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Sorption preconcentration of microcomponents for chemical analysis

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Abstract. Data on the methodology of sorption preconcentration are surveyed and the key concepts and quantitative parameters are given. The approaches to the preconcentration are considered, and various sorbents are characterised. Examples of using cellulose, styrene–divinylbenzene sorbents with grafted complexing groups, polyurethane foams and non-covalently modified silica gels, including those prepared by the sol–gel strategy, for preconcentration of inorganic and organic substances and development of combined and hybrid methods of analysis are given. The bibliography includes 357 references.

I. Introduction

Sorption, in particular, ion exchange, methods for the isolation, separation, and preconcentration of substances are widely used in the chemical and hydrometallurgical processes. The high efficiency of sorption processes in combination with high feasibility ensure the priority development of these methods. Sorption processes are also used on a large scale in analytical chemistry, for example, in chromatography. An essential place is occupied by sorption methods in solving problems of analytical preconcentration.

Preconcentration of microcomponents for determination is used, first of all, in those cases where the sensitivity of direct determination of these components is too low. Preconcentration is also necessary if the component is inhomogeneously distributed in the specimen. In addition, when physical methods of analysis are used, preconcentration makes it possible to manage without a large number of reference samples, in particular, standard samples, because preconcentration provides concentrates on a unified base, for example, in a carbon powder (in the case of atomic-emission analysis). During preconcentration, it is also convenient to introduce so-called internal standards if necessary. Therefore, preconcentration methods play an exceptionally important role in analytical chemistry.

Development of preconcentration methods, especially during the last two decades, has demonstrated appreciable advantages of sorption preconcentration as a relatively non-laborious process ensuring high preconcentration factors of substances. In particular, of interest is the mobile version of this method, which eliminates the necessity of separating the phases after preconcentration and opens up the way for automation of the whole cycle of analysis including sample preparation.

Thousands of original publications have been devoted to the sorption preconcentration of trace amounts of inorganic and organic compounds. General aspects of this topic have been considered in a number of monographs.[1–5] The sorption preconcentration has been employed to develop combined and hybrid methods for the analysis of environmental objects and industrial, geological, and biological objects. However, the design of new sorbents with specified properties for quantitative recovery of substances from diverse objects remains a topical task. The search for new approaches to determination of compounds after the isolation by sorption, in particular, directly in the sorbent phase, and development of quick, sensitive and simple determination methods are equally important.

This review, based on published data and authors' research, covers the strategy of sorption preconcentration of inorganic and organic compounds and characteristic features of recovery of substances on various sorbents, discusses the approaches to rational coupling of preconcentration methods with methods used for the subsequent determination, and considers the use of sorption preconcentration in the analysis of diverse objects. The review is based on authors' studies carried out together with colleagues at the Preconcentration Laboratory of the Chair of Analytical Chemistry at the Department of Chemistry of the Moscow State University. The purpose of the review is to draw attention to modern sorption preconcentration techniques, to characterise promising sorbents and to reveal their advantages and drawbacks.

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II. Theoretical grounds of the selection of sorption systems for preconcentration under dynamic conditions

Some advantages of dynamic preconcentration have already been noted. To extend the scope of this method, one can also use non-equilibrium conditions for dynamic sorption. For example, the

selectivity of the collection of a component may be increased by using kinetic features of its sorption and the preconcentration efficiency may be increased when non-equilibrium forms of components are recovered. Despite the good prospects offered by the last-mentioned approaches, they have been little developed as yet.

The last 15 – 20 years have seen vigorous development of flow analysis techniques which include the stage of dynamic sorption preconcentration (so-called on-line version). In this case, sorption, desorption and determination of components are performed in a cyclic mode, which implies repeated use of the sorbent without a change in its properties. However, not any determination method can be implemented in the on-line mode. Despite the attractive features of this approach, it cannot be applied, for example, for neutron activation or X-ray fluorescence determination of chemical elements. It is also noteworthy that the necessity of desorption leads inevitably to dilution of the concentrate and its dispersion in the flow on the way to a flow-type detector. In addition, the use of on-line preconcentration is expedient only provided that the preconcentration time is commensurable with the time of subsequent detection; otherwise, nonproductive expenses related to the no-load running of the detector will increase. This is especially tangible when expensive equipment and valuable consumables, for example, inert gases, are used.

Thus, if on-line detectors are inapplicable, it is expedient to use the off-line version of flow preconcentration to attain high preconcentration factors. In this version, the preconcentration and determination steps are independent of each other and are separated in time. The off-line methods are difficult to automate; however, they possess certain advantages and their existence is thus justified. For example, many molecular-spectroscopic, atomic-spectroscopic and electrochemical methods impose similar requirements on the gross composition of the concentrate for determination of toxic elements (heavy metals) in the environmental objects and foodstuffs. In the preconcentration of the elements, it is necessary to separate the major matrix elements of the sample, first of all, alkali and alkaline earth metals, and organic substances, for example, fulvic acids. When effective sorbents are used in the off-line mode, preconcentration methods can ensure the development of unified sample preparation procedures. The practically facile off-line flow sorption preconcentration of water samples of various types, extracts from soils and plants, *etc*., yields liquid or solid concentrates, which are suitable for long-term storage and transportation and which can be analysed by a variety of methods.

The use of the off-line and on-line options for preconcentration is determined by the sorbent properties or, strictly speaking, by the relationship between the properties of all components of the sorption system, which includes the sorbent, the solvent (most often, water), and the solutes including the trace component to be concentrated. In view of the sorbent inhomogeneity, the large numbers of components in solutions encountered in real-world tasks, and the diversity and complexity of the chemical and mass transfer processes that occur under non-equilibrium conditions of the dynamic preconcentration, one must admit that strict description of sorption systems is a highly complicated problem. However, without solving this problem, it is difficult to choose properly efficient sorbents and preconcentration systems. Most often, these are chosen empirically, taking into account the chemical properties of the functional group of the sorbent, the mechanical properties of the sorbent and other data. This is a labour-consuming procedure that requires screening of properties of sorption systems. This can be confirmed by tens of thousands of publications dealing with the use of various sorbents for the dynamic preconcentration of elements. Since most publications describe preconcentration of a small number of elements from a rather limited range of solutions, it can be stated that hundreds of variants have been proposed for the solution of similar tasks.

Meanwhile, in chromatography and chemical engineering — which have traditionally used sorption processes — mathematical models have been developed that establish the relationship between the physicochemical properties of the sorbent, the microcomponent to be recovered, and other sorption parameters.[6,7] Vast experimental material on the physicochemical properties of sorption systems has been accumulated. The development of the theoretical grounds of the dynamic sorption preconcentration using these models has allowed researchers to minimise the amount of experimental studies needed to choose sorbents for preconcentration of elements, to outline the ways for the development (synthesis) of new efficient sorbents, and to propose computation methods for the optimisation of experimental conditions.[8]

1. Parameters of the dynamic sorption preconcentration

Like any other preconcentration technique, the dynamic sorption preconcentration is described by the following key parameters.[1,4]

1. Preconcentration factor K_{conc} defined as the ratio of the component (element) concentration in the concentrate to that in the initial sample. For the case where the sorbent phase functions as the concentrate, $K_{conc} = c_s / c_{0\,liq}$ (c_s is the average concentration of microcomponent in the sorbent bulk, $c_{0\,liq}$ is the starting concentration of the microcomponent in the solution).

2. Recovery of the microcomponent (R) is the ratio of the amount of the substance in the concentrate m_s to that in the bulk of the initial solution $m_{0\,liq}$ ($R = m_s / m_{0\,liq}$). It is significant that the R values for preconcentration of a microcomponent from solutions with different compositions should remain constant; otherwise, when determining a component by a combined method including the preconcentration stage, it would be impossible to use calibration dependences plotted for 'pure' solutions.

3. Preconcentration rate. This value is determined by the time of preconcentration stage t_{conc}. In the ideal case, t_{conc} should not exceed the time of the subsequent instrument determination of the microcomponent. For the use of advanced instrumental methods of analysis, characterised by high sampling frequency (above 100 element determinations per hour), this parameter becomes not less important than the two previous parameters. In some cases, this value determines whether a system is suitable for dynamic preconcentration.[9–14]

4. Factors that describe the enhancement of the analytical signal. In flow analysis, sorption preconcentration is often characterised by parameters that reflect the growth of the analytical signal due to preconcentration, for example, the enrichment factor (EF).[9,14,15] The EF is calculated as the ratio of the analytical signals obtained before and after preconcentration,[16,17] or as the ratio of the higher and lower concentrations of the analyte responsible for the same magnitude of the analytical signal without and after preconcentration.[18] It has also been proposed to define the EF as the ratio of the sensitivity coefficients of the determination method attained after and without preconcentration, respectively.[19] Note that in flow systems that include desorption and detection steps, the increase in the analytical signal is not determined by the preconcentration factor alone, being an integrated characteristics of the whole analytical cycle. In the last-mentioned case, the EF should be called more correctly the enhancement factor.[9]

The dynamic sorption preconcentration can also be characterised by an integral criterion, namely, preconcentration efficiency CE, which was defined as the product of the enrichment coefficient attained through preconcentration and sampling frequency (min^{-1}).[13,14] According to this definition, the CE value is independent of the preconcentration or detection techniques and can be used to compare the efficiencies of various systems of flow analysis.[9,14]

The sorption preconcentration under dynamic conditions is characterised by a much higher CE value than that under static conditions. In the static mode, CE does not usually exceed 4 min^{-1}, whereas in flow analysis, CE reaches 30 – 60 min^{-1} or even more.[9,14] It has been noted[9] that with the use of advanced spectroscopic methods, the minimum CE value to justify the on-

line preconcentration compared to the off-line preconcentration from the economical standpoint is about 8 min^{-1}.

Meanwhile, this definition of the *CE* does not allow one to distinguish the contribution of the proper preconcentration stage to the overall efficiency of the flow analysis. Moreover, *CE* does not take into account the recovery of the microcomponent. We proposed defining the *CE* value for preconcentration as the preconcentration factor attained per unit time at a specified microcomponent recovery.[8] Note that the preconcentration efficiency defined in this way is proportional to the ratio of the solution space velocity (w) to the volume of the sorbent layer (V_{sorb}),

$$CE = \frac{Rw}{V_{sorb}}. \quad (1)$$

Thus, the *CE* value actually chartacterises the effective productivity of the sorption preconcentration. Note that for a column with a constant cross-section area S, the ratio of the liquid phase space velocity to the volume of the sorbent layer is equal to the ratio of the linear velocity of the liquid phase v to the length of the sorbent layer x_0. This can be easily seen if the numerator and denominator in expression (1) are divided by the column cross-section area S.

2. Comparison of the efficiency of sorption systems

For comparison of sorption systems under dynamic conditions and for elucidation of the optimal conditions of sorption, one should choose criteria describing the efficiency of such systems. This is done using a number of parameters, in particular, the preconcentration factor K_{conc}, the recovery R, the dynamic capacity up to breakthrough, t_{conc} and *CE*. These parameters are not independent;[9] therefore, efficient preconcentration systems and the optimal preconcentration conditions are usually chosen in the following ways.[20]

1. One parameter is varied, while the other are restricted. This method has found application in the design of low-output process units.

2. A unified optimality criterion is composed. In process engineering, this is an economical criterion that takes into account the contributions of all system parameters in terms of the cost per unit.[20,21]

When elucidating the optimal conditions of the dynamic sorption preconcentration, variable parameters are also distinguished (usually, the length of the layer and the size of sorbent particles, the column diameter, and the solution flow rate). The preconcentration conditions are chosen by experimental or calculation methods proceeding from the particular task and imposing restrictions on most of the parameters. As in the static version of sorption, the first item is to choose the optimal values for the parameters responsible for chemical reactions in the system: functional groups of the sorbent, pH, composition of the solution, *etc*.[9–14] Equally important are the sorbent weight, the size and the shape of the sorbent layer, the flow rate of the solution (the optimal values of these parameters have been determined in numerous publications).

In flow sorption spectroscopic systems, the signal-to-noise ratio directly related to the *EF* is often used as the optimality criterion.[9–12] This criterion has been used to determine the optimal solution flow rate during the on-line preconcentration of cobalt on alumina modified by nitroso-R-salt;[22] seven elements on a cellulose sorbent with ethylenediaminetriacetic acid groups;[23] antimony on the CPG-8Q sorbent (glass with a controlled pore size and 8-hydroxyquinoline groups).[24] In the last-mentioned case, the recovery R provided an additional restrictive criterion. The optimal amount of the sorbent and the diameter of its layer at a constant length were determined for the on-line preconcentration of lead on basic alumina;[25] Cd, Cu, Ni and Pb on the Resin 122 sorbent;[26] the same elements as complexes with diethyldithiocarbamate on C_{18} silica gel;[27] and Al, Cr(III), Fe(III), Ti(IV) and V(IV) on the Muromac A-1 sorbent.[28] A significant contribution of hydrodynamic factors to the formation of the analytical signal has been noted.[29]

In a number of studies,[30–38] the efficiencies of systems with various sorbents under dynamic conditions have been compared using the microcomponent recovery R. However, this comparison is legitimate only provided that other conditions (the sorbent layer size and shape, the flow rate of the solvent, and the preconcentration ratio attained) are the same for all systems, which is far from being always the case.[30,31]

When the efficiencies of dynamic sorption systems were compared as regards the microcomponent recovery, restriction was imposed on K_{conc}. For example, the optimal flow rates of the samples were determined for the flow preconcentration of eight elements as complexes with 7-iodo-8-hydroxyquinoline-5-sulfonic acid on the BioRad AG MP 1 anion exchange resin;[30] with 8-hydroxyquinoline on Amberlite XAD-2[31] or with bis(carboxymethyl)dithiocarbamate on Amberlite XAD-4;[32] ten elements on Chelex-100[33] and Amberlite XAD-2 modified with 1-(2-thiasolylazo)-2-naphthol;[34] six elements from sea water as diethyldithiocarbamates on SiO_2-C_{18}, Amberlite XAD-2 and XAD-7;[35] Mo and W on the anion exchanger Amberlite IRA-93;[36] Pb on the Spheron-oxine sorbent;[37] Mn on the vinyl gel with immobilised 8-hydroxyquinoline.[38]

The microcomponent recovery has been used as the efficiency criterion in the choice of the optimal quantity of the sorbent and the column dimensions.[31,38] Having determined the recoveries of several elements, the researchers compared the efficiencies of four sorbents under dynamic conditions.[29] This criterion was used to determine the optimal amount of the sorbent, the length and the cross-section of its layer for preconcentration of cadmium from soil extracts[39] and various forms of copper and lead from natural water as dithiocarbamates on SiO_2-C_{18}.[27]

The R value is related to the system capacity 'before breakthrough', which stands for the amount of the substance collected by the sorbent up to the instant where the recovery drops below a specified value.[40] For most tasks, it is taken that $R = 0.95$. The ratio of the average attained concentration of the microcomponent a to its equilibrium concentration a_0 in the solid phase characterises the fraction of the sorbent capacity that has been spent before the breakthrough (the dynamic sorbent capacity before the breakthrough). In other studies,[40–44] this parameter was used to compare the efficiency of different systems. The dynamic capacity before breakthrough depends, in particular, on the size and the shape of the sorbent layer, the solution flow rate (the pattern of this dependence was determined only in a few cases[40]). It has been noted that by using microcolumns with a great length-to-diameter ratio, one can attain fuller recovery of the microcomponent and a larger before-breakthrough capacity, especially at high *CE* values.[40]

The *CE* value was also used as the efficiency criterion; in this case, restrictions were imposed on K_{conc} and R. Thus, the efficiencies of the Chelex-100, CPG-8Q and Resin 122 sorbents in the preconcentration of heavy metals were compared;[45] the optimal flow rate of the solution for gold preconcentration on Amberlite XAD-7 and XAD-8[46] and cobalt and cadmium preconcentration on CPG-8Q[47] were determined. In the latter case, the optimal amount of the sorbent and the layer shape were also found.

In a number of studies, computation techniques were used to optimise the geometric parameters and the hydrodynamic operating conditions of microcolumns-reactors meant for determination of physiologically active compounds based on the reaction products in flow-injection systems. The formation of the analytical signal in flow-injection systems was described using layer-by-layer models.[48–51] The analysis productivity served as the efficiency criterion, the degree of substance conversion served as the analogue of the recovery and the size of the analytical signal served as an approximate analogue of the preconcentration factor. The efficiency of operation of the reactor was estimated

from the magnitude of the analytical signal (determined by the degree of conversion of the analyte and the longitudinal dispersion of its zone); restrictions were imposed on the system productivity. The layer-by-layer model parameters determined experimentally were used to calculate the optimal volume and the inner diameter of the reactor, the grain diameter of the filler, and the solution flow rate.[51] By imposing additional restrictions on the hydrodynamic resistance, the optimal size and the length of the reactor, and the corresponding reagent and sample consumptions were determined. The calculated parameters were employed to compare the efficiency of reactors of different types.[49] The general principles of their construction were formulated.[50] The possibility of influence of the rate of chemical reactions[48, 50, 51] and the substantial contribution of the longitudinal dispersion to the formation of the analytical signal in these systems have been noted. When the analytical signal is used as the criterion of the efficiency for flow injection systems, the last-mentioned factor can become crucial. This indicates that not only the sorption preconcentration stage, but also the subsequent desorption should be considered separately and perhaps optimised.

Modelling of the sorption dynamics was also employed to calculate the amount of the sorbent and sorption time for the dynamic preconcentration of palladium and platinum on the POLIORGS XI-N sorbent[52] on the basis of previously determined physicochemical parameters. The required flow rate of the solution and recovery were specified for the calculation. Good agreement between the calculated and experimental parameters was noted.

Thus, the dynamic sorption preconcentration is characterised by a set of parameters that depend in an intricate manner on one another and on the physicochemical properties of the system. Therefore, when comparing the efficiencies of various dynamic sorption systems, these parameters should be considered together (this was done, in particular, by Fang[9]). The search for the optimal preconcentration conditions (the region of the highest efficiency of a sorption system) has been performed both empirically and using various theoretical models.

To elucidate the legitimate criteria for comparison of the efficiency of dynamic preconcentration sorption systems, we proposed the use of mathematical models of sorption dynamics.[6–8]

3. Mathematical models of sorption dynamics

The sorption under dynamic conditions is a complex heterogeneous process consisting of several successive stages:[6, 7] the transport of the substance in the solution to the sorbent surface; the transport of this substance in the sorbent phase to the point where the chemical reaction takes place; the chemical reaction between the substance and functional groups of the sorbent; the transport of the reaction products in the sorbent phase; the transport of the reaction products from the sorbent surface to the solution bulk. The full mathematical description of processes that occur in the system implies taking into account the contribution of each of these stages to the overall rate of mass transfer, which is a fairly complicated task. The mathematical models proposed for describing sorption include three equations: differential material balance and kinetic equations and the equilibrium equation (isotherm) with initial and boundary conditions.[7] Rather detailed models constructed in this way are called deterministic models. In many cases, these can be simplified by averaging the concentrations of the sorbed substance over some volume of the system. The models thus obtained are called aggregated.[7, 20] If the concentration of the microcomponent in the solution is averaged over some volume of the liquid phase, these models are called layer-by-layer ones.[20, 53] The layer-by-layer method is used to describe the dynamics of sorption of substance mixtures when combined allowance for all kinetic parameters is impossible.[7, 20] As applied to chromatographic systems, it is widely used under the name of the method of 'theoretical plates.'

Methods for the solution of sets of partial differential equations describing the dynamics of sorption are well developed and presented in a number of monographs.[54, 55] Analytical solutions have been obtained only for limiting cases, in particular, for linear and rectangular sorption isotherms, external- and internal-diffusion kinetics.[54] In more complicated cases, approximate and numerical methods are used.[56, 57] The developed algorithms have been implemented as software programs. By using them, it is possible to obtain solutions for any case of diffusion kinetics (external, internal and mixed diffusion).[58–64] The numerical solutions of the problem of external diffusion dynamics for the linear sorption isotherms are tabulated.[64]

4. The use of the mathematical model of sorption dynamics for description of preconcentration problems

Dynamic sorption is widely used for various purposes, first of all, for the isolation, preconcentration and separation of substances. However, the efficiency criteria of sorption systems differ appreciably in various applications, depending on the task to be solved. For example, in solving most of process engineering problems, the key criterion is represented by the 'specific reduced costs.' During dynamic preconcentration, it is important to quantitatively isolate the microcomponent from the solution using the smallest possible amount of the sorbent (*i.e.*, the capacity before breakthrough should be high) over the shortest period of time (*i.e.*, the flow rate of the solution should be high), which is especially important in flow systems. Thus, of the parameters describing dynamic preconcentration, the preconcentration efficiency CE and the preconcentration factor K_{conc} are most general.

Note that the CE does not reflect in any way the true value of the preconcentration factor K_{conc} or, in other words, the dynamic capacity of the sorbent. Thus, the problem of preconcentration, unlike technological problems, can be formulated as follows: in a sorption system, it is necessary to attain the highest possible CE value at a specified K_{conc} or, *vice versa*, the highest K_{conc} at a specified CE value. The former version rather applies to the solution of off-line problems where a microcomponent is to be collected from large solution volumes. The latter is more important in on-line systems where the dimensions of the column and the flow rate of the solution are restricted by the system design, the preconcentration being limited by column capacity. In any case, the CE and K_{conc} values considered simultaneously ensure a well-posed characterisation of the efficiency of the sorption system for preconcentration of the given microcomponent.

Let us consider the mathematical model of sorption dynamics.[8] Let the η value mean the fraction of the total sorbent capacity that has been used by the end of preconcentration,

$$\eta = \left[\int_0^l a(x,t)\mathrm{d}x\right] / \Gamma c_0 ,$$

where a is the concentration of the microcomponent in the bulk of the solid phase, t is time, Γ is a dimensionless distribution coefficient of the microcomponent (ml ml^{-1}), $\Gamma = K_{conc}/\eta$, c_0 is its initial concentration in the solution. Note that within the bounds of the chosen and substantiated mathematical models, the η value can be calculated as a function of the dimensionless variables, X and T (the dimensionless sorption length and time), where $X = \beta x/v$; $T = \beta t/\Gamma$ (β is the effective mass transfer coefficient for the microcomponent in the solution, v is the linear velocity of the flow of the liquid phase).

For further calculations, it is convenient to represent η as isolines in the $X-T$ plane (Fig. 1). The limiting value of η is 1, *i.e.*, the limiting value of K_{conc} is Γ. This provides the limitation for the sorbent capacity, namely, the Γ value cannot be lower than the required K_{conc}.

The second limitation is related to the allowable breakthrough level χ. This means that the substance loss during sorption cannot be higher than a particular fraction of all substance that entered the layer, namely:

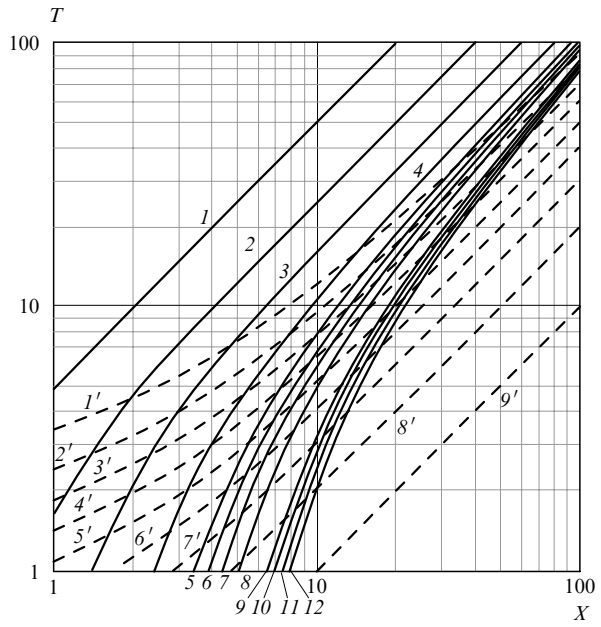


Figure 1. Theoretical function of the specific cumulative breakthrough χ (continuous lines) and fractions of the sorbent used η (dashed lines) in the case of external diffusion dynamics and linear sorption isotherm in the $X-T$ coordinates used to determine the maximum attainable preconcentration efficiency.
χ: 0.8 (*1*), 0.6 (*2*), 0.4 (*3*), 0.2 (*4*), 0.1 (*5*), 0.07 (*6*), 0.05 (*7*), 0.03 (*8*), 0.01 (*9*), 0.007 (*10*), 0.005 (*11*), 0.003 (*12*);
η: 0.9 (*1′*), 0.8 (*2′*), 0.7 (*3′*), 0.6 (*4′*), 0.5 (*5′*), 0.4 (*6′*), 0.3 (*7′*), 0.2 (*8′*), 0.1 (*9′*).

$$\chi = \frac{m_{\text{liq}}}{m_{0\,\text{liq}}} = \frac{m_{0\,\text{liq}} - m_{\text{s}}}{m_{0\,\text{liq}}}.$$

Note that the χ value is related to R by a simple relation $\chi = 1 - R$. It can also be calculated as a function of X and T for each type of kinetics and is represented as a series of theoretical curves.[64] Like the function η, this function is convenient to depict as isolines in the $X-T$ plane (see Fig. 1).[8]

The values of $\eta(X,T)$ and $\chi(X,T)$ found numerically using appropriate software are tabulated.[64]

A remarkable feature of this way of tackling the preconcentration problem (where it is necessary to attain a specified K_{conc} without losing more than m_{liq} of the microcomponent weight) is that the problem can be solved in terms of dimensionless variables with the restrictions already made. If metrological requirements have been specified as definite η and χ values, the only X_{opt} and T_{opt} values corresponding to them can be found by a simple graphical operation, in particular, by matching two plots for η and χ in the $X-T$ plane (Fig. 1).

Thus, in terms of dimensionless variables, we have a unique solution for the dimensionless length X_{opt} and the sorption time T_{opt}. The dimensional expressions for x_{o} and t_{o} are defined, in the case of external diffusion, by the relations

$$x_{\text{o}} = \frac{X_{\text{opt}} v}{\beta}, \quad t_o = \frac{T_{\text{opt}} \Gamma}{\beta}, \tag{2}$$

and for the internal-diffusion sorption kinetics, by the relations

$$x_{\text{o}} = \frac{X_{\text{opt}} d^2 v}{4D\Gamma}, \quad t_o = \frac{T_{\text{opt}} d^2}{4D}, \tag{3}$$

where d is the diameter of sorbent particles, D is the internal diffusion coefficient.

The X_{opt} and T_{opt} values determine the corresponding $CE_{\max}$, *i.e.*, the maximum preconcentration efficiency attainable in the system with specified K_{conc} and R (because η and χ are specified).

Thus, we arrive at an important conclusion — in any sorption system and for specified preconcentration ratio and recovery of the microcomponent, one can calculate the maximum attainable preconcentration efficiency $CE_{\max}$, which can serve as a universal criterion for comparison of the efficiency of dynamic sorption systems as regards their application for preconcentration of microcomponents.

The value of $CE_{\max} = T_{\text{opt}}\Gamma / X_{\text{opt}} t_{\text{o}}$ depends on t_{o}, which is determined by expressions (2) and (3); hence, it is related unambiguously to the v, d and Γ parameters. It follows from (2) and (3) that the smaller the grain size of the sorbent and the higher the flow rate of the liquid phase, the higher the preconcentration efficiency. However, it is clear that v cannot be increased and d cannot be decreased infinitely if for no other reason than from hydrodynamic considerations.

For analysis of the reasons for different efficiencies of sorption systems in preconcentration processes, it is necessary to estimate the degree to which the thermodynamic and kinetic sorption parameters and the particle size of the sorbent influence the generalised efficiency criterion, $CE_{\max}$, for specified K_{conc} and R. To solve this problem, $CE_{\max}$ values were calculated for various Γ, β, D and d.[8] The calculations were carried out for different kinetic mechanisms of sorption (Tables 1 and 2).

Table 1. Maximum attainable preconcentration efficiency $CE_{\max}$ (s^{-1}) calculated for the external-diffusion mass transfer mechanism ($K_{\text{conc}} = 1000$, $R = 95\%$).

$10^{-3}\,\Gamma$ /ml ml^{-1}	β /s^{-1}				
	0.01	0.05	0.1	0.5	1.0
1.11	1.8×10^{-4}	9.1×10^{-4}	1.8×10^{-3}	9.1×10^{-3}	1.8×10^{-2}
1.25	3.89×10^{-4}	1.95×10^{-3}	3.89×10^{-3}	1.95×10^{-2}	3.89×10^{-2}
2.0	1.2×10^{-3}	6.0×10^{-3}	1.2×10^{-2}	6.0×10^{-2}	1.2×10^{-1}
5.0	2.4×10^{-3}	1.2×10^{-2}	2.4×10^{-2}	1.2×10^{-1}	2.4×10^{-1}
10 (see [a])	2.85×10^{-3}	1.43×10^{-2}	2.85×10^{-2}	1.43×10^{-1}	2.85×10^{-1}

[a] Here and in Table 2, obtained by extrapolation.

It follows from the data of Table 1 that in the case of external-diffusion sorption kinetics, an increase in the mass transfer coefficient by a factor of 10 results in an identical change in the $CE_{\max}$, while the same increase in the distribution coefficient results in an approximately 16-fold increase in the $CE_{\max}$, *i.e.*, the thermodynamic sorption parameter impacts $CE_{\max}$ to somewhat a greater extent than the kinetic one.

In the case of internal-diffusion sorption kinetics, $CE_{\max}$ depends on the thermodynamic parameter to a markedly greater extent than on the kinetic one. Indeed, an 8-fold increase in Γ induces an increase in $CE_{\max}$ by more than two orders of magnitude; a similar change in the $CE_{\max}$ requires an increase in D (and $1/d^2$) also by two orders of magnitude (Table 2).

The efficiency criterion of sorption systems for preconcentration ($CE_{\max}$ at specified K_{conc} and R values) and the method for its

Table 2. Maximum attainable preconcentration efficiency $CE_{\max}$ (s^{-1}) calculated for the internal-diffusion mass transfer mechanism ($K_{\text{conc}} = 1000$, $R = 95\%$).

$10^{-3}\,\Gamma$ /ml ml^{-1}	$4D/d^2$ /s^{-1}				
	1×10^{-10}	1×10^{-8}	1×10^{-6}	1×10^{-4}	1×10^{-2}
1.25	8.9×10^{-8}	8.9×10^{-6}	8.9×10^{-4}	8.9×10^{-2}	8.9
2.0	4.44×10^{-7}	4.44×10^{-5}	4.44×10^{-3}	4.44×10^{-1}	44.4
5.0	2.79×10^{-6}	2.79×10^{-4}	2.79×10^{-2}	2.79	279
10 (see [a])	9.71×10^{-6}	9.71×10^{-4}	9.71×10^{-2}	9.71	971

calculation allow a legitimate comparison of sorption systems. The following procedure was proposed for the selection of an efficient sorption system for dynamic preconcentration.[8]

1. Published data or experimental results (obtained, for example, by the method of dynamic breakthrough curves) are used to determine the kinetic sorption mechanism and the Γ (or the distribution coefficient K_d), β or D values. This is done using mere matching of the theoretical and experimental curves.

2. Proceeding from the preconcentration factors K_{conc} needed to attain the specified detection limit in a combined method involving a sorption preconcentration stage, the required η value is calculated, the allowable breakthrough value χ is specified (usually, it is equal to 0.05). Then the intersection point of the calculated X_{opt} and T_{opt} curves (corresponding to these η and χ) is found in the $X-T$ coordinates (Fig. 1). These values are used to calculate the maximum preconcentration efficiency CE_{max} attainable in this system. The sorption system that ensures the highest CE_{max} value, all other factors being the same, is the most efficient.

III. Preconcentration of metal ions on polymeric sorbents with conformationally mobile aminocarboxyl groups

Complexing sorbents are often used for preconcentration of metal ions from solutions. Sorption in these systems is highly efficient if the solid-state metal compounds are stable and are formed at a high rate. When reacting with a metal ion, the sorbent acts as a ligand whose heteroatoms fill the metal coordination sphere either completely or partially. Various approaches to ensuring the efficiency and selectivity of these sorbents have been proposed and are successfully developing. These approaches are based, first of all, on the formation of a functional group required for optimal filling of the metal coordination sphere.

A traditional way is to design the sorbent taking into account the basicity of the heteroatoms of functional groups and the basicity of the species to be preconcentrated. In this case, the complexing groups are chosen on the basis of extensive knowledge accumulated in the field of monomeric analytical reagents. The geometric (spatial) factors are taken into account to a lesser extent.

1. Development of new sorbents

Complexing sorbents of new types are developed deliberately, proceeding from the expected structure of the complex of an element with the monomeric ligand. The ability of the metal ion to form the optimal coordination polyhedron from a set of heteroatoms offered depends on the basicity of the donor atoms of the functional groups of the ligand and on the conformational mobility of these atoms, the latter being mainly determined by the possibility of bond angle and bond length distortions in these functional groups. Unlike solutions, the mobility of donor atoms in the complexing groups grafted onto a polymer matrix is restricted by both the conformational rigidity of the matrix and the length and the conformational mobility of the spacer, *i.e.*, the fragment that links the polymer matrix to the complexing group. The grafting density of the functional groups on the polymer is also important. (In the case where the polymer matrix is modified by polydentate ligands able to saturate the coordination sphere of the element, the requirement of high density of complexing groups and relatively long spacers become less stringent, because the complexation capacity is determined only by the conformational mobility of the grafted polydentate ligand.) The lower efficiency of interaction of metal ions with grafted groups compared to the corresponding monomeric reagents in solution is due, first of all, to the distortion of the resulting coordination polyhedron. In our opinion, an increase in the coordination mobility of the donor atoms incorporated in the functional groups of sorbents should reduce the steric hindrance to the formation of the coordination sphere required for the given element.[65]

The complexation scheme considered[65] is not universal and has some limitations. In some cases, an increase in the number of donor atoms and in the spacer length can result in enhanced steric hindrance to complexation. However, generally, this scheme can show the way to the perfection of known and the development of new complexing sorbents.

Within the bounds of the proposed approach, sorbents based on polystyrene and poly(vinyl chloride) containing diethylenetriaminetetraacetate (DETATA) groups were synthesised. The synthesis was carried out by condensation of chlorine-containing compounds with amines followed by treatment of the aminated products with monochloroacetic acid in an alkaline medium.[66,67] Gel-type chloromethylated polystyrene with a cross-linking degree of 2% (grain diameter 40–80 μm) and poly(vinyl chloride) fibre with a fibre diameter of 8–12 μm were used. Cellulose-based sorbents were synthesised using a fibre (with a diameter of 10–20 μm) and 'blue ribbon' grade filter paper.

The results of experiments carried out under static conditions showed the advantage of sorbents with conformationally mobile groups over 'usual' aminocarboxyl sorbents, caused by the formation of stable coordinatively saturated complexes in the sorbent phase (Fig. 2).[65,66] Thus the equilibrium distribution coefficients K_d for the sorption of Mn(II), Ca, Co(II), Cu(II) and Zn on the polystyrene-based DETATA sorbent in the pH range most favourable for sorption are 1–1.5 orders of magnitude higher than those for the sorption of the same metals on the widely used Dowex A-1 sorbent (an analogue of Chelex 100) with iminodiacetate (IDA) groups. The dynamic capacity before breakthrough can serve as a criterion for comparison of dynamic sorption systems. As mentioned above, the use of this criterion is not completely legitimate[8] but fairly illustrative, for example, for the comparison of sorption filters (Table 3).[66] All other factors being the same (composition of the solution, solution flow rate, filter size), the capacity of DETATA filters is several times higher than that of the previously synthesised filters with IDA groups or EDTA-type groups in which one nitrogen atom is quaternary.

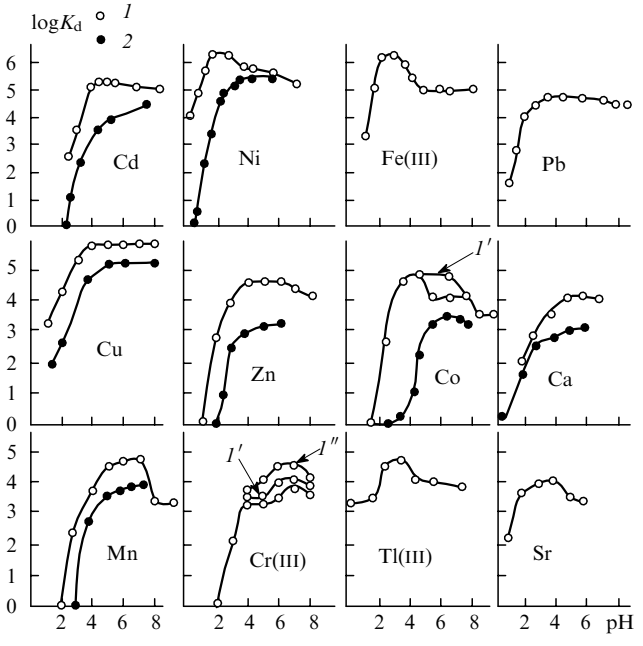


Figure 2. Distribution coefficients of some metals on aminocarboxyl sorbents.
(*1*) Polystyrene sorbent with DETATA groups; (*2*) Dowex A-1 sorbent; V_{soln} = 100 ml, m_{sorb} = 50 mg, 20 °C; t = 0.5 (*1*, *2*), 1 (*1′*), 3 h (*1″*).

Table 3. Capacity before breakthrough of some filters with aminocarboxyl groups (v = 1.0 ml min^{-1} cm^{-2}, pH 5.0).

Filter	Before-breakthrough capacity of the filter /μmol litre^{-1} g^{-1}			
	Co(II)	Zn	Mn(II)	Fe(III)
EDTA	197	209	–	160
IDA	171	157	–	109
DETATA	771	671	445	340

2. Preconcentration of elements on DETATA sorbents

Under dynamic sorption conditions, sorbents are used most often in columns (columns, cartridges or cylinders) or as filters. The column version is preferred as regards the subsequent desorption because the dead volume of a column is much smaller than those of devices used for filter locking-up. In our studies, the elements were collected on microcolumns with a sorbent (d = 2–3 mm; l = 10–15 mm, V_{col} = 0.03–0.12 ml) and on cellulose filters with the same grafted groups (filter diameter, 25 mm; filter thickness, 0.15 mm, diameter of the filtering surface, 22 mm).[68–71]

A study of the mass transfer kinetics for metals during sorption on DETATA sorbents has shown[72] that high thermodynamic and kinetic sorption parameters and small size of sorbent grains and fibres ensure the quantitative recovery of metals even with exceptionally high flow rates of the solution. For example, it was found that Cd, Co, Cu, Fe, Mn, Pb and Zn (in a concentration of 0.01 μg ml^{-1}) are quantitatively recovered from 100 ml of a 0.1 M solution of ammonium acetate (pH 5) on a 0.03-ml column at a solution flow rate of up to 20 ml min^{-1} (see Ref. 73). An increase in the flow rate of the solution through a two-filter tandem to 4 ml min^{-1} cm^{-2} (14 ml min^{-1} through the filtering surface with d = 22 mm) does not lead to a loss in Cd, Co, Cu, Fe, Mn, Ni, Pb or Zn at the preconcentration stage (V_{soln} = 100 ml).[74] Thus, quick preconcentration of metals from large solution volumes is possible.

a. Study of the effect of the major inorganic components of solutions on the sorption of heavy metals

It has been found that Cd and Pb are quantitatively collected on a column with a sorbent even in the presence of 10 g litre^{-1} of Ca and Mg and 100 g litre^{-1} of Na. Similar results have been obtained for Co, Cu, Ni and Zn. Some decrease in the recovery (down to 85%–90%) at high concentrations of alkali and alkaline earth metals was observed only for Mn sorption.[73,75]

The recovery of Cd and Pb does not decrease either in the presence of iron (up to 0.1 g litre^{-1}), whereas aluminium (0.05 g litre^{-1}) suppresses appreciably their sorption. With an iron concentration of 10 g litre^{-1}, the recovery of lead is equal to 96%. The pronounced influence of aluminium on the sorption of Cd and Pb may be due to the higher stability of complexes of the macrocomponent with respect to those formed by the microcomponents in the sorbent phase. Lead forms more stable complexes with functional groups than cadmium (and, apparently, iron), and is successfully recovered from solutions in the presence of this macrocomponent.[75]

A potential masking reagent for Al, Ca and Fe, namely, the citrate ion almost does not decrease the distribution coefficients or the recovery of Cd and Pb during sorption on DETATA sorbents and, therefore, it can be used to bind the macrocomponents when collecting these elements from solutions of complex composition.[75] For example, in the presence of citrate, the recovery of Cd and Pb from solutions with high contents of Al and Fe increases, quantitative extraction of microcomponents being observed when the citrate concentration is equimolar to the concentration of the macrocomponent.

In order to choose conditions for the preconcentration of lanthanides in the presence of the key matrix components of sedimentary rocks and elements creating noise in determination of lanthanides by inductively coupled plasma atomic emission (ICP-AES), sorption of Al, Ba, Cr(III), Fe(III), Mo(VI), Sr, Ti(IV), V(V), W(VI) and Zr was studied. It was found that DETATA polymers do not exhibit high selectivity with respect to lanthanides. To reduce sorption of interfering elements, 5-sulfosalicylic acid was proposed as the masking reagent. In the presence of this reagent, sorption of other elements was suppressed and lanthanides can be recovered quantitatively over a broad pH range.[76,77]

Chromium(III) is recovered quantitatively on the DETATA sorbent at pH 7, while chromium(VI), at pH 3; in addition, these pH values allow almost complete separation of these chromium forms. However, during sorption of this element, the equilibrium is attained slowly. The efficiency of chromium collection under both static and dynamic conditions increases when sorption is carried out in a microwave field.[78]

The sorption of Ag, Bi(III), In and Tl(III) from sea water on microcolumns with the DETATA-sorbent based on polystyrene has been studied under dynamic conditions. An increase in the content of alkali and alkaline earth metal salts in water to 200 g litre^{-1} does not decrease the recovery of the target elements.[79]

The experiments dealing with the effect of Na, K, Mg and Ca on the sorption of Cd, Cu(II) and Zn on DETATA filters were carried out over a broad range of concentrations of macrocomponents (0 to 100 mg litre^{-1}), which is fairly typical of the surface fresh water.[74] It was shown that potassium has a minor influence on sorption of copper and cadmium. In terms of their influence on the sorption of copper and cadmium, other macrocomponents can be arranged in the sequence Mg > Ca > Na.

The sorption of trace amounts of Mn(II) and Zn on DETATA filters as a function of the concentration of the same salt components in natural waters has been studied by the radioisotopic tracer method.[66,70] These elements are recovered quantitatively even when the concentrations of macrocomponents exceed markedly the natural level. Similar results have been obtained for the preconcentration of Bi, Cd, Co, Cu, Fe, In, Mn, Ni, Pb, Tl and Zn from sea water.[74] For increasing the recovery of heavy metals at high concentrations of inorganic components, it is better to use a tandem of two or three filters.

b. Effect of some organic substances on the sorption of heavy metals

Fulvic acids are the major organic components of natural water and soil extracts able to affect the sorption of metals. In fresh water, they account for 60%–90% of the dissolved organic compounds, while in sea water, almost 100%. Fulvic acids are involved in complex formation mainly through the carboxy and hydroxy groups.[74]

The sorption of cadmium and lead on microcolumns with the DETATA sorbent from model solutions containing fulvic acids isolated preliminarily from river water has been studied.[74,75] The presence of up to 50 mg litre^{-1} of fulvic acids barely influences the recovery of the target elements.

The dependence of the recovery of Cu(II) and Cd on filters on the colouring of model solutions caused by the presence of fulvic acids has been studied. The concentration of fulvic acids typical of the superficial land water has little influence on the recovery of Cu and Cd on DETATA filters.[74]

The high stability of heavy metal complexes in the DETATA sorbent phase suggests that these elements could be preconcentrated from juices or wines and other alcoholic beverages. It was found that a key complexing macrocomponent in these solutions, namely, citrate, does not influence the sorption of cadmium and lead on microcolumns up to a concentration of 0.2 mol litre^{-1} (Ref. 75). Similar results were obtained in the cadmium and lead preconcentration from tartrate-containing solutions.[72]

The conditions chosen for the dynamic preconcentration of Cd and Pb were applied to study the recovery of Co, Cu, Mn, Ni and Zn from various waters and solutions obtained after autoclave digestion of some foodstuffs.[80] The recovery of all elements on a 0.03-ml microcolumn at a flow rate of 6 ml min^{-1} (200 sorb-

ent volumes per min) or on DETATA filters from solutions containing inorganic and organic macrocomponents amounts to 96%–99%. Quantitative recovery of Cd and Pb from solutions obtained after the autoclave digestion of soil (clay loam) is attained by adding 0.02 mol litre^{-1} of citrate.[75]

3. Methods for determination of elements that include dynamic preconcentration on DETATA sorbents

The techniques of the dynamic preconcentration of heavy metals have been used to develop highly sensitive combined methods for determination of these elements in various objects. The high efficiency of the chosen preconcentration systems ensured better metrological characteristics of these methods compared not only to direct methods but also to the methods proposed previously that involve sorption preconcentration.

a. Methods involving preconcentration and determination of the elements directly in the solid concentrate

The advantage of this combined approach is that high preconcentration factors (10^3–10^4 and more) are attained and, as a consequence, the detection limits are reduced compared to those attained in direct determination. However, the drawbacks of these combined methods are rather significant. As a rule, it is necessary to dry the concentrate and to transfer it from the preconcentration system into the system for determination. In the optimisation of the conditions for element determination by the combined method, it is necessary to take into account the influence of the solid matrix of the sorbent on the formation of the analytical signal; these effects can be more pronounced with solid concentrates than in the case of liquid ones. Methods that include determination of elements in solid concentrates usually cannot be fully automated. Some important analyses carried out by this method are considered below.

1. Sorption coupled with X-ray fluorescence determination of As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, V and Zn in potable, natural and waste waters. X-ray fluorescence analysis (XFA) is known to be a widely used instrumental method for determining the elemental composition of natural and industrial materials, which is due to the simple instrumentation (especially in recent years), the possibility of multiple-element determination, high reproducibility and relatively low cost. However, until recently, this method has found only limited application for determination of minor concentrations of elements, in particular, in environmental objects due to low sensitivity.

For XFA determination of elements, it is useful to employ cellulose filters as substrates, as the fluorescence of the filter elements (C, H, N, O) does not fall in the spectral range covered and the small thickness and low density of the filters minimise the absorption and scattering of the primary and fluorescence emission. The data we obtained on the sorption of elements from solutions of complex composition on the DETATA filters were used to develop simple procedures involving sorption and X-ray fluorescence determination of a number of elements in potable, natural and treated waste waters and in urine.[70, 71, 74, 81]

When developing these procedures, three different spectrometers were used: an energy-dispersive spectrometer (a Si–Li semiconductor detector with a resolution of 180 eV at the MnK_α line, a Kevex X-ray tube with an Ag anode and a Link Analytical spectrometer tract) and portable single-crystal diffraction Spark-1M and Spectroscan-001 instruments. The detection limits of elements in solutions were 1–5 μg litre^{-1}, the relative standard deviation (s_r) of the results did not exceed 0.06 over broad ranges of element concentrations.[70, 74, 81]

2. Determination of chromium forms in water by sorption coupled with atomic-absorption spectrometry (with electrothermal atomisation).[78] The procedure proposed for separate preconcentration of Cr(III) and Cr(VI) on the polystyrene-based DETATA sorbent made it possible to develop a procedure for determination of these species in river water. Chromium(III) and chromium(VI) were extracted from solutions at pH 3 and 7 on a microcolumn with the sorbent (0.03 ml) placed in a microwave oven. Chromium was determined in solid and liquid concentrates by the atomic-absorption method with electrothermal atomisation at a wavelength of 357.9 nm, the background absorption being corrected based on broadening of the resonant absorption line. The detection limit of chromium (both in the case of determination in an aqueous suspension of the sorbent and after desorption with 6 M HCl) amounted to 30 ng litre^{-1} (K_{conc} = 100). The method shows a high reproducibility; the s_r value did not exceed 0.05 in the region of chromium concentrations of 0.2–10 μg litre^{-1}.

3. Determination of Ag, Bi, Cd, In, Pb and Tl in natural waters by sorption coupled with atomic-absorption spectrometry (with electrothermal atomisation).[79, 82] Two-chamber graphite atomisers of the crucible–cell type with independent heating of the vaporisation and atomisation zones, Saturn-2 and AAS-3 spectrometers and an experimental multichannel atomic-absorption/atomic-fluorescence setup were used. The atomiser crucibles with the bottom made of a porous graphite filter (disc) were employed as the microcolumns for dynamic preconcentration of elements. The dynamic preconcentration in the crucible/microcolumn with subsequent electrothermal atomic-absorption determination resulted in the following detection limits of elements: 0.3–1 (Ag, Cd) and 2–10 ng litre^{-1} (Bi, Pb, Tl). The relative standard deviation for a single determination of elements was 0.1–0.3, which complies with the goals of geochemical and ecological studies.

4. Determination of elements in waters by sorption coupled with neutron activation analysis. It has been demonstrated that the dynamic preconcentration of a broad range of elements can be easily combined with neutron activation determination.[83] For element preconcentration and determination, a special quartz cell acting as a microcolumn was used. The concentrates obtained were exposed to a neutron flux directly in these cells in an IR-8 reactor (the neutron flux density $n \times 10^{14}$ n cm^{-2} s^{-1}). The spectra were recorded using an HPGe detector (resolution 1.8 keV on the 1332.5 keV line) connected to a NUC-810 multichannel analyser. Two analysis protocols were used: (1) irradiation of the sorbent with the concentrate for 5–10 h, storage the samples for a week after irradiation and determination of Au, Ba, Cd, Co, Cr, Eu, Fe, Hg, La, Mn, Sc, Sr and Zn; (2) irradiation of the sorbent with the concentrate for 40–60 s for determination of Cu, In, Mn, V and some lanthanides.

b. Flow analysis for determination of elements involving preconcentration on sorbents with aminocarboxyl groups

A decrease in the proportion of human labour in performing analyses is a priority task in analytical chemistry. The extensive use of microprocessor-based units provided the possibility for the development of automated analytical systems characterised by high sampling frequency, good metrological characteristics and relatively low cost. Unfortunately, automated systems are still seldom used in the environment monitoring and quality control of foodstuffs where it may be necessary to take urgent measures on the basis of analysis of large series of samples.

It is relatively simple to automate analytical systems with flow detectors: atomic absorption, atomic fluorescence, inductively coupled plasma atomic emission, spectrophotometric, some electrochemical detectors and so on. A popular and rapidly developing way for automation of the sample preparation in the analysis of solutions is the use of flow-injection devices. Despite the relative simplicity of this equipment (usually this includes one or two peristaltic pumps, one to three injection valves and a simple electronic control device), its use not only ensured automation of numerous methods of analysis but also substantially increased the sampling frequency and improved the metrological characteristics, first of all, the sensitivity and reproducibility of the analysis.

In our opinion, for using sorption systems in flow methods of analysis, it is necessary and sufficient that the following conditions be met:[84]

— the microcomponent should be recovered quantitatively on a sorbent at a high flow rate of the solution (this ensures accumulation on the column of an amount of the analyte needed for reliable detection);

— the microcomponent is desorbed quickly and quantitatively by a desorbing solution suitable for detection; the sorption properties should not change after repeated sorption – desorption cycles;

— the capacity of the sorbent in the column should be sufficient for the recovery of the microcomponent from the solution under analysis in amounts exceeding the absolute limits of the subsequent detection;

— to decrease the dispersion of the concentrate zone in the stream, the dimensions of the column with the sorbent should be as small as possible;

— the sorbent should be sufficiently selective for the recovery of the target microcomponents in the presence of other components of the solution.

In flow analysis systems involving preconcentration, the analytical signal is formed under non-equilibrium conditions — when the concentrate zone resulting from the element desorption passes through the flow detector.[84] Attaining the maximum signal-to-noise ratio under the non-steady-state conditions existing in the flow system requires optimisation of the conditions for the desorption of metals from the column (the composition and concentration of the desorbing solution and the flow rate of this solution), conditions for analytical signal processing and some design factors of the flow system: flow distribution at various stages of the analysis cycle, some pipeline diameters, and the shape and dimensions of the column with the sorbent.

The sorption systems we proposed were chosen to ensure the highest efficiency, and they comply with most of the above requirements. The use of these systems in combination with flow detectors made it possible to develop automated highly sensitive flow techniques for determination of a large number of elements and to extend the range of objects suitable for analysis.

1. Flow sorption coupled with atomic absorption for determination of Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in potable, natural and waste waters, soil extracts and solutions obtained after digestion of soils and foodstuffs.[75, 80, 84–86] A set of procedures for determination of toxic elements in natural, potable and waste waters, soils and soil extracts, food raw materials, and foodstuffs have been proposed. The procedures were certified by Gosstandart of the Russian Federation. The procedures for determination of Cd, Co, Cu, Mn, Ni, Pb and Zn in potable, natural and treated waste waters and Cd and Pb in soils and soil extracts have been included in the Public Register of the Procedures Approved for the State Environmental Control (PND F 14.1:2:4.59-96 and PND F 16.14-97).

The limits of detection of elements by the flow sorption/atomic-absorption method (a KVANT AGA spectrometer) for preconcentration time of 1 min and atomisation in the propane – butane – air flame were 0.05 (Cd), 0.2 (Cu), 0.5 (Co, Mn, Zn), 1.0 (Pb), 2.0 (Ni) μg litre^{-1} (see Ref. 85). For the quantification of metals present in amounts 10 times as high as the detection limits, the relative standard deviation was 0.02 – 0.03. It should be noted that low detection limits of metals and high reproducibility of the results were attained with complete automation of the whole analysis cycle. The duration of the analysis cycle (with preconcentration for 1 min) was 95 – 105 s (depending on the time of column flushing), and the sampling frequency was up to 37 samples per hour. An increase in the preconcentration time results in lower detection limits of elements and better reproducibility of the determination results.

2. Flow sorption coupled with ICP AES for determination of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn in natural waters.[69, 73] The inductively coupled plasma atomic emission spectrometry (ICP AES) is a highly informational method for solution analysis. The use of a polychromator allows simultaneous determination of a large number of elements (up to 50) for sample consumption of 1 – 5 ml. In our studies, we have accomplished a combination of the flow sorption preconcentration on the DETATA sorbent and ICP AES determination of metals within a single automated cycle.

The non-stationary signals formed during flow determination by sorption coupled with atomic emission spectrometry of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn have been studied. It was found that desorption of all ten elements takes place simultaneously and requires the same period of time (equal signal widths).

The signal recording in the flow sorption coupled with ICP AES determination of elements requires identification of the zone of the concentrate which enters the spectrometer detector in the flow of the desorbing solution. The integration time of analytical signals determined by the size of the concentrate zone in the flow and the pre-integration time, which corresponds to the time it takes for the desorbing solution moving ahead of this zone to pass through the detector, are the key parameters for optimisation of the determination conditions. In the case of desorption of elements from the polystyrene-based DETATA sorbent, both parameters depend on the concentration of the acid in the desorbing solution and the flow rate of this solution. It was shown that all the ten elements can be desorbed with 2 M HNO_3. The optimal flow rate of the desorbing solution is 2 ml min^{-1}. With this flow rate, the integration time for all the elements to be quantified is 20 s and the pre-integration time is 7 s.

Under the conditions chosen, the limits of detection of the elements in solutions by a flow method were 0.2 – 1 μg litre^{-1} and the enhancement factors of the analytical signal due to preconcentration (EF) with respect to those in the direct ICP AES determination (after preconcentration for 1 min) were 17 (Cu), 15 (Cd, Zn), 14 (Co), 11 (Cr, Mn, Pb) and 10 (Fe, Ni, V). The relative standard deviation in the determination of elements present in concentrations of 10 μg litre^{-1} was 0.02 – 0.06.

3. Flow sorption coupled with ICP AES for determination of rare earth elements in solutions of complex composition.[76, 77] To attain the highest signal-to-noise ratio, the composition and the flow rate of the desorbing solution were optimised. The range of quantifiable rare earth metal concentrations (for simultaneous determination) in solutions was $1 - 1 \times 10^{-4}$ μg ml^{-1}.

4. Flow sorption coupled with voltammetry or with X-ray fluorescence for determination of metals in solutions ('stopped-flow systems'). Coupling of the dynamic sorption preconcentration with the electrothermal atomic absorption, inversion voltammetry and X-ray fluorescence implies a discrete analytical cycle. The specific feature of this approach is that the concentrate zone is identified in the flow of the desorbing solution and stopped in the area of analytical signal measurement. 'Stopped-flow systems' are promising, as they combine the advantages of the dynamic preconcentration and the determination methods involved. In the case where the preconcentration time is commensurable with the detection time, automation of the analysis cycle is expedient. It is especially convenient to combine preconcentration of a group of elements with simple and readily available methods of simultaneous multielement determination. Thus dynamic preconcentration of heavy metals on the DETATA sorbent can be coupled with their determination in the concentrates (solutions) by inversion voltammetry or XFA.[87]

X-Ray fluorescence analysis alone does not ensure determination of elements whose concentrations are at the MPC level. The time of measurement for the simultaneous determination of 9 elements using a Spectroscan spectrometer is about 15 min. A simple calculation shows that a 15-min preconcentration by forcing a solution through a DETATA microcolumn at a flow rate of 6 – 7 ml min^{-1} ensures $K_{conc} \approx 200$ (the volume of the desorbing solution is 0.5 ml). When the sorption technique is combined with the stopped flow, the time required for element determination remains the same (during the detection, the elements from the next sample are preconcentrated), while the detection limits markedly decrease. The following detection limits were attained for a frequency of 4 samples per h: 0.005 (Co, Ni); 0.02 (Cu, Fe, Mn, Pb, Zn); 0.05 (Cr) and 0.07 (V) μg ml^{-1} (see

Ref. 87). Owing to the high reproducibility of the results ($s_r = 0.03-0.06$ over a broad range of element concentrations) and the stability of spectrometer operation with time, this method can be recommended for the monitoring of continuous industrial processes.

IV. Preconcentration on polyurethane foams

Polyurethane foams (PUF), an important product of the industrial organic synthesis, are of interest for the sorption preconcentration of substances. These sorbents are distinguished by high efficiency, versatility, chemical and mechanical stability, stability against organic solvents, relatively low cost and ready availability. The sorption properties of these synthetic polymeric materials are largely due to the combination of various hydrophobic (hydrocarbon, aromatic) and hydrophilic (urethane, amide, urea, ester, ether and terminal toluidine) groups, which allows the use of these materials for efficient sorption of both non-polar and polar compounds. A part of the solid phase in PUF is replaced by air,[88] which occurs in the polymer as numerous cells, thus forming an ordered system of solid quasispherical membranes. Owing to the system of cells, the sorbed substance can penetrate inside the sorbent. Thus, the substances are collected not only due to adsorption but also as a result of absorption; therefore, the capacity of PUF is fairly high. Polyurethane foams actually 'dissolve' sorbates in the membranes. This is a unique feature of PUF, which distinguishes them from many other sorbents.

Polyurethane foams have been used in analytical practice since the early 1970s.[89-91] At present, a large body of facts concerning sorption of organic compounds and elements on PUF have been accumulated. The publications generalised in a monograph [92] and reviews [93-98] discuss the reasons for the high efficiency of these sorbents, the factors that influence sorption and the ways of optimisation of the preconcentration and separation conditions of microcomponents. Below we consider (mainly, relying on our data) the characteristic features of sorption of various substances on PUF and discuss the potential of hybrid methods of analysis based on sorption preconcentration coupled with spectroscopic determination directly in the concentrate.

1. Characteristic features of sorption on polyurethane foams

Development of combined and hybrid methods of analysis based on the use of PUF requires study of the laws of sorption processes and elucidation of sorption mechanisms. The knowledge of the chemistry of sorption of substances on PUF can facilitate the selection of practically important sorption systems and to explain (in favourable cases, even to predict) the conditions of sorption in systems not yet studied.

a. Effect of the sorbate hydrophobicity

Comparative estimation of the hydrophobicity of six industrial PUF samples based on ethers (PUF-ET) and esters (PUF-ES) [99] indicates that the surfaces of all these polymers are nearly equal in hydrophobicity. Their hydrophobicity proved to be higher than that of sorbents based on cellulose, cellulose triacetate, polyacrylate (Amberlite XAD-8), silicas (Diasorb-C_4, -C_8, -C_{16}, -phenyl, -carboxyl) but lower than the hydrophobicity of the activated carbon AX-21.

Due to their hydrophobic properties, PUF efficiently sorb molecules containing hydrophobic fragments (for example, polycyclic aromatic hydrocarbons, PAH).[100, 101] The distribution coefficients of PAH are linearly related to their hydrophobicity parameters, *i.e.*, the Hansch's parameters (the logarithms of the distribution constant in the n-octanol – water system, $\log P_{ow}$), by correlation (4) (Table 4). The correlation equations (4) – (7) describe satisfactorily the sorption on PUF of not only PAH but also other aromatic hydrocarbons: the calculated and experimental distribution coefficients of benzene, toluene, acenaphthene, fluorene and fluoranthene are in good agreement with each other.[101]

Table 4. Types of correlations describing the sorption of various organic compounds on PUF.

Class of compounds	Correlation [a]	Correlation coefficient
PAH, aromatic hydrocarbons	$\log K_d = a + b \log P_{ow}$ (4)	0.980 – 0.997
Cationic surfactants of the alkyltrimethylammonium series	$\log K_d = a + b\, n_C$ (5)	0.970 – 0.989
Phenols, phenolcarboxylic acids	$\log K_d = a + b \log P_{ow} - c\, pK_a$ (6)	0.963 – 0.996
Xanthene dyes, cationic metal chelates with 1,10-phenanthroline	$\log K_d = a + b\, \Delta H$ (7)	0.967 – 0.997

[a] a, b, c are constants.

The sorption of homologues of cationic surfactants of the alkyltrimethylammonium series increases with an increase in the chain length, which is indicative of an important role of hydrophobic interactions of the hydrocarbon parts of the cationic surfactant molecules with the PUF hydrophobic matrix and with one another.[102] The $\log K_d$ values follow a linear dependence on the number of carbon atoms in the alkyl radical (n_C) [relation (5) in Table 4].

For phenols with close pK_a values, differences in the sorption are also determined by the hydrophobicity difference. In the series phenol – 3-cresol – 1-naphthol, $\log K_d$ values follow a linear correlation with the hydrophobicity parameter of the phenol on any of the PUF studied [relation (6) in Table 4].[103, 104] Similar regularities are observed in the sorption of phenolcarboxylic acids.[105] The distribution coefficients, the limiting sorption values and the sorption constants of xanthene [106] and sulfophthalein dyes [107] increase with an increase in the hydrophobicity of their molecules in the following sequences: rhodamine 6G < rhodamine 3B < butylrhodamine, thymol blue < bromocresol purple < bromothymol blue < bromocresol green. An important role of hydrophobic interaction in the sorption of dyes was also pointed out in a study.[108]

The sorption of 4-nitrophenylazo derivatives of phenols increases with an increase in the hydrophobicity of the azo component on passing from phenol to 2-cresol and then to 1-naphthol.[109] For the associates formed by cationic surfactants of the alkyltrimethylammonium series with the bromothymol blue (BTB) anion [110] and with phenol and 1-naphthol 4-nitrophenylazo derivatives,[111] it has been shown that sorption increases with an increase in the hydrophobicity of the alkyl radical of the cationic surfactant in the sequence $C_{10} < C_{12} < C_{14} < C_{16} < C_{18}$. In the presence of cationic surfactants, the dependence of $\log K_d$ of ion associates formed by 4-nitrophenylazophenol and 4-nitrophenylazo-1-naphthol on the number of carbon atoms in the alkyl radical of the cationic surfactant is described by linear equations (5) (Table 4).

b. The ability to form hydrogen bonds

As a rule, organic compounds containing a hydroxy group are sorbed more efficiently on PUF-ET, which, in the opinion of many researchers,[104, 105, 112-116] attests to the formation of a hydrogen bond (ether groups are known to be more prone to form hydrogen bonds than the ester groups). In the sorption of compounds containing hydrophobic fragments in addition to a hydroxy group, two factors should be taken into account, in particular, hydrophobicity and the ability to form intermolecular hydrogen bonds. It was shown that the logarithms of the distribution coefficients of phenols [104, 111] and phenolcarboxylic acids [105] are related to their hydrophobicity parameters and the

pK_a values by two-parameter correlation equations [relation (6) in Table 4].

c. The concentration and the nature of the partner ion

Ionised compounds are most often sorbed on PUF as ion associates.[117] The concentration and the nature of the partner ion are important factors influencing their sorption. Typical dependences of the recovery of associates on the concentration of partner ions are curves with saturation.

The sorption of associates of xanthene dyes [106] and cationic metal chelates with 1,10-phenanthroline [118, 119] increases with an increase in the size and hydrophobicity of the anion in the sequence Cl^-, $Br^- < NO_3^- < I^- < SCN^- < ClO_4^-$. A linear correlation is observed between logK_d and hydration energies of anions (ΔH, kJ mol^{-1}) [relation (7) in Table 4]. The distribution coefficients of the associates formed by 4-nitrophenylazophenols [109, 111] and sulfophthalein dyes [107, 108, 119] on PUF-ET in the presence of alkali metal ions increase in the sequence $Li^+ < Na^+ < Rb^+ < K^+$ (the maximum value is observed for potassium). Similar dependences are observed for the sorption of anionic metal complexes (mainly thiocyanate complexes).[120–123] This means that the polyether units of PUF bind selectively alkali metal ions, especially potassium ions. The resulting positively charged fragments of the sorbent promote the recovery of anions.

d. The structure of the PUF polymer unit

The influence of the structure of the PUF polymer unit shows itself in different ways for different groups of sorbates. The sorption of PAH [100, 101] and hydrophobic ion associates, for example, those of cationic surfactants with 4-nitrophenylazophenols,[111] is the same on PUF having different structures but identical hydrophobicities. As the sorbate hydrophobicity increases, the difference between the sorption properties of PUF differing in the structure of the polymer unit becomes less pronounced.[124] Conversely, the effect of the polymer base is essential when specific interactions are present in the system. As a rule, PUF-ET are more efficient for such compounds. In most cases, PUF-ET sorb more efficiently metal thiocyanate complexes,[120–123] heteropoly acids,[125, 126] singly and doubly charged anions of the sulfophthalein dyes,[107, 108, 119] anionic surfactants [102, 119] and 4-nitrophenylazo phenol derivatives.[109, 111] The recovery increases on passing from propylene oxide-based PUF to ethylene/propylene oxide-based PUF and then to ethylene oxide-based PUF.[124]

e. The charge of ions, the composition of the aqueous phase and solution acidity

The sorption of ion associates depends on the charge of ions they contain. Doubly charged ions are sorbed less efficiently on any PUF than singly charged ions, all other factors being the same.[117]

The sorption of associates is influenced also by the solution composition and the pH. Depending on the pH, the compounds sorbed can exist as different species, either as singly or doubly charged species or as neutral molecules.[106, 107, 127] In addition, the sorption properties of PUF can change with the acidity and salt composition of the solution, as they can be modified by hydroxonium and alkali metal ions. It is known that PUF are protonated on contact with mineral acid solutions.[124, 128]

Let us consider some examples. The maximum recovery of phenols [103, 104] and phenolcarboxylic acids [105] is observed for pH $\leqslant$ pK_a-2, where the hydroxy group is not dissociated. As the pH increases to pK_a+2 and further, the recovery of phenol decreases almost to zero. Conversely, the sorption of PAH does not depend on the acidity of the initial solution over a broad pH range (from 4 M HCl to pH 13).[100, 101] The maximum recovery of the oxidised and reduced forms of heteropoly acids on PUF is attained in the range from 4 M HCl to pH 2, which coincide, on the one hand, with the stability region of the corresponding heteropoly anions in an aqueous solution, and on the other hand, with the pH of the maximum extraction of these compounds with oxygen-containing extractants.[124, 125] The quantitative recovery of thiocyanate complexes is attained in the pH ranges of pH 2–3 (Cu), 5–1 M HCl (Co), pH 2–1 M HCl (Fe) and pH 1–2 M HCl (Ti), which coincides with the regions of quantitative extraction of these compounds with oxygen-containing solvents.[124]

2. Chemisorption of polyurethane foams

The chemisorption processes involving the functional groups of macromolecules of polyurethane foams and accompanied by the formation of intensely coloured products have been studied by diffuse reflectance and IR spectroscopy.[129–134] It was found that the terminal toluidine groups of PUF enter into heterogeneous chemical reactions typical of aromatic amines: diazotisation with sodium nitrite, azo coupling with 4-nitrophenyldiazonium tetrafluoroborate, the reaction with active chlorine, and condensation with formaldehyde. The chemisorption of the above-listed substances takes place under relatively mild conditions (aqueous solutions, room temperature, atmospheric pressure), the coloured products are formed rapidly and at rather low concentrations of the compounds in aqueous solutions. The main factors influencing these processes were elucidated, in particular, pH and the acid composition of the aqueous phase, the time of phase contact, the structure of the monomeric unit in the polymer and the concentrations of the reactants. The high efficiency of chemisorption preconcentration of free active chlorine and nitrite and nitrate ions, the intensive colour of the sorbent thus attained, the ready availability and the low cost of the sorbent proved to be attractive for the use of PUF as new polymeric reagents.[129, 130, 133, 134]

3. The state of sorbed molecules in the polyurethane foam matrix

Study of the state of the sorbed molecules in the polyurethane foam matrix is important for extension of the analytical potential of hybrid methods of analysis based on sorption coupled with spectroscopy. In a series of studies (Refs 100, 101, 109–111, 118, 119, 122–125, 127, 135) using the diffuse reflectance spectroscopy and luminescence, the spectroscopic characteristics of the coloured and luminescent sorbates have been studied. If hydrophobic (as in PAH) [100, 101] or electrostatic (as in thiocyanate metal complexes) interactions are the predominant type of intermolecular interactions in the sorbed compounds, no pronounced changes in their spectroscopic characteristics take place.[122–124] The normalised fluorescence, fluorescence excitation, absorption and diffuse reflectance spectra for these groups of compounds incorporated in a PUF matrix or occurring in solution are shifted with respect to each other by not more than 10 nm.

For other groups of sorbed compounds, the changes in the spectral characteristics can be more pronounced. For example, the maxima of the diffuse reflectance spectra of oxidised forms of heteropoly acids as sorbates are shifted bathochromically by 55, 45 and 65 nm for molybdosilicic, molybdophosphoric and molybdovanadophosphoric acids, respectively, with respect to the absorption spectra of aqueous solutions, which is indicative of strong interaction between the heteropoly anion and the polymeric matrix.[125]

The diffuse reflectance spectra of 4-nitrophenylazo phenol derivatives [109, 111] or sulfophthalein dyes [119] as sorbates are shifted bathochromically with respect to those in the absorption spectra of aqueous solutions by 50–60 nm, which may be due to the change in the nature of the ionic bond in the associates caused by ionisation processes taking place in the PUF phase and resulting in the separation of ion pairs to give solvated ions. As shown in a study,[136] PUF membranes contain polar microregions in addition to the hydrophobic ones. Similar structural changes have been observed previously for the ion pairs formed by alkali metal ions with hydrophobic anions in the presence of crown ethers.[137]

On storage of some sorbates, for example, 4-nitrophenylazophenols [111] or acridine yellow,[127] in air, the diffuse reflectance spectra change, in particular, the amplitude decreases or new bands appear. Most often, these processes are reversible and are

related to acid–base interactions taking place in the PUF matrix upon the contact of sorbed compounds with acid or ammonia vapour present in the laboratory air. A method for stabilisation of the colour of 4-nitrophenylazo phenol derivatives as sorbates consisting of treating the material with a solution of tetrabutylammonium hydroxide has been proposed.[111]

In some cases, reactions that are impossible in solutions take place in the PUF matrix. Thus the diffuse reflectance spectrum of Cu(II) thiocyanate sorbed on PUF-ET exhibits a broad band with a maximum at 480 nm, which is shifted bathochromically by 130 nm compared to that in the absorption spectrum of the aqueous solution. The Cu(II) thiocyanate complexes in an aqueous solution and in the PUF matrix were compared by EPR. The hyperfine splitting constants and the g-factors for aqueous solutions and sorbates were determined. It was shown that the $Cu(NCS)_4^{2-}$ complexes in which copper is coordinated by four equivalent nitrogen atoms predominate in aqueous solutions, whereas the PUF matrix incorporates mainly $Cu(NCS)_3^-$ complexes whose inner coordination sphere contains one oxygen-containing group of the polymer.[124]

The product formed in the reaction of PUF-immobilised diphenylcarbazide with chromium(VI) in the presence of tetraphenylborate ions BPh_4^- differs in spectral characteristics from the product formed in the presence of other anions.[122, 123] In the presence of BPh_4^- in highly acidic media (1.5–4.5 M H_2SO_4), the diffuse reflectance spectra of the sorbate exhibit a bathochromic shift (40 nm) and a hyperchromic effect ($\sim$5-fold). The formation of intensively coloured compounds on the PUF surface in the presence of BPh_4^- is also typical of other potent oxidants (O_2, MnO_4^-, $S_2O_8^{2-}$), which may be used for their combined determination at a level of 10^{-8} mol litre^{-1}, the detection limit of chromium being decreased by almost an order of magnitude.

Comparative analysis of the fluorescence spectra of the PAH sorbates allows one to classify all these compounds into two groups.[100, 101] One group includes naphthalene, phenanthrene, acenaphthene and fluorene, for which the fluorescence excitation wavelength (λ_{ex}) is smaller than 310 nm. The fluorescence spectra of these compounds coincide with the fluorescence spectrum of PUF; therefore, it is difficult to quantify them by the solid-phase luminescence technique. The second group includes anthracene, pyrene, fluoranthene and 3,4-benzpyrene, for which λ_{ex} is greater than 310 nm. These compounds develop intensive fluorescence in the PUF matrix in the region where no sorbent fluorescence is observed. The characteristics of the luminescence spectra of binary and ternary mixtures of the PAH sorbates were studied. It was found that the presence of feebly fluorescing naphthalene, phenanthrene, fluorene and/or acenaphthene molecules (even in a 100-fold amount) in the PUF phase together with intensely fluorescing anthracene, fluoranthene, pyrene and 3,4-benzpyrene has virtually no influence on the emission intensity from the latter group. By changing the excitation wavelength, it is possible to distinguish between PAH present as binary or ternary sorbate mixtures in comparable amounts and to identify them on the basis of characteristic bands in the spectrum.[100, 101]

For all the coloured and luminescent compounds, the change in the sorbate concentration does not change either the positions of peaks in the diffuse reflectance or fluorescence spectra or the spectral patterns. Within the linear sections of sorption isotherms, there exists a linear correlation between the Kubelka–Munk function values or the fluorescence intensity and the concentration of the compounds being sorbed in an aqueous solution, which is the reason why these polymers can be used to develop hybrid methods of analysis based on coupling of sorption with photometry or luminescence measurements.[100, 109, 110, 118, 122–124]

4. The technique of preconcentration on polyurethane foams

The technique of preconcentration of elements and organic compounds on PUF differs from that with other sorbents. The sorption preconcentration and separation of PUF can be accomplished in either static or dynamic mode.

The static sorption is performed by two ways. A traditional method is based on shaking (stirring) of the solution under analysis with a known amount of the sorbent, from which air bubbles have been removed. Usually PUF are used as cubes, cylinders, cylindrical discs (tablets) cut or stamped out from a polymer sheet. The PUF cubes or discs occurring in the solution should be squeezed at intervals either manually (for example, by means of the bottom of a glass measuring cylinder) or using special automatic devices.

The dynamic version of sorption implies passing of the solution under analysis through chromatographic column filled with PUF cubes or cylinders. A number of methods for packing of these columns have been developed; a vacuum method is the most popular among them. Yet another specific mode of preconcentration on PUF called the method of 'pulsating column' is implemented by pumping the solution through a sorbent layer situated in a glass or plastic medical syringe. Owing to the sorbent elasticity, the cylindrical core of polyurethane foam can be easily compressed and released by movement of the syringe piston. The pulsating column technique suits perfectly for process automation in the sorption–desorption mode. More detailed information concerning various modes of sorption on PUF from aqueous solutions can be found in monographs[92] and reviews;[93, 94] these publications also describe various types of samplers used for sorption preconcentration of organic compounds in air.

The efficiency of preconcentration on PUF can be increased by increasing the sample volume (Table 5), decreasing the sorbent weight within reasonable limits or by performing successive sorption.[138, 139] In the last-mentioned case, the same sorbent tablet is successively brought in contact with fresh portions of the solution to be analysed. Due to the presence of linear sections on sorption isotherms, high recovery values and the ease of separation of the sorbent from the solution, this method provides efficient preconcentration of compounds from dilute solutions. The absolute amount of the substance that has passed to the PUF phase is equal, to a good approximation, to nqR (n is the number of successive sorptions, q is the absolute amount of the substance in the sample, μg), and R is the recovery.

Table 5. Recoveries and preconcentration ratios for the ion associate formed by 4-nitrophenylazo phenol derivative with cetyltrimethylammonium (4-NPA $\cdots$ CTMA)[138] and for pyrene[139] and sorption time of these compounds from different volumes of aqueous solutions on polyurethane foams.

V /ml	4-NPA $\cdots$ CTMA			Pyrene		
	R (%)	$10^{-2} K_{conc}$	t /min	R (%)	$10^{-2} K_{conc}$	t /min
25	95	7.3	40	99	4.5	10
50	95	16.1	50	98	8.7	15
100	95	27.6	60	99	17.0	20
200	73	45.0	90	98	33.0	30
250	–	–	–	98	41.0	40
500	–	–	–	96	81.0	60

The sorbent capacity, *i.e.*, the greatest amount of the preconcentrated component per unit weight of the sorbent is an important parameter as regards the subsequent isolation of the preconcentrated substances in reasonable amounts. Here the advantages of PUF are obvious, as the preconcentration takes place throughout the whole sorbent volume. The sorption capacities with respect to anionic metal complexes vary from 0.2 to 2 mmol per gramme of the sorbent, *i.e.*, they reach 10% of the sorbent weight.[89, 140–146] Taking into account the sorption sites and the limiting sorption values for pyrene and heteropoly acids, the areas occupied by these compounds in the PUF phase have been calculated.[100, 124, 125] They were found to exceed the specific surface area of PUF by factors of 10 to 340.

It has been noted in a number of publication that PUF have a number of advantages over other polymeric sorbents and carbons for preconcentration of polychlorobiphenyls,[147–150] PAH,[139,150–152] phenols,[113,114,138] organophosphorus and chlorinated acaricides and organophosphorus insecticides [153,154] from waters.

5. Polyurethane foams in sorption spectroscopic and test methods of analysis

The methods of analysis combining sorption and spectroscopic determination are based on the sorption preconcentration of the component to be quantified on PUF, the formation of a coloured or luminescent product on the PUF surface, and its subsequent determination directly in the sorbent matrix by measuring the optical density, diffuse reflectance, luminescence intensity or chromatic characteristics. The sorption preconcentration combined with measurement of the analytical signal on the sorbent surface decreases the limit of detection of the target components by several orders of magnitude, while the use of sorbents modified by specific analytical reagents increases the selectivity of analysis.

Depending on the way of measurement of the analytical signal, the methods based on sorption coupled with spectroscopy can be classified into solid-phase spectrophotometry, sorption photometric and sorption luminescence methods and chromaticity measurements.

The solid-phase spectrophotometry is based on direct measurement of light absorption by the sorbent after it has collected the target component.[155–161] To this end, a thin parallelepiped with dimensions matching the cell dimensions ($2 \times 1 \times 0.1$ cm) is cut out of a PUF plate, a coloured compound is sorbed on it, the sorbent is transferred into the cell filled by an organic solvent and the optical density is measured. The solvent serves as the immersion liquid which decreases light scattering. Methods have been developed for determination of bismuth as the iodide complex,[155] cobalt as the thiocyanate,[156] phosphate ions as the reduced molybdophosphoric heteropoly acid,[157] zinc and bismuth [158] and Hg(II) chloride and phenyl chloride [159] as dithizonates, chromium as blue peroxychromic acid and as the diphenylcarbazide complex.[160,161] These methods are characterised by a rather narrow ranges of linearity of the calibration plots and relatively low reproducibility of the results.

In the method of analysis where sorption is coupled photometry, the appearance or change of the sorbent colour due to sorption of the component under analysis on its surface can be recorded by measuring the diffusion reflectance (Refs 109–111, 119, 121–124, 129, 130, 133, 135, 162–172). The method involving sorption and luminescence measurement is based on preconcentration of the component by a solid substrate followed by determination directly in the sorbent phase using luminescence spectroscopy.[100,173–175] The procedural aspects of the quantitative measurement of diffuse reflectance and luminescence intensity for the sorbates on PUF have been considered.[176] The key characteristics of the analysis of organic compounds, anions and elements based on sorption coupled with photometric determination or with luminescent determination are summarised in Table 6.

In the chromaticity measurements, colour coordinates serve as the analytical signal determined in the sorbent matrix. A method including chromaticity measurements and numerical estimation of the colour intensity of substances sorbed on PUF by means of an office scanner and computer software for digital image processing has been proposed.[177]

Test methods of analysis are quick, simple and cheap techniques for detection and determination of substances that do not require any essential sample preparation, the use of complex instrumentation, complex laboratory equipment or highly qualified personnel.[178] The analytical signal used in test methods is the appearance or a change of the sorbent colour upon collection of the analyte on its surface as a coloured analytical form. Most often, this change is detected by sight, although in some cases, recording by simple instruments is also possible.[178] The possibility of using PUF in test methods of analysis was first noted in 1974.[179] Determination was performed after preconcentration of elements on chromofoams (the term was proposed by Braun [179]), *i.e.*, PUF modified by photometric reagents. On contact of these foams (as small cubes) with the solution to be analysed, the initially white polymer acquires a colour typical of the given photometric reaction. These reactions are highly sensitive. The detection limits for sorption under static conditions and for a sample volume of not more than 1 to 2 ml are tenth or even hundredths of a μg (as, for example, for Co,[179] Cu,[179–181] Cd,[180] Pd,[181] Pb,[179] Cr,[182] Mo [183]).

A different way of using PUF in test methods that does not require the preparation of modified PUF has also been proposed. In a number of studies, [110,118,129,130,138,163,164,184] tablets of non-modified PUF in combination with tubes containing a reagent solution were used as test systems. The reproducibility of the results (s_r) of visual determination against a colour scale varies from 0.1 to 0.5. Test systems based on PUF for determination of Co, Ni, Fe(III), nitrite ions, active chlorine, the total content of phenols and anionic and cationic surfactants have passed the metrological certification procedure at the Urals Research Institute of Metrology of the Russian Federation Gosstandart, have been included in the register of test system types and are now manufactured commercially by the ecological and analytical association Ekoanalitika. The test kits based on PUF are easily manufactured, reliable in operation and can be used to determine environmentally toxic compounds in various types of water

Table 6. Characteristics of determination methods of organic compounds, non-metals and metal ions based on sorption on polyurethane foams and spectroscopy.

Analyte	Quantifiable concentration range /mg litre^{-1}	Detection limit /mg litre^{-1}	Ref.
Diffuse reflectance spectroscopy			
Phenol	0.01 – 0.8	0.003	109, 111
1-Naphthol	0.01 – 1	0.003	111, 163
Gallic acid	0.1 – 10	0.04	164
CTMA [a]	0.2 – 3	0.04	110, 119
CP [b]	0.8 – 8	0.2	110, 119
DDC [c]	1.2 – 50	0.30	118, 119, 165
Si(IV)	0.008 – 0.04	0.003	166
Nitrite ions	0.1 – 4	0.02	129, 133, 134
Nitrate ions	2 – 50	0.5	133, 134
Free active chlorine	0.2 – 15	0.07	130, 134
Fe(III)	0.004 – 0.6	0.001	121 – 123, 167
Co(II)	0.07 – 6	0.02	121 – 123, 168
Cu(II)	0.2 – 10	0.05	124
Ti(IV)	0.008 – 0.5	0.002	123
Sn(II)	0.2 – 4	0.08	124
Ascorbic acid	0.3 – 2.4	0.1	169
Ascorbic acid [d]	0.6 – 4	0.2	135
Ni(II)	0.04 – 4	0.01	121 – 123, 170
Cr(VI)	0.001 – 0.2	0.0004	122, 123, 172
Luminescence spectroscopy			
Anthracene	0.02 – 0.7	0.006	100, 101
Pyrene	0.001 – 0.1	0.0003	100, 101
3,4-Benzpyrene	0.001 – 0.06	0.0004	100, 101
Ru(IV)	0.002 – 0.1	0.0004	174
Se(IV)	0.001 – 0.1	0.0003	174, 175
Cr(VI)	0.01 – 0.4	0.008	173

[a] CTMA is cetyltrimethylammonium bromide, [b] CP is cetylpyridinium chloride, [c] DDC is sodium dodecyl sulfate, [d] the reduction was performed in a microwave field.

including potable and mineral water, soil extracts and juices. If necessary, the test form can be preserved and analysed in a laboratory using diffuse reflectance spectroscopy or (after desorption of the compounds) by HPLC.[138, 139]

V. Preconcentration on non-covalently modified silicas

Silicas differ favourably from other inorganic and organic sorbents: they do not tend to swell, ensure a rather high mass exchange rate, possess chemical stability and mechanical strength, and in some cases, also fairly high hydrolytic stability.[185–188] On the basis of silica, a large number of diverse modified materials that possess chemical features of the immobilised compound and the properties of silica as a solid have been produced.[185–192] Covalently and non-covalently modified silicas can be distinguished.

For preconcentration and determination of metal ions, a number of chemically modified silicas have been prepared and studied, the chemical modification being performed by mono-, di-, tri- and tetramines,[185, 193–195] eriochrome black T,[196] naphthoquinone,[197] carbazides,[194] purpurogallin,[198] nitrogen-containing heterocycles (1,10-phenanthroline, 2,2′-bipyridine, 8-hydroxyquinoline, *etc.*),[199] iminodiacetic,[185, 200] aminophosphonic[201] and carboxylic[202] acids.

Yet another approach is non-covalent immobilisation of analytical reagents on silicas. Depending on the chemical nature and the structure, analytical reagents can undergo electrostatic, donor-acceptor, hydrophobic and other types of interaction with the silica surface groups and thus become attached to the surface.[203] It has been proposed to use immobilisation both to improve the chemicoanalytical properties of the reagents and to design new organic reagents.[204] The non-covalent modification of silochromes and other silica gels by complexing analytical reagents has been studied fairly comprehensively.[205–235]

Terada *et al*. have prepared and described silica gels modified by 2-mercaptobenzothiazole,[205–207] 2-mercaptobenzoimidazole, 2,5-dimercapto-1,3,4-thiadiazole,[207] thionalide,[208, 209] *p*-dimethylaminobenzylidenerhodanine[210] and 1-nitroso-2-naphthol.[211] Ukrainian researchers immobilised on silica gels dodecylaminoethyl-β-triodidoammonium iodide, high-molecular-mass quaternary ammonium salts,[212, 213] 1,10-phenanthroline,[214, 215] dithizone and zinc dithizonate,[216] 1-(2-thiazolazo)-2-naphthol[217] and other reagents[218–221] and found that a substantial contribution to the retention of reagents is made by the formation of hydrogen bonds between the donor atoms of the reagents and the silanol groups on the silica gel surface.[212, 217] For attaching of readily water-soluble organic complexing reagents such as nitroso-R-salt,[222] eriochrome black T,[223] calcion,[224] titanium yellow[225] and zincon[226] to silica gels, Kocjan *et al*. have proposed that the reagent to be fastened should be preliminary extracted into chloroform as an ionic associate with methyltricaprylammonium chloride (Aliquat 336) and, after treatment of silica gel, chloroform was removed by evaporation. Heterocyclic azo compounds were immobilised on silica gels of various brands through sorption from aqueous and water–organic solutions.[227–235] Ivanov and co-workers prepared and characterised silica gels modified by 4-(2-pyridylazo)resorcinol (PAR),[228, 229] 1-(2-pyridylazo)-2-naphthol (PAN),[228–232, 234] 4-(2-thiazolylazo)resorcinol,[233] 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PAAP).[234, 235]

Complexing sorbents based on non-covalently modified silica gels are often used for preconcentration under static conditions to determine metal ions, including radioactive ones.

The few papers dealing with non-covalently immobilised redox reagents show that the redox properties change upon immobilisation.[236–239] Examples of the practical use of redox sorbents are virtually missing. We have prepared and studied a number of complexing and redox sorbents. Diverse analytical reagents were immobilised in two ways, either sorbed on the surface of modified silicas containing hydrophobic and ion exchange groups or incorporated into xerogels of silicic acid using the sol–gel process.

1. Preparation and characteristics of modified silicas

a. Hydrophobised silicas and capillary columns modified with complexing reagents

In the mid-1990s when we started our studies, only a few examples of non-covalent modification of hydrophobised silicas were known.[240–245] We have studied immobilisation, on reverse-phase silica gels with alkyl (SG-C_1, SG-C_8, SG-C_{16}), nirtile (SG-CN) and phenyl (SG-P) groups and in capillary columns with hydrophobic inner surface, of the following reagents: hydroxyquinolines [2-methyl-8-hydroxyquinoline (MOx),[246, 247] 8-hydroxyquinoline (Ox),[246–248] 5-phenylazo-8-hydroxyquinoline (PAOx)[246, 247]; oximes [nioxime (NIO),[246, 247] dimethylglyoxime (DMGO),[246, 247] salicylaldoxime (SAO)[246, 247]; β-diketones [benzoylacetone (BA),[246, 247] thenoyltrifluoroacetone (TTA),[246, 247] 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP)[246, 247, 249]; bis(2-ethylhexyl) hydrogen phosphate (BEHHP);[246, 247, 249] azo compounds [PAR,[246, 250] PAN,[246, 251–253] sulfochlorophenolazorhodanine (SCPAR),[246, 250] 1-(6-bromo-2-benzothiazolylazo)-2-naphthol (BBT),[246, 250] lumogallion (LG),[246] cadion (CD),[246, 250, 251] hexaoxacycloazochromium (HOCAC),[246, 253] pyrogallol and bromopyrogallol red[246, 252]; triphenylmethane and xanthane derivatives [xylenol orange (XO),[246, 251, 252, 254] crystal violet (CV)[246, 250]; N,O,S-macrocyclic compounds[246, 255–257] and octaethylporphyrin (EEP),[246, 255] sodium diethyldithiocarbamate (DDTC),[246, 249, 252] sodium rhodizonate,[246, 252] 1-nitroso-2-naphthol (NN),[246, 249, 252, 258, 259] 4-dimethylaminobenzylidenerhodanine (DMABR),[246] 2,2′-dipyridine (D),[246, 252, 258] 1,10-phenanthroline (P),[246, 252, 258] diphenylcarbazone (DPCone),[246] diphenylcarbazide (DPCide),[246] quinalizarin (QL).[246, 260]

We proposed capillary columns with a hydrophobic inner surface for the on-line sorption preconcentration and separation of metal ions. For this purpose, the inner surface of quartz capillary tubes (internal diameter 0.45–1.1 mm, length 1–10 m) was chemically etched and then modified *in situ* with organosilicon compounds (dimethyldichlorosilane S-C_1, methylhexyldichlorosilane S-C_6, diphenyldichlorosilane S-P) and their polymeric analogues (S-polyC_1, S-polyC_6, S-polyP).[257, 253, 260] It was found that the major contribution to the retention of reagents on hydrophobised surfaces is made by the distribution mechanism, which determines the behaviour of the reagents in organic solvent–water extraction systems. As the reagent and surface hydrophobicities increase, for example, with an increase in the number of atoms in the carbon chain, $C_1 < C_8 < C_{16}$, the capacity increases. All the reagents we studied are strongly held on 'phenyl' hydrophobic surfaces, apparently, due to non-specific π–π-interactions between the aromatic systems of the reagents and the surface. In the sorbents we studied, the interaction between the donor atoms of the reagents and the surface silanol groups does not make a substantial contribution to the retention of the reagents (apparently, due to the high density of grafting of hydrophobic groups).[246, 247, 250–253, 260, 261]

The strongest retention of the reagents is observed in slightly acidic and neutral media in which the molecular forms of the reagents predominate.[246–261] In the presence of non-ionic surfactants (Triton X-100 and Bridge 35), the capacity of a hydrophobic surface markedly increases.[246, 262] Probably, a hydrophilically hydrated reagent becomes hydrophobically hydrated in micellar media, which enhances the hydrophobic interactions.[263]

The service life of complex-forming sorbents (the reproducibity of the retention times of metal ions) prepared based on hydrophobised silicas is rather long: for example, the Ox/SG-C_{16} sorbent can be used 30 times in the sorption–desorption mode[248] and sorbents based on PAOx, diaza-18-crown-6 (DAC) and OEP withstand up to 100 cycles.[246]

The modification of hydrophobised surfaces under dynamic conditions allows one to obtain complex-forming sorbents within

several minutes. Conditions for modification – regeneration of packed micro and capillary columns in an automated mode have been selected; after modification for 30 – 120 s, capillary columns can be used in continuous flow analysis systems for up to 15 h.[246, 249, 251, 260]

Dynmic sorption of Ca, Mg, Al, Mn(II), Fe(III), Co(II), Ni, Cu(II), Zn, Cd, Pb and Ag(I) on modified silica gels and capillary columns has been studied in the off-line and on-line modes.[246 – 261] The key factors affecting the sorption behaviour of metals include the nature of immobilised complexing reagent (first of all, the set of donor atoms) and the sample pH and flow rate.

The conditions for quantitative sorption of metals are virtually the same as the optimal conditions for the reactions of these metals with free reagents in solutions.[246 – 261] Therefore, the enormous body of data accumulated on the complexation of metal ions with analytical reagents in solutions (in particular, for solvent extraction) can be utilised to design sorbents with specified properties.[246]

To increase the selectivity of sorption, the most selective complexing reagents have been immobilised; mixed sorbents [246, 248, 261, 264, 265] and exchange sorption [249] have been used. Sorbents containing at least two sorts of functional groups (complexing, ion exchange, and so on) are referred to as mixed sorbents. If the compound to be sorbed reacts with both sorts of group, its retention can be smoothly controlled by varying their ratio.[264] Mixed sorbents are used in chromatography to enhance the separation of organic substances [266 – 269] or metal ions.[270] Examples of modification of the substrate simultaneously by hydrophilic and hydrophobic reagents have been reported.[268, 269] Mixtures of ion exchangers have been used for simultaneous determination of cations and anions from the same sample;[271] and mixed metal hydroxides and phosphates have been used for selective sorption preconcentration of Ca, Mg, Sr and Ba.[272] We have proposed preparing mixed sorbents by modification of hydrophobised surfaces with mixtures of complexing reagents with different sets of donor atoms. The sorption behaviour of metals can be controlled (for example, to ensure that a required metal is eluted first) by mere variation of the ratio of complexing reagents in the modifying solution.[246, 248, 261, 264] Mixed sorbents have been used to increase the selectivity of sorption preconcentration,[246, 248, 261, 265] including that in the on-line mode,[261] and for TLC separation.[264]

Exchange sorption is also employed to increase the selectivity of the sorption process. The immobilised complexing reagent is loaded with a metal ion and then used to recover another metal ion.[249] It is obvious that this approach resembles exchange solvent extraction; however, the sorption version does not require the presence of an organic solvent and implies a much lower consumption of the reagent; this version is faster and can be more easily automated. The metal ion-loaded complexing sorbents based on non-covalently modified hydrophobised silicas ensured a record selectivity of the sorption preconcentration of Cu(II) and Fe(III).[249]

Non-covalently immobilised complexing reagents have been used to develop hybrid methods for metal determination that combine sorption preconcentration and separation.[246 – 261, 265, 273]

b. Hydrophobised silicas and ion exchangers modified by redox reagents

The immobilisation of quinone imines (2,6-dichloroindophenol, 2,6-dibromoindoguaiacol, indophenol blue, Bindschedler's green, variamine blue, phenol blue), thiazine dyes (methylene blue, toluidine blue), *N*,*N*-diethyl-*p*-phenylenediamine (DPPDA) and benzidine on Silochrome S 80 (SG), reverse-phase silica gels (SG-P, SG-C_{16}, SG-CN) and ion exhange resins with sulfo groups (SG-SO_3^-) and tetramethylammonium groups (SG-TA) has been studied.[274 – 278] In addition, benzidine was grafted covalently to silica gel and cellulose [278] and quinone imine was immobilised on ion exchangers obtained by modification of SG-CN by solutions of cationic and anionic surfactants.[277]

The retention of reagents depends substantially on the nature of the sorbent and the solution pH. Silica gels retain strongly thiazine dyes (methylene blue, toluidine blue) and DPPDA (apparently, due to the formation of hydrogen bonds between the amine and imine nitrogen atoms of the reagents and the silanol groups of the substrate surface).[274, 275] In weakly acidic and neutral media (when molecular species predominate), quinone imine derivatives are firmly held on SG-P. Indophenols are held on an anion exchanger (SG-TA) in an alkaline medium where indophenolates predominate. The protonated forms of indamines and benzidine are held on cation exchangers (SG-SO_3H).[276, 277]

The redox equilibrium involving non-covalently immobilised reagents is attained within a few minutes.[276, 278] In the mode of successively repeated oxidation – reduction cycles, indophenol- and indanine-based sorbents are almost completely reversible. Non-covalently immobilised 2,6-dichloroindophenol can be used in 50 cycles and 2,6-dibromoindoguaiacol and Bindschedler's green, in 20 cycles.[277]

The nature of substrates has a pronounced influence on the acid – base and redox properties of the reagents. Whereas sorption on reverse-phase silica gels does not change the acid – base properties, sorption on cation exchangers markedly enhances the acidic properties of reagents.[277] Indophenols and indamines have been used as examples to elucidate the influence of non-covalent immobilisation on the redox properties of reagents. For Bindschedler's green, the greatest difference between the formal redox potentials in a solution and on a sorbent surface was found in the case of SG-P.[277]

The redox sorbents considered were used to develop hybrid methods for determination of sulfur-containing reducing agents, ascorbic acid, free active chlorine and aniline.[274 – 278]

c. Xerogels of silicic acid modified by analytical reagents

The sol – gel process is now widely used to obtain materials with specified properties. Sol – gel materials are characterised by high strength and high thermal and light stabilities, many of these being optically transparent. Using sol – gel process, it is possible to modify materials by various substances, in particular, analytical reagents.[187, 279 – 285]

Sol – gel materials based on silica (xerogels, XG) are used most often for analytical purposes. The sol – gel process is performed in the presence of catalysts. The porosity and the specific surface area of xerogels depend substantially on both the conditions of the sol – gel process (the composition of the mixture subjected to hydrolysis, the nature of the catalyst, and the pH) and on the drying conditions.[279 – 284]

Modified sol – gel materials can be prepared either by using functionally substituted alkoxysilanes containing alkyl, amino, vinyl, epoxy, mercapto and other groups [187, 280, 285 – 287] or by adding the compound to be grafted at the sol formation stage.[286 – 323] The latter approach is obviously more versatile and has an almost infinite potential, because in this case, retention is mainly provided by the mechanical capture of substances by the network silica structure formed during the gelation.

The immobilisation of an analytical reagent (rhodamine 6G) on a sol – gel material was first accomplished in 1984.[289] However, intensive research along this line started only in 1990 when Avnir and co-workers [290] concluded, based on the data accumulated at that time, that substances incorporated in sol – gel materials can participate in chemical reactions. The materials now obtained include silica-based monoliths and films modified by acid – base indicators (azo, phthalein and sulfophthalein compounds and by porphyrins),[291 – 295] complexing organic reagents (ethylenediaminetetraacetic acid, 1,10-phenanthroline, alizarin, quinalizarin, 1-nitroso-2-naphthol, dimethylglyoxime, sodium rhodizonate, hydrorubeanic acid, cuproin, gallocyanin, morin, eriochrome cyanine, diphenylcarbazide) [286, 290, 296 – 303] and metal salts.[290] Sol – gel process is a convenient way of immobilisation of biological molecules (proteins, enzymes, antibodies); interesting data concerning this issue have been reported in reviews.[304 – 306]

The protolytic reactions involving acid – base indicators incorporated in sol – gel materials have been studied fairly comprehensively.[292, 294] Complexation reactions have been less investigated [only the nickel – dimethylglyoxime,[286] iron(II) – 1,10-phenanthroline,[287] aluminium – morin,[300] copper(II) – eriochrome cyanine (ECC) systems have been studied in detail].[300] It has been noted that the retention of complexing reagents and their interaction with metal ions depends appreciably on the material porosity.[286, 300]

The sol – gel materials modified by analytical reagents have been used for determination of metal ions by solid-phase spectroscopy[298 – 300] and by test methods (indicator tubes),[287, 296, 297] for the design of spectroscopic[301 – 317] and electrochemical sensors[318, 319] and as sorbents.[187, 286, 320 – 323] A study of affinity sorbents — sol – gel materials modified by polyclonal antibodies — has demonstrated a better selectivity of the antigen – antibody interaction.[322, 323] A substantial limitation hampering the extensive use of sol – gel materials in analysis is the long time it takes for sorption equilibrium to be established (in some cases, up to several days).

Good results have been obtained in gas and liquid chromatography used to separate organic compounds on capillary columns modified by ion exchange or hydrophobic sol – gel films.[324 – 328] The use of capillary columns containing sol – gel monoliths has been proposed.[327]

Our studies[246, 250, 273, 329 – 344] have promoted extensive introduction of sol – gel materials modified by analytical reagents into the chemical analysis practice in Russia. We have developed a new method for the preparation of silicic acid xerogel powders with specified physicochemical properties (specific surface area, pore diameter, concentration of the immobilised reagent).[329] These were used to immobilise analytical reagents promising for preconcentration, separation and determination of metal ions, anions and a number of organic compounds including those whose immobilisation had been studied on hydrophobic surfaces: hydroxyquinolines [Ox,[246] 5,7-dibromo-8-hydroxyquinoline (5,7-dibromo-8-Ox)[246, 342]; azo compounds [PAN,[246, 250, 331, 332] PAR,[246, 250, 333] 4-(2-thiazolylazo)-2-naphthol,[246] SCPAR,[246, 250] BBT,[246, 250] LG,[246] CD,[246, 250] HOCAC,[246] sulfarsazene (SA)[246]; triphenylmethane and xanthone derivatives [chromazurol (CAZ),[246, 334, 335] sulfochrome (SC),[334] ECC,[246, 334] XO,[246, 331, 336] CV[246, 250]]; 1,10-phenanthroline,[246] bathophenanthroline (BP),[246] DPCide,[246, 335] DPCone,[246, 336] morin,[246] chrompyrazol 1 (CP 1),[246] copper(II),[246] cobalt(II),[246, 337] iron(III),[246, 338] molybdophosphoric acid and its ammonium salt, Vavele reagent (VR) (a mixture of 12- and 18-row molybdophosphoric acids),[246, 339 – 341] aromatic hydroxy compounds [1- and 2-naphthols, 2,7-dihydroxynaphthalene, *N*-(1-naphthyl)ethylenediamine, *p*-hydroxydiphenyl],[246, 342] 4-aminoantipyrine (4-AAP),[246, 343] disodium 4,4′-dithiobis(8-chloro-1-hydroxy-2-phenylazonaphthalene)-3,6-disulfonic acid (BAS) and butyrylthiocholine (BTCI).[344] Methods for the synthesis of modified sol – gel materials with a specified concentration of an analytical reagent, in particular, those modified by mixtures of reagents [a complexing reagent and a surfactant,[333, 334] molybdophosphoric heteropoly compound and copper(II),[246, 341] and BAS and BTCI] have been developed.[344]

Data on the thermodynamics and kinetics of heterogeneous reactions involving immobilised analytical reagents have been obtained. It was shown that inclusion of complexing reagents of various classes or 1-naphthol and 4-aminoantipyrine into silicic acid xerogel powders enhances the acid – base properties of the reagents.[246] Apparently, this is due to the reaction of active hydrogen atoms of immobilised compounds with the silanol groups in the bulk of the xerogel matrix. The formation of complexes in xerogels of silicic acid is possible upon immobilisation of both a complexing reagent and a metal ion. Complexes with a metal : reagent ratio of $\leqslant 1:3$ are formed in the xerogels. The equilibrium constants of heterogeneous reactions vary in parallel with the stability constants of complexes in solutions, which makes it possible to predict the analytical properties of reagents incorporated in xerogels of silicic acid.[246] Xerogels modified by molybdophosphoric heteropoly compounds (HPC) withstand at least 30 oxidation – reduction cycles. It was found that the oxidative ability of molybdophosphoric HPC is enhanced upon their inclusion into xerogels of silicic acid.[339 – 341] Various reactions can take place in xerogels of silicic acid: azo coupling, diazotisation – azo coupling and oxidative condensation.[246, 342, 343] For example, in xerogels modified by aromatic hydroxy compounds (the best results were attained with 1-naphthol), reactions with diazotised anilines yield azo dyes.[246, 342] The xerogel modified by a mixture of sulfanilic and chromotropic acids reacts with nitrite ions (diazotisation – azo coupling reactions).[246] The selectivity of oxidative condensation of phenolic compounds in 4-aminoantipyrine substantially increases in xerogels.[246, 343]

The conditions of interaction of choline esterase with BAS and BTCI contained in a xerogel have been selected: first, enzymic hydrolysis of BTCI takes place and then the resulting thiocholine reacts with BAS, which is accompanied by a sharp colour change.[344]

In two publications,[246, 330] reactions of inorganic and organic compounds with modified xerogels have been considered from the standpoint of the general mass transfer theory as sequences of the following processes: diffusion of a reactant from the bulk to the surface of modified xerogel particles (external diffusion), diffusion inside the pores (internal diffusion) and the proper chemical reaction with immobilised reagents. The rate-limiting steps were established and the rate constants for diffusion processes were determined.[246]

Interesting data on the effect of microwave radiation and ultrasound on the rate of heterogeneous processes involving sol – gel materials have been obtained. The microwave radiation intensifies all stages of the heterogeneous process. The time it takes to attain the equilibrium decreases three- to four-fold, while the rate constants for diffusion processes are almost doubled. It was shown that it is expedient to use 200 – 600 W microwave radiation.[246, 330] To accelerate the processes whose duration is determined by external diffusion, ultrasonic treatment was used. The high intensity of stirring, and apparently cavitation phenomena markedly accelerate heterogeneous reactions by intensification of, most of all, the external diffusion (the rate constants for external diffusion increase by a factor of almost three).[246, 330]

In powders of sol – gel materials, heterogeneous reactions proceed much faster than in monolithic structures: whereas the complexation of copper(II) with the monolith modified by eriochrome cyanine requires 48 h,[300] the reaction with a powder modified with the same reagent (pore diameter 40 Å) takes place over a period of 5 min.[334] An increase in the average pore diameter in the powders from 20 to 200 Å (which can be easily attained by using the method for the preparation of xerogels we developed) results in a higher rate of internal diffusion, which almost halves the time required to reach the equilibrium.[246]

To accelerate the reactions between molybdophosphoric HPC immobilised on xerogels and reducing agents, we synthesised xerogels containing simultaneously molybdophosphoric HPC and copper(II) as the catalyst for their reduction. The results indicate a substantial acceleration of the heterogeneous reaction, *i.e.*, a catalytic reaction takes place.[341]

2. The use of non-covalently modified silicas in analysis

Due to the simplicity of preparation of silicas non-covalently modified by analytical reagents with a high concentration of firmly attached reagents and to the high rate of sorption, these materials can be regarded as promising sorbents. They have been used for sorption preconcentration and separation of metal ions, including that in the on-line mode,[246 – 252, 255, 257, 259 – 261, 265] and for the solid-state spectroscopic and test determination of metal ions, anions, reducing agents, oxidants and organic compounds.[246, 254, 258, 274 – 278, 330 – 344]

a. Determination of metal ions by sorption coupled with atomic absorption spectrometry or photometry

The sorption preconcentration of metal ions on reverse-phase silica gels and xerogels of silicic acid non-covalently modified by complexing reagents results in high preconcentration factors (up to 5×10^3). The capacities before breakthrough of the complexing sorbents with respect to metal ions are rather high (5–100 μmol g^{-1}). The high preconcentration efficiency is determined by rather high flow rates of the sample: from 3–4 ml min^{-1} (for complexes) to 20 ml min^{-1} (for ion associates).[246–248, 250–253, 259, 273]

An obvious advantage of complexing sorbents based on modified silicas is the high selectivity attained by immobilisation of selective complexing reagents, choice of appropriate conditions and by using mixed sorbents [246, 255, 261, 265] or exchange sorption.[246, 249]

For sorption preconcentration of metal ions, the use of cartridges filled with hydrophobic silica gels modified by complexing reagents (XO, PAN, CD, Ox and DMABR) has been proposed. If necessary, modification can be carried out under field conditions on the sampling site.[246, 248]

The procedures proposed for determination of Ag, Cd, Cu(II), Fe(II), Mn(II) and Pb using sorption preconcentration coupled with atomic absorption or photometry allow the use of serial, readily available and cheap spectrophotometers and flame atomic absorption spectrometers to determine traces of metals in natural, potable and waste waters, atmospheric precipitates and industrial solutions at the MPC level (Table 7). The sorption–atomic absorption procedure for determination of Cd, Pb and Zn in atmospheric precipitates or natural and waste water using preconcentrating cartridges filled with reverse-phase silica gel SG-P non-covalently modified by XO has passed the state metrological certification procedure (PND P 14.1:2.81-96) and was approved for the use in the state ecological monitoring.[246]

b. Continuous flow analysis

Flow analysis of samples has a high sampling frequency and good reproducibility and requires small amounts of samples and reagents. Currently, the development of flow analysis is related to the possibility of performing sorption preconcentration and separation and solid-state detection under dynamic flow conditions (often, on a micro scale).[345]

The reasonable efficiency ($CE = 5–95$) and high selectivity of complexing sorbents based on non-covalently modified silicas determine the success in using them for the on-line sorption preconcentration and separation of metal ions.

A study [273] describes a flow distribution system for automated photometric determination of 0.009–0.3 mg $litre^{-1}$ of aluminium in waters and beverages including the on-line sorption preconcentration on a microcolumn filled with xerogel of silicic acid modified by chromazurol (50 samples per hour).

We developed a universal flow distribution system for determination of metal ions. The system core is a sorption column. This can be either a microcolumn packed with reverse-phase silica gel or a capillary column with a hydrophobic inner surface, which is modified alternately by various complexing reagents that ensure the retention of different metal ions (Fig. 3). The system allows automated sorption separation of metal ions, preconcentration of one ion and separation of the interfering metal ions; hence, a number of analytical problems can be solved. Automated highly productive procedures for determination of traces of metal ions [Cd, Pb, Co(II), Cu(II), Fe(III)] or for simultaneous determination of two metal ions [Ca–Mg, Co(II)–Fe(III), Pb–Fe(III)] in atmospheric precipitates have been developed. The high selectivity of the flow photometric determination of metal ions with on-line sorption preconcentration is ensured by the appropriate choice of the sorbent and by the sorption–desorption and photometric detection conditions. Advantages of capillary columns over packed microcolumns include higher sampling frequency and better metrological characteristics of the determination. The main reason is the decrease in sample diffusion in the case of capillary columns (Table 8).[246, 251, 259–261]

For determination of Pb(II), Co(II), Mn(II) and Fe(III) traces in natural waters, the versatile gas distribution system was supplemented by a block for on-line sample preparation (destruction of the metal complexes with humic and fulvic acids) in a microwave field (see Fig. 3).[346]

The flow distribution systems for the simultaneous determination of cadmium and zinc, aluminium and manganese(II) have been developed on the basis of on-line sorption separation on

Table 7. Characteristics of metal determination by sorption on non-covalently modified silicas ($n = 3$, $p = 0.95$) coupled with atomic absorption spectrometry and photometry.

Sorbent	Analyte	Quantifiable concentration range /mg $litre^{-1}$	Detection limit /mg $litre^{-1}$
Atomic absorption spectrometry			
N_4/SG [a]	Co(II)	0.025–0.15	0.02
	Cu(II)	0.020–0.12	0.01
DMABR/SG-C_{16}	Ag(I)	0.002–0.1	0.001
Ox/SG-C_{16} (see [b])	Cd	0.0009–0.06	0.0003
	Pb	0.06–0.2	0.03
CD/SG-P	Cd	0.006–0.1	0.002
QO/SG-P [c]	Cd	0.0005–0.01	0.0002
	Pb	0.001–0.1	0.0006
	Zn	0.01–0.1	0.004
Ox/SG-C_{16} + Cu	Fe(III)	0.38–3.61	0.25
BEHHP/SG + Zn	Fe(III)	0.03–1.70	0.02
PMBP/SG + Co	Cu(II)	0.06–0.85	0.03
BBT/XG	Cd	0.006–0.1	0.002
Spectrophotometry			
PAN/SG-P	Mn(II)	0.0006–0.01	0.0003
QO/SG-P	Fe(III)	0.001–0.03	0.0005
$(DDTC)_2$Pb/SG	Cu(II)	0.13–3.20	0.02
CV/XG	Cd	0.01–0.34	0.002

[a] N_4 is the tetraaza analogue of dibenzo-18-crown-6; [b] joint determination of Cd and Pb; [c] joint determination of Cd, Pb and Zn.

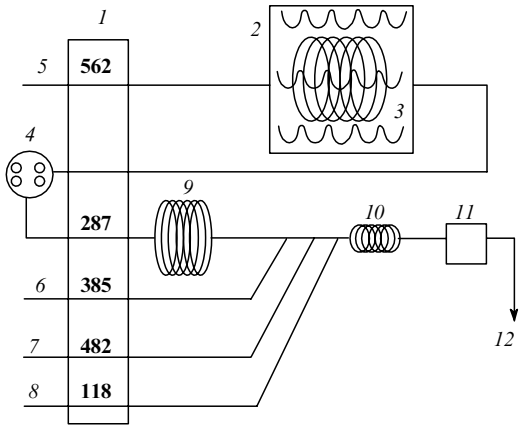


Figure 3. Flow distribution system for photometric determination of metals in natural waters.
(*1*) Peristaltic pump, (*2*) microwave oven, (*3*) reaction helix, (*4*) sampler, (*5*) inlet of the modifying solution, the sample and the rinsing solution, (*6*) inlet of the photometric reagent, (*7*) inlet of the buffer solution, (*8*) air inlet, (*9*) capillarty column, (*10*) mixing helix, (*11*) flow photometer, (*12*) discharge.
The values typed in bold in this and in the next Figure are the corresponding flow rates in μl min^{-1}.

Table 8. Characteristics of flow photometric determination of metals with the on-line sorption preconcentration and separation on microcolumns (SG-P) and capillary columns (S-P).

Analyte	Modifying reagent	Column	Quantifiable concentration range /mg litre^{-1}	Sampling frequency, samples per h
One-component systems				
Copper(II)	PAN	SG-P	0.006 – 0.06	19
	PAN	S-P	0.003 – 1.5	19
Cobalt(II)	QO	SG-P	0.005 – 0.05	18
	QO	S-P	0.003 – 0.9	18
Iron(III)	QO	SG-P	0.02 – 1.0	17
	QO	S-P	0.005 – 3.0	17
Lead	HOCAC	S-P	0.01 – 1.0	17
Two-component systems				
Zinc + iron(III)	QO	SG-P	0.5 – 6.5 0.3 – 1.7	30
	QO	S-P	0.5 – 6.5 0.3 – 1.7	60
Copper(II) + manganese(II)	PAN	SG-P	0.06 – 4.0 0.3 – 1.7	30
	PAN	S-P	0.06 – 4.0 0.3 – 1.7	51
Calcium + magnesium	Quinalizarin	S-P	2 – 32 0.1 – 2	55

mixed sorbents.[246] For automation of routine agrochemical analyses, a flow distribution system for simultaneous photometric determination of three components — manganese(II), aluminium and iron(II)[261] — has been developed; the system combines the on-line sorption separation on a mixed sorbent with twice repeated flow detection (23 samples per hour) (Fig. 4).

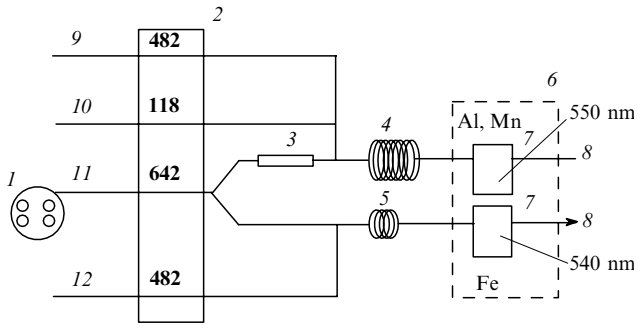


Figure 4. Flow distribution system for simultaneous photometric determination of Mn(II), Al and Fe(III) with the on-line sorption separation and double detection.
(*1*) Sampler, (*2*) peristaltic pump, (*3*) microcolumn, (*4*, *5*) mixing helices, (*6*) flow photometer, (*7*) flow cells, (*8*) discharge, (*9*) inlet for the solution of XO in a buffer solution, (*10*) air inlet, (*11*) inlet of the sample and the rinsing solution, (*12*) inlet of a XO solution in 0.1 M nitric acid.

c. Solid-state spectroscopy and test methods

Due to the simplicity and high sensitivity of the determinations, the title methods are now attracting considerable attention of researchers. The determination is based on a chromogenic heterogeneous reaction carried out under static conditions (as a result of sorption of pre-synthesised coloured compounds by appropriate sorbents or the reaction of the analyte with immobilised chromogenic reagents) and measurement of the spectroscopic characteristics of the solid phase. The spectroscopic characteristics of the indicator powders are recorded, after the sorption equilibrium has been established, by diffuse reflectance spectroscopy, solid-state spectrophotometry or chromaticity measurements.[347, 348]

When the colour can be estimated by sight or portable instruments can be used, test versions of these methods can be developed.[178, 349]

Solid-state spectroscopy has found the most extensive application for determination of metal ions. To this end, ion exchange resins,[348] fibrous materials and fabrics with ionogenic groups filled by ion exchangers,[350 – 352] cellulose sorbents,[348] silochromes[212 – 221, 228 – 235] and sol – gel materials (monoliths and films)[298 – 300] have been used.

The high porosity and optical transparency of silicas modified by analytical reagents and the possibility of implementation of various heterogeneous reactions in the solid phase ensured further development of methods based on solid-state spectroscopy. Highly sensitive and simple procedures for determination of Mn(II), Cu(II), Zn, Mo(VI), Cd, Pb; nitrate, nitrite, fluoride and phosphate ions; the total content of sulfur-containing anions, ammonium ions, anionic surfactants, ascorbic acid, hydrazines, asymmetric dimethylhydrazine, anilines, phenols, naphthols and esters have been developed (Table 9, 10). The procedures are fairly quick; it takes only 5 – 20 min to attain the sorption equilibrium.[246, 274 – 277, 330 – 343]

Quantification by these procedures does not imply the use of expensive instrumentation and can be performed by portable photometers and reflectometers; in the test version, this is also done using colour scales. The procedures proved useful in analysis of field samples: water, industrial process solutions, foodstuffs, pharmaceuticals and biological liquids.[246]

Test systems based on indicator powders have passed metrological certification procedure at the State Metrological Scientific Centre based on Urals Research Institute of Metrology; they have been included in the register of test system types, approved for the use and are now manufactured commercially by the limited liability company MedEkoTest (Moscow).

Table 9. Characteristics of solid-state spectrophotometric determination of inorganic and organic substances using modified silicas ($n = 3$; $p = 0.95$).

Analyte	Indicator powder	Quantifiable concentration range /mg litre^{-1}	Detection limit /mg litre^{-1}
Ag	SCPAR/XG	0.5 – 8.0	0.1
Cd [a]	BBT/XG	0.02 – 0.2	0.01
		0.005 – 0.2	0.005
Cu(II)	ECC/XG	0.002 – 0.2	0.001
Zn	PAR + CP/XG	0.4 – 10	0.2
Mn(II)	PAN/XG	0.5 – 5.0	0.5
Mo(VI)	LG/KG	0.2 – 6.0	0.2
Pb	CP 1/XG	0.01 – 4.0	0.005
F^-	QO/XG	0.5 – 10.0	0.3
Cl^-	DPCone/XG	1.0 – 30.0	0.5
Free active chlorine	DPPDA/SG-SO_3^-	0.02 – 0.8	0.01
Hydrazines	PB + Cu(II)/XG	0.2 – 2.0	0.1
Ascorbic acid	PB + Cu(II)/XG	1 – 50	0.3
Naphthols	Co(III)/XG	0.1 – 4.0	0.05
Esters	Fe(III)/XG	17 – 450	11
Aniline	1-Naphthol/XG	0.05 – 10	0.02
		0.1 – 10 [a]	0.05 [a]
Phenols	4-AAP/XG	0.03 – 0.5	0.01

[a] Determined by diffuse reflectance spectroscopy.

d. The method of indicator tubes

This method is based on the direct proportionality between the length of the coloured segment of the indicator powder located in the tube and the concentration of the analyte. The main advantage

Table 10. Characteristics of test systems based on modified silicas for determination of inorganic and organic compounds.

Analyte	Quntifiable concentration range /mg litre^{-1}
Indicator powders	
Manganese(II)	0.5 – 5.0
Copper(II)	0.001 – 0.1
Zinc	0.1 – 10
Molybdenum(VI)	0.2 – 60
Silver	0.5 – 80
Cadmium	0.001 – 0.01
Lead	0.01 – 1.0
Nitrate ions	0 – 1
Nitrite ions	0.01 – 10
Fluoride ions	1.0 – 10
Asymmetric *N*,*N*-dimethylhydrazine [a]	0.2 – 50
Aniline	0.05 – 10
Phenolic index	0.0005 – 0.1
Naphthols	0.1 – 4.0
Esters	40 – 450
Anionic surfactants	0.1 – 50
Indicator tubes	
Mixture of heavy metals [b]	$(0.001 - 1) \times 10^{-3}$ (see [c])
Tin(II)	10 – 200
Copper(II)	0.1 – 65
Iron	0.05 – 50
Aluminium	0.3 – 3.0
Chromium(VI)	0.5 – 50
Cobalt(II)	0.06 – 6.0
Cadmium	0.3 – 3.0
Nickel	0.2 – 30
Nitrate ions	0.5 – 20
Nitrite ions	0.1 – 5
Chloride ions	0 – 2000
Iodide ions	100 – 800
Free active chlorine	0.05 – 3.0
Ascorbic acid	3.0 – 330
Aniline	0.02 – 2.5
Anionic surfactants	0.1 – 150
Cationic surfactants	10 – 150

[a] The test system has passed the state metrological certification procedure, registered under the number TS-224.01:11/008-2004 and approved for the use by the Problem Commission of the RF Ministry of Health; [b] the test system has passed the state metrological certification procedure and is registered under the number TS-224.09/009-2004; [c] in mol litre^{-1}.

of this approach is the possibility of reliable test determination based on the easily measurable stain length rather than on the degree of colour or tint change (as in most test methods). The method is widely used to analyse gases and aerosols, in particular, in military chemistry.[353]

We have applied the indicator tube method for analysis of solutions (environmental objects, waste waters, foodstuffs and beverages, biological liquids).[246, 252, 254, 258, 274 – 276, 331, 336, 339, 344] For the preparation of indicator powders, analytical reagents were either non-covalently immobilised on reverse-phase silica gels and silica gel-based ion exchangers directly in the indicator tube [246, 252, 254, 258, 274 – 276, 354] or incorporated in xerogels of silicic acid.[246, 331, 332, 335, 336, 339, 344]

On the basis of studies of the dependence of determination sensitivity on the physicochemical characteristics of the indicator powders, the flow rate and the mode of supply of the analyte solution to the tube, and the tube length and internal diameter, requirements to the selection of indicator reactions and analysis protocols have been formulated. To ensure high accuracy of determination, the time of passage of the solution through the tube should be 10 – 20 times longer than the characteristic time of the chemical reaction.[355]

Two modes were employed to feed analyte solutions to the indicator tubes: rising of the liquid due to capillary forces (the 'sinking' mode) and pumping the solution through the tube, for example, by means of a medical syringe (the 'passing' mode). The former mode markedly facilitates and accelerates the procedure of analysis, while the latter ensures a higher determination sensitivity due to the larger solution volume.[246, 254, 258, 274 – 276, 331, 332, 335, 336, 339, 344, 354]

Indicator tubes for determination of heavy metal mixtures, Al, Cr(VI), Fe, Co(II), Ni, Cu(III), Cd and Sn(III); nitrate, nitrite, chloride and iodide ions; the total content of sulfite, thiosulfate and sulfide ions, ascorbic acid, free active chlorine, cationic and anionic surfactants, sulfur-containing reducing agents, aniline and hydrazines; and the choline esterase activity have been developed (see Table 10). The indicator tubes have been used to analyse environmental objects, industrial process solutions, foodstuffs (after the appropriate sample preparation), beverages, and biological liquids.[246, 254, 258, 274 – 276, 331, 332, 335, 336, 339, 344, 354]

The metrological characteristics of indicator tube analyses are comparable to those for instrument methods. The relative standard deviation for determination using indicator tubes is 0.02 – 0.15 and the analysis time is 2 – 10 min.

Test systems based on indicator tubes have passed metrological certification procedure at the State Metrological Scientific Centre based on the Urals Research Institute of Metrology; they have been included in the register of test system types, approved for the use and are now manufactured commercially by the limited liability company MedEkoTest (Moscow).

Test systems for determination of nitrate, nitrite and chloride ions and Cu(II) and Fe in natural waters have passed state interbranch tests. The test system for determination of asymmetrical dimethylhydrazine ensures reliable quantification of this toxic substance in soils and in special rinsing solutions.

Indicator tubes are used to determine Sn(II) in the reagents for the preparation of radiopharmaceuticals by the ^{99m}Tc generator. The test system for determination of nitrate ions is used for clinical urine and blood serum analyses. The indicator tubes for determination of chloride ions in sweat and the choline esterase activity in biological liquids have been recommended for detection of mucoviscidosis in babies and general intoxication in patients.

Thus, non-covalent immobilisation on the surface-modified silicas and incorporation into xerogels of silicic acid has imparted new analytical properties to the fixed analytical reagents, which determined their use in the practice of chemical analysis. In our opinion, silicas modified by analytical reagents can be successfully used to develop flow methods of analysis, in particular, electroinjection [356] and sequential injection analyses and analysis with particle injection.[357] Of particular interest is the design of microelectrodes and microanalytical systems on microchips.

VI. Conclusion

The information presented in the review demonstrates the substantial achievements in the development of sorption preconcentration techniques aimed at solving topical tasks of chemical analysis. First, this is the pronounced increase in the number of sorbents that allow quantitative and in some cases fairly selective recovery of trace amounts of metal ions (including complex ions), various ionised and non-ionised organic compounds and simple inorganic anions. Second, this is the appreciable progress attained in the quantitative description of sorption processes, in the investigation of the interaction mechanism, in the development of the strategy for the *a priori* estimation of the sorption conditions and even in the deliberate selection of sorbents for particular purposes. Third, fundamental research has resulted in the development of a large number of combined and hybrid methods for the analysis of diverse objects, including environmental objects. Some of these methods are routinely used in chemical analysis.

A prominent place in the approaches and methods considered belongs to dynamic sorption preconcentration and flow preconcentration. This provides a way to automation of the analysis; numerous examples of automated analyses are currently known, mainly represented by flow injection analysis. A significant contribution to the development of analytical sorption preconcentration was made by the researchers of the Department of Chemistry of the Moscow State University.

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