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Polyurethane foams in chemical analysis: sorption of various substances and its analytical applications

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Abstract. Data on the sorption properties of polyurethane foams including their modified forms are surveyed. Examples of application of polyurethane foams for the separation and preconcentration of inorganic and organic compounds are given. The mechanisms of sorption on polyurethane foams described in the literature are analysed. Advances in the development of combined and hybrid methods of analysis with the use of these sorbents are discussed. The bibliography includes 259 references.

I. Introduction

Polyurethane foams (PUF), or foamed polyurethanes, represent an extensive class of synthetic materials prepared from polyurethanes — heterochain polymers that contain urea, amide, ether, ester, or other groups in addition to urethane groups. Polyurethanes were first synthesised by Bayer and co-workers in 1937.[1]

Later, industrial production of PUF was started on the basis of these polymers and polyesters or their analogues (Germany, 1944) and, subsequently, on the basis of cheaper polyethers (USA, 1957). Currently, PUF are produced in large amounts (millions of tons a year) in many countries all over the world. Polyurethane foams (in the household, these materials are called foam-rubbers) are widely used for domestic purposes: to produce soft furniture, car seats, mats, sponges, toys, and so on. In industry, PUF are employed as damping and heat insulating materials. Some similarity between the characteristic functional groups present in polyurethane molecules and in macromolecules forming living tissues provides grounds for assuming that PUF-based materials would be promising for use in medicine, all the more so, because polyurethane fibres have long been used in surgical practice as sutures and for the manufacture of vessel prostheses.

The possibility of using PUF as sorbents for extraction of metal ions and organic compounds from water and air was first established by Bowen in 1970.[2] Two years later, Braun and Farag proposed the use of PUF as solid polymer matrices for immobilisation of various organic reagents.[3,4] Since the mid-1970s, PUF have been used in analytical chemistry for preconcentration of inorganic and organic compounds from aqueous solutions or air and for the development of combined or hybrid analytical techniques. During the elapsed time, vast amounts of experimental information dealing with sorption by means of unloaded and loaded PUF has been accumulated and data on sorption mechanisms have been gained. The following practical applications of PUF have become traditional and most important: separation of mixtures in which elements and compounds are present in comparable amounts; isolation of components for preconcentration and subsequent determination directly in the sorbent phase using neutron-activation analysis, X-ray fluorescence, photometry, or another method; and isolation of components for preconcentration and subsequent determination in the eluate phase using chromatography, spectroscopy, or some other analytical technique.

The application of PUF in analytical chemistry is the subject of a monograph[5] (difficult to access for a Russian reader) and several reviews,[6–10] which, however, do not cover all applications of this class of sorbent. In addition, after the publication of the latest of the above-mentioned works (1992), the number of studies dealing with this topic has substantially increased and new trends in the use of PUF in chemical analysis have taken shape. This has stipulated the need for generalisation of the accumulated data at a qualitatively new level taking into account, first of all, the modern views on the mechanisms of sorption on PUF and the properties of these sorbents.

II. General characteristics of polyurethane foams

Polyurethane foams are prepared by polycondensation of isocyanates with polyols (glycols, triols, polyethers, or polyesters) followed by foaming of the polymer bulk by carbon dioxide. Polyether and polyester foams can be distinguished. In the industrial synthesis, polyethers with terminal OH groups and molecular masses of 400 – 6000 are used most often as the initial compounds, together with mixtures of 2,4- and 2,6-toluylene diisocyanates in 65 : 35 or 80 : 20 ratio. In the one-step process, diisocyanate, polyether resin, water, catalysts, stabilisers, and emulsifiers are mixed simultaneously. The reaction takes place immediately; foaming starts several seconds after mixing and is over after 1 – 2 min. Toluylene diisocyanates play an especially important role in the synthesis of PUF. The reaction between

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polyhydric alcohol and isocyanate is a chain propagation reaction, resulting in urethane derivatives

$$R^1-N=C=O + R^2-OH \longrightarrow R^1-NH-C(O)-O-R^2.$$

The reaction of isocyanate with water yields amine and carbon dioxide, which foams the polymer. Amine can react with excess isocyanate to give substituted urea derivatives

$$R^1-N=C=O + H_2O \longrightarrow [R^1-NH-C(O)-OH] \longrightarrow R^1NH_2 + CO_2,$$

$$R^1-N=C=O + R^1-NH_2 \longrightarrow R^1-NH-C(O)-NH-R^1.$$

Isocyanate can also react with urea and urethane derivatives giving rise to allophanate and biuret, which induce additional cross-linking of the polymer:

$$R^1-N=C=O + R^1NH-C(O)-NHR^1 \longrightarrow R^1-\underset{\displaystyle C(O)-NH-R^1}{\overset{\displaystyle |}{N}}-C(O)-NH-R^1$$

$$R^1-N=C=O + R^1NH-C(O)-OR^2 \longrightarrow R^1-\underset{\displaystyle C(O)-NH-R^1}{\overset{\displaystyle |}{N}}-C(O)-OR^2$$

Depending on the number of cross-links, flexible and rigid PUF are distinguished. The materials with low cross-linking density are called flexible PUF, while rigid polymers are characterised by high cross-linking density. Flexible PUF are usually synthesised from polyhydric alcohols with not very high molecular mass and low degrees of branching, while rigid ones are prepared from highly branched alcohols with low molecular mass. Detailed information on the synthesis of PUF can be found in monograph.[1]

Foamed polyurethanes contain different functional groups, namely, urethane [$-NHC(O)O-$], ether ($-O-$), ester [$-C(O)-O-$], amide [$-C(O)-NH-$], urea [$-NH-C(O)-NH-$], and terminal toluidine [$-C_6H_3(CH_3)NH_2$] groups and also both aromatic ($-C_6H_4-$) and aliphatic ($-CH_2-$) groups. The diversity of functional groups in the flexible polymer chains of PUF creates favourable conditions for the formation of intermolecular (secondary) bonds of various chemical natures and with different energies (ranging from van der Waals to hydrogen bonds), which has a substantial influence on the physicochemical properties of the materials.[11, 12] The hydrogen bonds arising upon the interaction of hydrogens of the proton-donating urethane groups with oxygens of the proton-withdrawing ether, ester or carbonyl groups play an especially important role. The type of hydrogen bond depends on many factors, in particular, on the proton-donating and proton-withdrawing capacity of groups, their concentrations and distribution along the polymer chain and on the steric conditions of the formation of the H-bonds. Exhaustive information on the types of hydrogen bonding has been obtained by IR spectroscopy.[13] Study of IR absorption of polyurethanes of different chemical structures in the region of NH stretching frequencies showed that most of the NH groups in polyurethanes are involved in hydrogen bonds. The vibration frequencies of NH groups perturbed by hydrogen bonding are different in the spectra of PUF based on polyethers and polyesters. This may be due to different types of H-bonding in these systems. From analysis of the IR spectra, it was concluded that the major type of hydrogen bond in polyester-based polymers is that between the hydrogen atom of the urethane group and the carbonyl oxygen of the ester group, while in the polyether foams, this is the bond between the urethane-group hydrogen and oxygen of the polyether chain; the hydrogen bond involving ether oxygen is stronger.[13]

Due to the strong hydrogen bonds which form in PUF a continuous three-dimensional network, in certain cases, linear polyurethanes, cross-linked only through physical bonding exhibit properties normally typical of chemically cross-linked linear chains.[13] Yet another structural feature of the three-dimensional network formed in PUF is lability. The ability of the network to be destroyed and reconstructed on heating, treatment with solvents or mechanical stresses suggests that this network can be likened to thixotropic structures, well-known in colloid chemistry. The presence of the labile structural network accounts for many specific properties of PUF. For example, the tensile and compression strengths of PUF are believed to be mainly due to the presence of intermolecular interaction. In the case of pronounced deformations (bending, stretching, *etc.*), the secondary bonds are destroyed, while the primary (chemical) bonds remain intact. Evidently, the ability of polyurethanes to 'heal' the defects arising upon deformations can be explained by the relative ease of network destruction and subsequent restoration. Therefore, after multiple compression, PUF is softened and its initial strength is restored after a certain 'rest'.[11]

Polyurethane foams are foamed plastics in which some of the solid has been replaced by gas, usually air, which exists in the polymer as numerous bubbles (cells). Depending on the relationship between the rate of the macromolecule growth and the rate of gas evolution at the foaming stage, the cell walls are either broken (ruptured) or not; this gives rise to polymers with open-cellular or closed-cellular structure, respectively. As a rule, flexible PUF have an open-cellular structure and rigid ones are characterised by a closed-cellular structure. If the volume occupied by gas bubbles is less than 76% of the total volume of the specimen, the bubbles can be spherical; if this volume is greater than 76%, the bubbles are shaped most likely as quasi-spherical polyhedra, mainly, pentagonal dodecahedra.[5, 6, 9] The polymer itself forms the walls of the bubbles, which are actually polyurethane membranes. In open-cellular PUF, at least two membranes (faces of the pentagonal dodecahedron) are ruptured.

Among the properties of PUF, one should mention the lightness (the apparent density is 0.015–0.045 g cm^{-3}), enhanced stability against thermooxidative destruction (180–220 °C), and chemical and radiation stability. The properties of PUF do not change (not counting the reversible swelling) on contact with hydrochloric (up to 6 M), sulfuric (up to 4 M), nitric (up to 2 M), or glacial acetic acid, solutions of sodium hydroxide or ammonia (up to 2 M), and many organic solvents such as benzene, tetrachloromethane, chloroform, diethyl ether, other ethers or esters, methyl isobutyl ketone, alcohols. Poluyrethane foams based on esters are less stable in acidic or alkaline media than those based on ethers because the former are more susceptible to hydrolysis. Both types of PUF are soluble in concentrated sulfuric acid or a hot solution of arsenic(III) chloride; they are destroyed on treatment with concentrated nitric acid and oxidised by an alkaline solution of $KMnO_4$.[2]

Estimation of the purity of PUF of various brands showed that the content of inorganic impurities in them is comparable with or even less than that in other sorbents such as active (activated) carbons, synthetic ion exchange resins or chelating sorbents.[5] It was found by neutron activation analysis that the major impurity in PUF is tin, its content being substantially lower in polyester PUF.[14] This may be due to the fact that organotin catalysts are used in the synthesis of PUF based on ethers. In addition, small amounts of Na, Mg, Al, Mn, V, Cl, Br and I have been found in PUF.

The organic impurities extracted from industrial PUF specimens by various methods, namely, on treatment with solvents,[15, 16] by thermodesorption[17, 18] or by supercritical fluid extraction[19] have been identified by a combination of gas chromatography and mass-spectrometry techniques. The impurities were mainly toluylene diisocyanates,[15] various aliphatic and aromatic amines[16, 18] and fluorocarbons (Freons).[17, 19] The composition of the impurities depends on the solvent used and on the features of the PUF manufacturing process.†

† It is known[1] that amines and Freons are used as catalysts and as additional foaming agents, respectively, in the production of some sorts of PUF.

The specific surface area of PUF can be determined from isotherms of low-temperature adsorption of nitrogen [20, 21] or carboxy-^{14}C-stearic acid.[22] The specific surface areas of the PUF specimens studied were 0.007–0.035 $m^2\ g^{-1}$, which is much smaller than the values found in sorbents such as Tenax GC (6.4–25 $m^2\ g^{-1}$) or XAD-2 (300–360 $m^2\ g^{-1}$).

As applied to PUF, a method for the estimation of the microenvironment hydrophobicity, based on the interfacial partition of pyrene between water and the medium to be tested, has been developed.[23] The partition coefficient of pyrene between the sorbent and water, aqueous acetonitrile or aqueous ethanol is used as a measure of hydrophobicity. A comparative estimate of the surface hydrophobicities for six industrially manufactured specimens of PUF based on ethers and esters and for other sorbents such as Diasorbs C_4, C_8, C_{16}, phenyl and carboxyl, XAD-8, cellulose, cellulose triacetate and activated carbon AX-21 showed that the PUF specimens studied are characterised by approximately equal surface hydrophobicities and that, regarding this parameter, they should be placed between Diasorb C_{16} and activated carbon AX-21.

Fluorescence spectroscopy has been demonstrated to provide extensive possibilities in investigations of the properties of polyurethane foam membranes.[24, 25] Using pyrene as the fluorescence probe, the polarity of the pyrene microenvironment (ε_{ef}) in the matrix of various PUF has been estimated.[24] For low degrees of filling of the sorbent phase (0.3–0.9 μmol g^{-1}), the ε_{ef} value ranges from 24 to 39, polyether PUF being less polar than polyester PUF; for high degrees of filling of the sorbent phase (4.2–5.6 μmol g^{-1}), the polarity of the pyrene microenvironment decreases, the ε_{ef} values being 10–19 for polyester PUF and ~2 for polyether PUF. The polarity of the pyrene microenvironment in the matrices of protonated PUF proved to be higher than those for the initial PUF. The data on quenching of the fluorescence of pyrene sorbed on PUF by quenchers of different natures, namely, potassium iodide and bromoform, gave rise to the suggestion that solid-phase foamed polyurethane membranes contain polar and hydrophobic microregions characterised by different physical properties.[25] Lower values for the calculated Stern–Volmer constants for pyrene in the PUF matrix compared to the values for aqueous solutions point to a decrease in the mobility of pyrene and quencher molecules, related, first to the their transition to a thicker medium and, second, to the rigid fixing of these molecules at particular sections of the polymer chain. The fact that the pyrene molecule is rigidly fixed in the PUF matrix is also indicated by the absence of the excimer band in the fluorescence spectra of pyrene sorbates, even when it is sorbed from suspended media.[25]

In a study of the protolytic properties of PUF, it was shown that stepwise protonation of PUF takes place in aqueous solutions of mineral acids (pH < 3).[25, 26] The protonation constants were calculated; it was suggested that the terminal toluidine groups in the PUF molecules are the first to be protonated.

Thus, PUF are foamed plastics with a 'membrane-like structure' characterised by a relatively low specific surface area and high chemical stability and purity.

III. Sorption of elements and organic compounds on unloaded polyurethane foams

1. Sorption of elements

At present, the sorption of ~50 elements on unloaded PUF has been studied. Most often, PUF adsorb elements as metal acido complexes,‡ more rarely, as heteropolyacids, ion associates or metal chelates. Sorption in the form of metal acido complexes is observed for most elements able to form negatively charged halide, cyanide, and thiocyanate complexes (Table 1). Sorption of chloride and thiocyanate metal complexes is the most widespread. Data on the sorption of fluoride,[27–30] bromide,[2, 49, 52] iodide [39, 53] and cyanide [54] complexes are scarce.

Table 1. Sorption of elements by unloaded PUF from solutions in mineral acids.

Sorbable forms of elements	Element	Ref.
MF_6^-	Nb, Sb, Ta	27–30
MCl_n^{q-n}	Au	2, 31–34
	Fe	2, 33, 35–40
	Ga	2, 20, 33, 35, 36, 41
	Pt	42–45
	Rh	46, 47
	Sb	2, 48
	Sn	21, 33
	Te	49
	Tl	50, 51
MBr_4^-	Ag, Au	2, 52
	Te	49
MI_4^-	Bi	39, 53
$M(CN)_4^-$	Au	54
$M(NCS)_n^{q-n}$	Au, Fe, Ga, Hf, In, Mo, Nb, Pa, Sb, Sc, Sn, Ta, W, Zr	33
	Cd	55
	Co	56–67
	Cu	39, 66
	Fe	55–57, 60, 63, 64, 66, 68–70
	Ga	33, 71
	Hf, Zr	33, 72
	Hg	14, 73, 74
	In	14, 33, 73
	Ir, Rh	75, 76
	Mo, W, Tc	39, 66, 71, 77
	Os, Ru, Pd	78, 79
	Pd	60, 80, 81
	Pt	82
	Ti	83
	Zn	55, 57, 73, 84, 85
$UO_2(NO_3)_2$	U	2, 36, 86, 87
$H_nMMo_{12}O_{40}$	As	88, 89
	Ge	90
	P	91–95
	Si	90, 91, 95

The sorption of metal acido complexes is carried out both from solutions of hydrohalic acids and from mixtures of alkali metal salts with mineral acids, for example, LiCl–HCl, KNCS–HCl and KNCS–H_2SO_4. The use of these mixtures is especially typical of sorption of thiocyanate complexes. The time required for sorption equilibrium to establish depends on the nature of the sorbed acido complex and varies from several hours (for metal chloride complexes) to 10–30 min (for thiocyanate complexes).

It should be noted that the conditions for sorption of metal acido complexes on PUF are the same as conditions for extraction of these complexes with oxygen-containing solvents, in particular, diethyl ether. Polyurethane foams adsorb metal acido complexes as one- and two-charged anions of the composition MF_6^-, MX_4^- [X = Cl, Br, I, CN, NCS and $M(NCS)_4^{2-}$] with high partition coefficients ($n \times 10^2 - n \times 10^4$ ml g^{-1}). The sorption capacity is also high, varying from ~0.2 to ~2 mmol per gramme of the sorbent, which makes up to 10% of the sorbent weight. As a rule, PUF based on polyethers sorb metal acido complexes better than polyester foams. The metal acido complexes can be quantitatively desorbed from PUF on treatment with acetone or dilute solutions of hydrohalic acids.

‡ Acido complexes are complexes containing only acid anions as the ligands.

Sorption on PUF of acido complexes of platinum group metals has some specific features. Thus Rh(III) and Ir(IV) are poorly collected from thiocyanate solutions at room temperature; however, after short-term heating to 90 °C, sorption of these metals becomes quantitative.[76]

The selectivity of PUF with respect to chloride and, especially, thiocyanate metal complexes is relatively low and depends on sorption conditions, namely, solution acidity, supporting salts and other substances present in the solution. The sorption of metals from fluoride solutions proved to be more selective. Polyurethane foams quantitatively collect Ta(V) and Sb(V) from 0.1 – 5 M HF as MF_6^- complexes and do not adsorb Co, Zn, Fe(III), Hf, Zr, Sn(IV), Nb, Pa, As(V), Mo, or W.[27, 28]

Apart from metal acido complexes, PUF quantitatively sorb some elements, for example, As, Ge, P and Si, as heteropolyacids (see Table 1). In this case, too, the conditions of sorption of heteropolyacids on PUF coincide with conditions of their extraction with oxygen-containing solvents.

Like crown ethers and acyclic polyethers, PUF collect alkali and alkaline earth metals [59, 96 – 98] as well as Ag, Pb and Tl(I) [59, 98] in the form of ionic associates with large hydrophobic anion partners such as picrate or anilinonaphthalenesulfonate. The sequence of sorption of metal picrates is in agreement with the series of extractability of these metals with crown ethers, for example, 18-crown-6 or dicyclohexyl-18-crown-6. Polyether foams are better sorbents for these metals than polyester-based PUF.

The possibility of sorption of metal chelates on unloaded polyether type PUF has been demonstrated. Thus Hg, Pt(II) and Zn are sorbed as complexes with dithizone,[2, 99] Y is sorbed as a complex with 8-hydroxyquinoline,[100, 101] and Cd, Fe(II) and Eu, as complexes with 1,10-phenanthroline.[102 – 106]

2. Sorption of organic compounds

The interest in the use of PUF as sorbents for preconcentration of organic compounds is in many respects due to a study [107] demonstrating that ether-based PUF collect quantitatively polychlorinated biphenyls (PCB) from large water samples. In the subsequent years, several dozens of publications have been devoted to sorption on PUF of polycyclic aromatic hydrocarbons (PAH), PCB, phenols and some other organic compounds from various water [108 – 112, 125 – 127, 137 – 145, 147, 150 – 174] and air [113 – 124, 128 – 136, 146, 148, 149] samples (Table 2).

It was found in relation to aromatic compounds that the partition coefficients of substances between PUF and the aqueous phase are proportional to their partition coefficients for the extraction into diethyl ether.[108] Similar results were obtained in a comparison of sorption of 59 organic dyes (triphenylmethane, xanthene, sulfophthalein) by polyurethane foams from water or aqueous ethanol with the extraction of the same compounds into diethyl ether or ethyl acetate.[160] Sorption of dyes depends on the nature, the structure, and polarity of the dye. The pattern of the dependence of sorption of ionising organic compounds (phenols and carboxylic acids) on the solution pH attests that these compounds pass to PUF as neutral species.[108, 137, 138, 141, 142]

The efficiency of sorption of anionic [105, 171] and cationic surfactants [172] and 4-nitrophenylazo derivatives of phenols [161, 163, 164] increases if they are collected as ionic associates with large hydrophobic counter-ions. In this case, sorption is substantially dependent on the hydrophobicity of the cationic and anionic components of the associate, the size and charge of the ions they contain, the concentration and the nature of the counter-ion, the composition of the aqueous medium, and the chemical structure of the sorbent.[25, 105, 167 – 169]

The capacity of PUF with respect to volatile organic compounds sorbed from air has been studied to elucidate the dependence of the volume before breakthrough on the key parameters of the process: flow rate of the mobile phase, temperature, sample volume and some other.[114, 115, 119 – 121, 129, 130] The relationship between the size of the PUF block, the volume of the air under analysis and the volume before breakthrough has been elucidated in relation to PCB. It was found that PUF blocks with thicknesses of 4 and 7 cm collect 90% of PCB from 500- and 900-m^3 air specimens, respectively.[130] It was noted [132] that a 15 cm-thick PUF block completely absorbs hexachlorobenzene, 3,3′-dichlorobiphenyl and 2,4′,5-trichlorobiphenyl impurities from air specimens with volumes of 250, 330, and 2880 m^3, respectively. Pankov [119] demonstrated that the relationship between the specific retention volume of a compound on PUF ($v_{g,293}$) and the vapour pressure ($p^0_{L,293}$) of the pure target compound is described by correlation equations:

$$\log v_{g,293} = -1.195 \log p^0_{L,293} - 1.884 \quad (r^2 = 0.989, \text{PAH})$$

and

$$\log v_{g,293} = -1.059 \log p^0_{L,293} - 1.764 \quad (r^2 = 0.950, \text{PCB}),$$

where r is the correlation coefficient.

Table 2. Sorption of organic compounds by unloaded PUF.

Type of compound	Sorbable compounds	Ref.
Aromatic hydrocarbons	monocyclic aromatic compounds	2, 108
	polycyclic aromatic compounds	109 – 125
	polychlorinated biphenyls	107, 124, 126 – 136
Hydroxy-containing aromatic compounds	phenols	2, 108, 122, 137 – 142
	carboxylic acids	108
	alcohols	143, 144
Esters	esters of phthalic acid	145, 146
	esters of acetic acid	147
Insecticides	organochlorine	127 – 129, 133, 148 – 150
	organophosphorus	133, 151 – 157
	acaricides	158, 159
Dyes	azo dyes	160 – 166
	xanthene	160, 167
	acridines	160, 168
	sulfophthalein	160, 169
	other	160, 166
Other compounds	anionic surfactants	105, 170 – 172
	cationic surfactants	172, 173
	alkylammonium salts	174
	bilirubin	175

A number of studies have been devoted to the transport of phenols [141] and organic dyes [166] through thin polyurethane membranes. Using a polyurethane membrane, ethanol has been isolated from aqueous solutions.[144]

3. The mechanisms of sorption on unloaded polyurethane foams

A critical analysis of the views on the mechanisms of sorption of metal complexes on PUF has been reported in a monograph [5] and in a review.[10] The mechanisms discussed as the most probable ones include extraction, anion exchange, cation chelation, ligand exchange and ligand addition mechanisms.

The views on the extraction mechanism, proposed by Bowen in his first study [2] and confirmed subsequently by other researchers are underlain by the fact that the conditions of extraction of metal acido complexes into diethyl ether are similar to the conditions of sorption of these complexes on PUF. The relatively high sorption capacity of PUF calculated on the basis of sorption isotherms of Au(III),[2] Fe(III),[2, 38] Hg,[73] Sb(V) [48] and Te [49] halide complexes and some ions (0.5–1.5 mmol g^{-1}) with relatively low specific surface area (0.03–0.08 m^2 g^{-1}) is regarded as evidence supporting this mechanism. Experimental data concerning the transport of Ga,[20, 36] Fe(III) [36, 37, 40] and Au(III) [34] halide complexes and uranyl nitrate [36, 86] through polyurethane membranes indicate that the membranes collect compounds not only due to adsorption but also due to absorption processes. A layer-by-layer microscopic study of polyurethane foam membranes after sorption of coloured compounds, for example, iodine showed that they are uniformly distributed throughout the sorbent bulk rather than concentrated on the surface.[2] In several studies devoted to sorption of Ga,[20, 35] Fe(III),[35, 38] Sb(III, V) [48] Sn(II, IV) [21] chloride complexes and Co and Fe(III) [56] thiocyanate complexes, PUF are characterised as solid polymeric analogues of oxygen-containing solvents.

Extraction of metal acido complexes by polyurethane foams increases in the presence of alkali metal salts, *i.e.*, a salting-out effect is observed, which is usually typical of liquid extraction. For example, when polyether-based PUF are used, the partition coefficient of Sn(IV) from 3 M HCl does not exceed 140 cm^3 g^{-1}, whereas for a solution containing 10 M LiCl and 0.12 M HCl, this value is 5600 cm^3 g^{-1} (see Ref. 21). A similar increase in the partition coefficient was also observed for PUF based on polyesters; however, the values are much lower in this case, namely, 120 and 730 cm^3 g^{-1}, respectively.

Actually, the extraction mechanism proposed in early studies [20, 35–37, 48] reflected the known ability of polymers to dissolve metal salts and organic compounds, which was later (1982) called solid-phase extraction,[176] but did not disclose the factors that made this dissolution possible.

Even the first investigations of the sorption properties of PUF showed that these sorbents possess low anion-exchange capacity. It has been suggested [2, 20] that these properties appear due to protonation of the electron-donating nitrogen and oxygen atoms incorporated in PUF macromolecules. Since the basicity constants of the groups present in the foamed polyurethane units are rather low, it has been considered that PUF can exhibit anion exchange properties only in highly acidic solutions.

In 1982, a cation chelation mechanism was proposed,[59] which provided a different interpretation of the anion exchange properties in PUF. In a study of sorption of thiocyanate metal complexes and some organic anions (in particular, picrate) in the presence of various salts, the researchers concluded [59] that polyester-based PUF exhibit complexing properties with respect to alkali and alkaline earth metal cations, Ag, Tl(I), Pb, NH_4, RNH_3^+, and H_3O^+. When binding cations, neutral macromolecules of foamed polyurethane are converted into macrocations with variable charge density. To maintain neutrality, an anion should be bound (or exchanged) together with the cation. Sorption of metal acido complexes and organic anions by polyether-type polyurethane foams increases in the sequence $Li < Na < Cs < Rb < K < NH_4 < Ag, Tl(I) \ll Ba < Hg < Pb$. Since the same sequence was observed for the sorption of these substances by many crown ethers [177] and acyclic ethers,[178, 179] it was suggested [59] that the selective binding of cations is ensured by the polyether segments of PUF, which are able to form a helix around the sorbed cation. To confirm the selectivity of cation binding, the sorption properties of PUF of various types were compared with the extraction capacity of macrocyclic ethers containing polymeric units similar to those found in foamed sorbents.[59] It was shown that the cation-binding capacity of PUF based on poly(ethylene oxide) is higher than that of PUF based on poly(propylene oxide). The results of a study of sorbates by IR spectroscopy attest in favour of the cation chelation mechanism of sorption of organic compounds on PUF. This study showed the presence of strong interactions between the ether units of PUF and sorbed thiocyanate metal complexes.[59] The presence of ester groups, which are conformationally more rigid, in the polymer chain of PUF has an adverse effect on the cation binding. This is confirmed experimentally by the facts that the sorption properties of polyester-based PUF are poorer than those of polyether-based PUF and that the pattern of influence of alkali metal halides on sorption changes. The sorption of anions by polyurethane foams based on esters varies according to Hofmeister lyotropic series: $Li < Na < K < Rb < Cs$.

The cation chelation mechanism has found quite a few advocates. This mechanism is believed to be responsible for the sorption on PUF of Cd,[55] Co,[59, 61] Fe(III),[55] Mo, W, Tc,[77] Os,[78] Pd,[81] Pt,[82] Ru,[79] Zn,[55] Zr and Hf [72] thiocyanate complexes from slightly acidic aqueous solutions and hexachloro platinum and iridium complexes from acetone and ethyl acetate.[42]

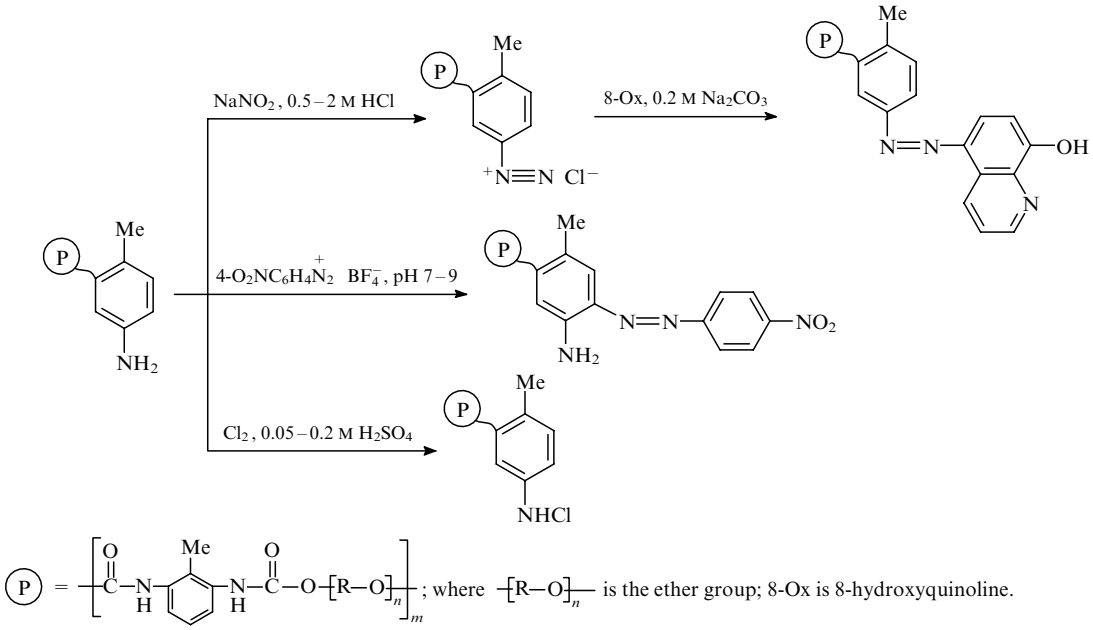
In the ligand exchange or addition mechanism, the polymer segments containing electron-donating nitrogen or oxygen atoms act as ligands able to coordinate metal ions. This 'ligand addition' has been considered to interpret the sorption of yttrium hydroxyquinolinate complexes [101] and iron thiocyanate complexes [39] on PUF. It was proved using IR spectroscopy that the role of the ligand is played by the urethane group (–CO–NH–).

Sorption of organic compounds on PUF is explained in most cases in terms of the extraction and cation chelation mechanisms. According to the extraction mechanism, PUF are regarded as solid polymeric extractants which dissolve organic molecules in the polymer films that form the framework of these sorbents.[108] A piece of evidence supporting the extraction mechanism is provided by the fact that the efficiency of extraction of organic compounds by polyurethane foams can be increased by introducing inorganic salts in the aqueous solution–PUF system.[108] In the presence of alkali metal salts, sorption efficiency increases in the series: $K < Na < Li$. Double-charged cations influence the extraction efficiency to a markedly greater extent than single-charged ones, *i.e.*, a salting-out effect typical of extraction is involved. The extraction mechanism has also been used to interpret sorption by polyurethane foams of PAH,[125] phenols,[108, 138, 141, 142] cationic dyes [160, 167, 168] and organophosphorus and organochlorine acaricides.[158]

Negatively charged forms of organic compounds such as anionic surfactants,[172] sulfophthalein dyes [160, 169] and azo dyes [160, 161] are extracted by PUF by the cation chelation mechanism. This is indicated by the data on the influence of alkali metal and ammonium salts on sorption. Sorption of these compounds increases in the following order: $Li < Na < Cs < Rb < K \sim NH_4$.

In some publications, the important role of hydrophobic interactions and interactions giving hydrogen bonds in the sorption of organic compounds is noted. A reliable correlation has been established between the main parameter of PAH sorption, the partition coefficient ($\log D$), and the hydrophobicity parameter of their molecules [the Hansch parameter defined as the partition coefficient in the 1-octanol–water system ($\log P_{ow}$)].[125] Two-parameter correlation equations relating the partition coefficients of phenols to their hydrophobicity parameters and

Scheme 1



medium pK_a values have been proposed.[142] The logarithms of the partition coefficients of cationic surfactant homologues were found to follow a linear dependence on the number of carbon atoms in the alkyl groups of these compounds.[25, 172]

Thus, various mechanisms of sorption of metal complexes and organic compounds by polyurethane foams have been proposed; each mechanism has its own adherents and has been confirmed by experimental data. A common drawback of the views in these mechanisms is that sorption is idealised. In most cases, consideration actually refers to special cases in which only one process takes place in the system, other processes being entirely suppressed. Meanwhile, real systems normally provide favourable conditions for the simultaneous occurrence of several processes.

4. Chemisorption processes involving polyurethane foams

Experimental data attesting to a previously unknown ability of the terminal toluidine groups of PUF to be involved in oxidation, diazotisation and azo coupling reactions have been reported.[180–182] When PUF samples are brought in contact with aqueous solutions of free active chlorine, sodium nitrite and 4-nitrophenyldiazonium tetrafluoroborate, chemisorption processes take place to give intensively coloured products. The composition of the products was determined using diffuse reflection spectroscopy, elemental chemical analysis and other techniques. The optimal conditions of heterogeneous chemical reactions with participation of PUF and the conjectural composition of the products are shown in Scheme 1.

The introduction of the diazo group into PUF provides activation of these materials toward covalent attachment of functional groups to their surface.[182] Diazotised PUF enter into azo coupling reactions with azo components such as 8-hydroxyquinoline (Scheme 1), 1- and 2-naphthols, phenol, aniline and other compounds to give intensely coloured products. Heterogeneous chemical reactions involving PUF proceed under relatively mild conditions (aqueous solutions, room temperature, atmospheric pressure), the coloured products being rapidly formed at relatively low concentrations of compounds present in the aqueous phase. Therefore, PUF were recommended as new polymeric reagents for determination of free active chlorine and nitrite ions.[180, 181]

IV. Sorption of elements on polyurethane foams loaded with organic reagents

Polyurethane foams can collect and retain substantial amounts of inorganic and organic compounds. This provides the possibility of modifying PUF to improve their sorption properties, while preserving the required hydrodynamic characteristics of the material. This is done using oxygen- and nitrogen-containing extractants or chelating organic reagents. The general information about sorption of elements on PUF loaded with various oxygen- and nitrogen-containing extractants and chelating reagents is presented in Table 3. The major application of loaded PUF is preconcentration with subsequent determination of metal ions and organic compounds in waters.

Two ways of immobilising reagents, differing in the method of fixing of compounds in the PUF matrix, have been described, namely, physical and chemical immobilisation. Physical immobilisation is used most often because chemical fixing of reagents, which is carried out during the polymer synthesis, is a more laborious procedure. Organic compounds can be introduced into the foaming material owing to the hydrophobic nature of the polymer matrix and its dissolving capacity with respect to various compounds. Immobilisation of liquid extractants is an exceptionally simple procedure; this is attained by keeping PUF pellets or small cubes in an appropriate liquid extractant or in its mixture with some organic solvent. Excess liquid is then removed and the PUF samples are dried between sheets of filter paper. Foams obtained in this way contain 50 mass % to 80 mass % of an organic compound. Immobilisation is performed for liquid extractants, for example, tributyl phosphate,[3, 183, 184, 187] trioctylamine,[196, 197] bis(2-ethylhexyl) hydrogen phosphate,[192] and for solutions of these compounds: tributyl phosphate in benzene,[185] trioctylphosphine oxide in diethyl ether, bis(2-ethylhexyl) hydrogen phosphate in nitrobenzene[190, 191, 193] or in dichlorobenzene.[194, 195]

Immobilisation of solid chelating reagents on PUF is carried out using two procedures. According to one procedure, the reagent is dissolved in a non-volatile organic solvent (plasticiser) and physically immobilised on PUF as described above. The other method consists of keeping the polymer in a solution of the reagent in a highly volatile solvent followed by removal of the solvent. In both procedures, it is required that the reactant solubility be rather high. This requirement is readily fulfilled in the second procedure because there is a wide choice of volatile solvents; however, the range of solvents suitable for the first procedure is substantially narrower. The solvents play a dual role in this case: they should efficiently dissolve the reagents and should also act as plasticisers for the polymeric sorbent. Tributyl phosphate[57, 192, 213, 215] and α-dinonyl phthalate[57, 209, 225] are used most often as plasticisers.

Table 3. Sorption of elements by polyurethane foams loaded with organic reagents.

Organic reagent	Element	Ref.	Organic reagent	Element	Ref.
Tributyl phosphate	Au	14, 183, 184	dithizone	Ag	211
	Bi	4, 57		Bi	212, 213
	Cr	185		Cd, Cu	214
	Nb	186		Hg	215 – 217
	Pd	4		Pb	218, 219
	U	162, 187		Zn	212, 218
Trioctylphosphine oxide	U	188, 189	diethyldithiocarbamates	As, Bi, Hg, Pb, Sb, Se, Sn	220 – 222
Bis(2-ethylhexyl) hydrogen	Ce	190, 191		Cd, Co, Cr, Cu, Fe, Mn, Ni	222 – 224
phosphate	Th	192		Hg	225, 226
	U	193 – 195		Sb	227
Trioctylamine	Co	196		REE	228, 229
	U	197, 198	diphenylcarbazide	Cr	230 – 232
Dibenzoylmethane	U	199, 200	benzoylhydrazone	Cu, Pd	233
Thenoyltrifluoroacetone	Co, Fe	201 – 203	phenylhydrazine	Mo	234
Dimethylglyoxime	Ni	204 – 206	dibenzo-18-crown-6	Pb	235
	Pd	207		AM [a]	236
1-(2-Pyridylazo)-2-naphthol	Au	14			
	Cd	57, 208			
	Co	57, 208 – 210			
	Fe, Mn	57, 209			
	Hg	14, 57, 73, 208			
	In	14, 73			
	Zn	57, 73, 208			

[a] AM are alkali metals.

Immobilisation of various chelating reagents on PUF has been described, for example, dimethylglyoxime,[204 – 207] 1-(2-pyridylazo)-2-naphthol,[14, 57, 208 – 210] dithizone,[211 – 219] ammonium pyrrolidinedithiocarbamate,[220, 221, 223] hexamethyleneammonium hexamethylenedithiocarbamate,[224] and sodium,[222] diethylammonium [225] and potassium [228] diethyldithiocarbamates. It was shown using numerous examples that the conditions of formation of compounds with PUF-immobilised reagents do not differ from the conditions of reactions taking place in aqueous solutions.

Parameters such as the strength of retention and the uniformity of distribution of the organic reagent in a polymer matrix are little studied. It was only found that on contact with large amounts of an aqueous phase (up to 1 litre), not more than 15% of the reagent is desorbed, whereas on treatment with acetone, ethanol and other organic solvents both the reagent and the resulting complex are removed from PUF almost completely.[217] It was shown in a study of operational characteristics of PUF loaded with 1-(2-pyridylazo)-2-naphthol,[210] that an increase in the reagent content leads to a poorer retention of the reagent on contact with water. The optimal amount of the reagent is 1 mass %.

As in the case of unloaded PUF, isolation and preconcentration of compounds on loaded PUF are carried out in either a static or dynamic regime. In the latter case, the flow rate of the analysed solution through the column can vary over a broad range, from 0.1 to 250 ml min^{-1}. The scope of the dynamic preconcentration technique can be extended by using plasticised PUF,[210, 225] as this allows quantitative collection of the analyte for flow rates exceeding 100 ml min^{-1}. Nevertheless, the solution flow rates used most often are 0.1 – 10 ml min^{-1}.

Physical immobilisation of organic reagents is usually carried out for polyether-type PUF. No results of comparative studies of the properties of different PUF have been found in the literature; only in one study,[209] was it noted that the use of polyether-type PUF allows a 4-fold increase in the solution flow rate with respect to that for the polyester foam in the collection of Co, Mg and Fe using the polymer loaded with 1-(2-pyridylazo)-2-naphthol.

V. Classification of sorption processes involving polyurethane foams

A classification of sorption systems involving PUF has been proposed,[25] based on the views of various types of sorbent – sorbate intermolecular interactions developed by Kiselev.[237] According to this classification, three types of sorption systems with participation of PUF can be distinguished, depending on the type of intermolecular interactions between the sorbent and the sorbate (Table 4).

The first type includes unloaded PUF in the polymer chains of which the active centres are represented by hydrophobic hydrocarbon chains and aromatic groups and electron-donating nitrogen and oxygen atoms contained in urethane, amide, ester, ether or terminal toluidine groups.

The second type comprises PUF loaded with alkali metal ions and mineral acids. This modification becomes possible due to protonation of nitrogen atoms incorporated in polar groups (first of all, terminal toluidine groups), which takes place in acidic solutions, due to introduction of cations capable of complexation with polyether (polyester) units in the polymer macromolecule. Upon binding alkali metal or ammonium cations or some other ions, polyurethane foams are converted into macrocations with variable charge density, which depends on the nature of the cation involved, salt concentration, and the nature of the PUF unit. Since this binding is less typical of PUF based on esters, it is possible to increase the selectivity of sorption on passing from polyether foams to those based on polyesters. The properties of the initial polymers would differ from the properties of PUF loaded in this way; thus, the latter can be used to recover negatively charged species.

Finally, PUF, loaded with various organic reagents upon immobilisation of the reagent without covalent bonding with the sorbent belong to the third type.

In the majority of cases, the main role in binding the sorbates on unloaded polyurethane foams is played by hydrophobic interactions and hydrogen bonds. Hydrophobic interactions play

Table 4. Classification of sorption systems with PUF according to the main types of sorbent – sorbate intermolecular interactions.

Type of sorption system	Main types of intermolecular interactions	Groups of compounds sorbed
Unloaded PUF	hydrophobic	polycyclic aromatic hydrocarbons
		ionic associates containing large hydrophobic cations
		ionic associates containing large hydrophobic cations and anions
		ionic surfactants
	hydrophobic + H-bonding	phenols
	H-bonding + donor – acceptor	heteropolyacids
	ion – dipole	alkali metal and ammonium salts
PUF loaded with alkali metal ions and mineral acids	ion – ion	metal acido complexes
	ion – ion + donor – acceptor	heterolyacids
	ion – ion + hydrophobic	sulfophthalein dyes
		anionic surfactants
		4-nitrophenylazo-derivatives of phenols
PUF loaded non-covalently with organic reagents	chemical bond between the metal and the functional group of the organic reagent	metal complexes with organic reagents

a crucial role in the collection of PAH, associates containing simultaneously large hydrophobic cations and anions and associates containing hydrophobic cations. Compounds of the two first-mentioned groups are sorbed quantitatively on unloaded PUF (95% – 99.9%); this can be used to develop procedures for preconcentration followed by spectroscopic determination of these coloured (luminescing) compounds.

The efficiency of sorption of compounds the molecules of which contain polar groups together with hydrophobic fragments is determined by a number of factors, which was demonstrated convincingly in relation to phenols.[142] Of the group of compounds under consideration, either molecules incorporating hydrophobic fragments with Hansch parameters (log P_{ow} in the octanol – water system) greater than 3 (*e.g.*, 1-naphthol), or relatively strong acids (*e.g.*, 2,4,6-trinitrophenol) can be of interest from the practical standpoint. The main types of intermolecular interactions involved in the binding of strong acids and alkali metal salts include hydrogen bonding and donor – acceptor and ion – dipole interactions. In the case of chemical interactions taking place due to high reactivity of the terminal toluidine groups, chemical individuality of the sorbed molecules is lost upon the formation of surface compounds and, thus, sorption becomes irreversible, unlike the cases described above.

Ion – ion interactions make a crucial contribution to the sorption on PUF loaded with alkali metal ions and mineral acids of compounds such as thiocyanate metal complexes, heteropolyacids, single- and double-charged anions of sulfophthalein dyes, anionic surfactants and 4-nitrophenylazo derivatives of phenols. Binding of negatively charged species to PUF, which has an electrostatic nature, can be enhanced by hydrophobic interactions of anions containing hydrophobic groups. Usually, the compounds listed above are quantitatively sorbed on PUF; most of them, are intensively coloured, which accounts for their high practical significance.

In sorption systems of the third type, PUF function as hydrophobic polymeric matrices that fix organic compounds, the key interactions being due to the formation of chemical bonds between metal ions and functional groups of the reagent.

VI. Analytical application of polyurethane foams

Polyurethane foams are of substantial interest for analytical chemistry. These sorbents are characterised by high efficiency combined with sorption capacity with respect to many classes of sorbates, chemical and mechanical strength and stability against organic solvents. The advantages of PUF include the presence of a membrane structure, which ensures good hydro- and air-fluid dynamics of the sorbents and allows preconcentration of trace elements and organic compounds from large samples of water and air. These sorbents are relatively inexpensive and readily available.

Sorption on PUF is used for separation, preconcentration and determination of trace elements and organic compounds from water and air. Determination of elements and organic compounds after preconcentration or separation can be carried out by a variety of methods. Most often, preconcentration by sorption is combined with photometry, diffuse reflection spectroscopy, atomic-absorption spectroscopy and chromatographic techniques. Determination can be done either directly in the sorbent or in a solution after desorption of the target components using an appropriate eluent. In some cases, determination is carried out after decomposition of the sorbent on treatment with mineral acids, for example, HNO_3 [184] or its mixture with HCl.[44, 54, 192]

1. Separation and preconcentration

The success of preconcentration and separation by sorption on PUF depends on a rational choice of the sorption system, the composition of the aqueous phase and on the procedure used for separation and preconcentration. The practice of preconcentration by sorption on PUF has some specific features differing from those used with other sorbents. Preconcentration and separation of elements and organic compounds on PUF can be performed in either a static or dynamic regime.

Static sorption can be performed in two ways. The traditional procedure is based on shaking (mixing) of the solution to be analysed with a known amount of the sorbent; air bubbles should be necessarily removed from the sorbent. Usually, PUF are used as cubes, cylinders, cylindrical discs or pellets cut out or knocked out of a polymer sheet. According to the second procedure, PUF blocks or discs situated in the solution under analysis are squeezed at some intervals either manually, for example, by the bottom of a glass measuring cylinder, or using a special automatic device.§

In the dynamic version of sorption, the solution under analysis is passed through a chromatographic column packed with PUF cubes or cylinders. Various methods for packing the columns have been developed; a vacuum procedure is used most often. In yet another specific method of preconcentration on PUF, called the pulsating column technique, the solution to be analysed is pumped through a sorbent layer located in a glass or plastic medical syringe. Since the sorbent is flexible, the cylindrical polyurethane foam plug can be easily compressed (or released) when the syringe

§ The automatic device consists of an eccentric shaft operated by an engine, which makes one or several glass or plastic pistons move up and down and thus forces the solution through the PUF sample placed under the piston.

piston moves. The pulsating column technique is very convenient regarding process automation in the sorption–desorption regime. More detailed information about different procedures of sorption on PUF from aqueous solutions can be found in the monograph [5] and in reviews.[9,10] Various types of samplers used for the collection of organic compounds from air by sorption are described in the same publications.

Numerous studies have been devoted to PUF for the separation and preconcentration of metals, mainly, as acido complexes. Some examples are presented below.

The separation of the Ta–Nb (from 1 M HF), Mo–Re, Mo–Tc (from 0.1 M HF + 1 M NH_4F) pairs on 4.5 × 0.9 cm columns packed by polyether-based PUF (0.27 g of the sorbent) has been described.[28] It was shown that Ta, Re and Tc are desorbed quantitatively from the column on treatment with 1 M HNO_3.[28] Separation of Ga and Fe in the presence of large amounts of aluminium (1 : 1000) is attained by sorption from 6–7 M solutions of HCl by polyether-based polyurethane foams.[35] Procedures for the separation of binary and ternary mixtures (W–La, W–Al, La–Ga, La–W, Ga–Al, Al–W–Ga and Mo–La–Al)[71] under dynamic conditions using columns packed with 1 g of PUF at a flow rate of 1–5 ml min^{-1} have been developed. The separation is based on different sorbability of elements from thiocyanate solutions, which increases in the series Al < Ga < La < Mo < W. The Mo and La ions are desorbed from the column with acetone, while Al, Ga and W, by 1 M HCl, 2 M NH_3 and an HCl–acetone mixture, respectively.

The difference between the rates of sorption of elements on PUF underlies the procedure of separation of Te and Se.[49] Tellurium is sorbed quantitatively (> 99%) over a period of 2 min from a solution containing 1 M HCl and 5 M NaBr, while quantitative sorption of selenium requires that the contact time be increased to 2 h.

Procedures for separation of Os from Ru,[78] Pd from Pt,[82] Rh from Ir[76] and Ru from Rh[79] based on the difference between the rates of formation of thiocyanate metal complexes have been developed. It was found that palladium can be collected at room temperature from a solution (0.002–0.006 M KNCS and 2 M KCl) in the presence of a large amount of platinum (1 : 20).[82] To separate Ru from Os or Rh, a 0.3–0.4 M solution of KNCS containing 2 M NaCl is heated for 5 min at 90 °C and the $Ru(NCS)_6^{3-}$ complex is sorbed by polyether-based polyurethane foams. The degree of recovery of Ru is 95%, while Os and Rh are sorbed under these conditions to not more than 5%.[78,79] For separation of Rh and Ir (0.2 M KNCS + 0.2 M LiCl), the solution is heated for 30 min at 90 °C; as this takes place, rhodium is transferred quantitatively in the $Rh(NCS)_6^{3-}$ complex. The complex is sorbed by PUF to 94±1% and iridium, to not more than 5%. The procedure allows separation of rhodium in the presence of a large amount of iridium (1 : 5).[76]

The preconcentration of cobalt and iron as thiocyanate complexes from large (up to 1 litre) samples on a PUF-packed column at a flow rate of 30 ml min^{-1} has been described.[56] The recovery of metals present in a concentration of 1 μg $litre^{-1}$ was 96%. An efficient method for preconcentration of Co, Fe and Zn on 5 × 2 cm columns packed with 1.5 g of PUF (v = 5 ml min^{-1}) has been proposed.[57] It was shown[73] that Zn, Hg and In are sorbed quantitatively on a PUF column from a 0.2 M solution of KNCS at pH 2–3 and at flow rates of 25–50, 10–25 and 20–50 ml min^{-1}, respectively. Zinc is desorbed using 1 M HNO_3, and mercury and indium, by 1 M KNCS in 80% acetone. Molybdenum is recovered from sea water using sorption of its thiocyanate complexes on PUF with subsequent desorption with acetone.[77]

A number of studies have been devoted to the use of PUF for the preconcentration of PCB,[107,126–128,153] PAH,[109,110,125] phenols,[139,140,165] organophosphorus and chlorinated acaricides[158,159] and organophosphorus insecticides from water. It was noted that PUF offer a number of advantages over other polymeric sorbents and carbons for preconcentration of PAH, PCB, and chlorine- and phosphorus-containing insecticides present in water.[118,127,132,135,136] Polyurethane foam sorbents provide highly efficient recovery and allow a very high sampling rate (up to 800 litres min^{-1}).

2. Photometry

Two variants of using PUF in photometric analysis can be distinguished. The simplest, although not the most popular method is based on the sorption of elements on PUF as coloured compounds, desorption by acetone and spectrophotometric determination in the eluate. A classical example of using this method is determination of Co, Fe, Mo and Cu,[66] Ti,[83] Co,[238] Fe[239] as intensely coloured thiocyanate complexes after desorption from PUF on treatment with acetone. This technique was used to determine iron in glass and ceramic materials.[103] The method includes the preparation of Fe(II) phenanthrolinate, its sorption on PUF as an ionic associate with perchlorate ions, desorption by acetone and spectrophotometric determination at 510 nm. The range of iron concentrations determined in this way is 0.05–3 μg ml^{-1}. The method for cadmium determination in industrial zinc oxide specimens is based on the sorption of the $[Cd(Phen)_2]^{2+}$ associate with dithizone as the counter-ion.[102] A method for platinum determination in glass with a limit of detection of 0.1 μg ml^{-1} has been developed.[99] This includes sorption of the complex with dithizone on PUF, desorption by HCl-acidified acetone and spectrophotometric determination at 530 nm.

In some cases, a different, more suitable reagent is added to the eluate to increase the sensitivity and selectivity of the spectrophotometric determination. A method for determination of cobalt in nickel salts and in steels is based on the collection of cobalt on PUF from thiocyanate solutions, desorption with 80% ethanol and the subsequent determination in the eluate using 2-(2-benzothiazolylazo)-2-cresol.[240] The method allows determination of cobalt in the presence of large amounts of Ni, Mo and Fe. A photometric method was described for arsenic determination in glass; the method includes preparation of the oxidised form of molybdoarsenic acid, its sorption on PUF, desorption with 0.1 M HNO_3 and determination in the eluate as the reduced form after the addition of $SnCl_2$.[89] A reported[84] method for determination of zinc in cadmium salts is based on sorption of zinc thiocyanate complexes on PUF, desorption on treatment with water and subsequent determination using 4-(2-pyridylazo)resorcinol. The same principle underlies determination of cobalt in natural waters.[210] The procedure includes preconcentration of cobalt from a 10-litre sample by sorption under dynamic conditions on a column with PUF loaded with 1-(2-pyridylazo)resorcinol.

The second variant is associated with the techniques of thin layer spectrophotometry, which rationally combines the preconcentration of elements on PUF with direct determination of the absorption of light by the solid phase.[53,62,94,185,214,216,230] The essence of the method is in the sorption of coloured compounds by a PUF specimen shaped like a thin parallelepiped with dimensions corresponding to those of the cell (2 × 1 × 0.1 cm), transfer of the sorbent into a cell filled with an organic solvent and measurement of the optical density. The solvent serves as an immersion liquid reducing light scattering. Methods have been reported for determination of bismuth as an iodide complex;[53] cobalt as the thiocyanate;[62] phosphate ions as the reduced form of the molybdophosphoric heteropolyacid;[94] zinc and bismuth,[212] divalent mercury chloride and phenylmercury chloride[216] as dithizonates; and chromium as blue peroxochromic acid and a complex with diphenylcarbazide.[185,230] However, these methods are characterised by relatively narrow ranges of linearity of calibrating plots and relatively low reproducibility of the results.

Good prospects for the use of PUF in a flow-injection system were first demonstrated in relation to photometric determination of zinc in specimens of biological origin.[85] In this system, zinc is collected in the 'on-line' mode as the thiocyanate complex on a

microcolumn with PUF (0.3 × 3 cm, 100 mg of the sorbent), eluted with water and determined with 4-(2-pyridylazo)resorcinol. A flow-injection system has been used [241] for the photometric determination of aluminium with methyl thymol blue after separation of the interfering ions as thiocyanate complexes by sorption on a microcolumn with PUF (0.3 × 7 cm, 200 mg of the sorbent). The calibration plot is linear in the 0.25–2.0 μg ml^{-1} range, the productivity of the method is 17 samples per hour. Determination of 1 μg ml^{-1} of aluminium can be carried out in the presence of large amounts of iron (1 : 170), zinc (1 : 100), copper and cobalt (1 : 50). This method has been used to determine aluminium in silicates and ores. The same procedure is employed to separate Fe, Cu, Zn and Co in a flow-injection method of determination of nickel in brasses, bronzes and silicates.[242] A method for determination of carbaryl with a limit of detection of 12 μg ml^{-1} after collection on a PUF microcolumn and desorption by dichloromethane has been proposed; on-line spectrophotometric detection was carried out at 280 nm.[243]

3. Diffuse reflection spectroscopy

The combination of preconcentration on PUF and subsequent determination of the sorbed substances by diffuse reflection spectroscopy is a promising expedient for analytical chemistry. The possibility of this combination was first discussed by Dmitrienko and coworkers.[63, 64] It was shown [25] that PUF offer a number of advantages over other sorbents regarding their use in sorption–photometric and sorption–luminescence procedures and in test methods. First of all, this facilitates the final stage of analysis because the sorbate can be easily separated from other components present in the sorption system, which looks like a coloured tight pellet; owing to the uniform distribution of the analyte over the sorbent matrix, PUF pellets can be used without any additional operations.

In diffuse reflection spectroscopy, the Kubelka–Munk function (F) is related to the analytical signal, diffuse reflection (R), and the sorbate concentration in the following way:

$$F = \frac{(1-R)^2}{2R} = 2.3\,\varepsilon\,c\,s^{-1},$$

where $\varepsilon = n \times 10^4$ is the molar extinction coefficient of the sorbate ($n = 1-10$), c is the sorbate concentration, s is the light scattering coefficient. Methodical aspects of the quantitative measurements of the diffuse reflection of sorbates on PUF are considered in a paper.[244] The main factors influencing the accuracy and reproducibility of diffuse reflection measurements, namely, sample layer thickness, sample humidity, the brand of the PUF used and the sorbate concentration, have been studied. For all the compounds studied, the Kubelka–Munk function was found to be linearly related to the sorbate concentration not only in the PUF matrix but also in aqueous solution within the limits of the linear sections of sorption isotherms. The limits of detection of intensely coloured ($\varepsilon \simeq n \times 10^4$) compounds in the PUF matrix reach $n \times 10^{-2}$ μg in a 0.04–0.07 g PUF pellet or $n \times 10^{-4}$ μg ml^{-1} for a sample volume of 25–100 ml.

Various methods are used to obtain a coloured compound in the sorbent phase. One method is based on the sorption on PUF of the coloured compounds formed in the solution under analysis upon the reaction between a specially added analytical reagent and the target component. Numerous publications have been devoted to determination of metal ions and organic compounds by this method. For example, in a sorption–photometric determination of cobalt [63–65] and iron,[63, 64, 69] they are transferred into coloured thiocyanate complexes and sorbed on PUF. The limits of detection are $n \times 10^{-3}$ μg ml^{-1}. To increase the selectivity of analysis, sorption is carried out in the presence of various masking compounds. A similar method was used to determine silicon as the oxidised and reduced forms of molybdosilicic acid with limits of detection of 3×10^{-3} and 1×10^{-2} μg ml^{-1}, respectively. A sorption–photometric procedure for determination of ionic surfactants using PUF is based on sorption of the associates formed by surfactants and coloured hydrophobic counter-ions. Sulfophthalein dyes are used as the counter-ions in the determination of cationic surfactants,[173] while tris(1,10-phenanthroline)iron(II) was used for anionic surfactants.[105, 171] This procedure makes it possible to determine ionic surfactants present at a level of $n \times 10^{-2}$ μg ml^{-1}. A sorption and photometric method for determination of phenols and 1-naphthol is underlain by sorption of their coloured azo derivatives.[161, 163–165] Azo derivatives of phenols were synthesised by azo coupling with 4-nitrophenyldiazonium tetrafluoroborate. To enhance the recovery, sorption was carried out in the presence of cetyltrimethylammonium bromide. This procedure provides determination of phenols with limits of detection of $n \times 10^{-3}$ μg ml^{-1}.

The second method is related to the use of loaded PUF. In this case, the coloured compound is formed directly in the sorbent phase due to complexation or redox reactions between the target component present in an aqueous solution and an analytical reagent immobilised on PUF. Polyurethane foam loaded with dimethylglyoxime was proposed for sorption–photometric determination of nickel,[64, 206] and diphenylcarbazide-loaded PUF was proposed for chromium(VI) determination.[64, 231, 232] A sorption–photometric determination of ascorbic acid is based on reduction of heteropolyacids immobilised on PUF.[245] The procedure allows determination of 0.3 to 2.4 μg ml^{-1} of ascorbic acid. The time of analysis is 75 min. When the reduction of heteropolyacid is carried out on exposure to microwave radiation, the duration of the analysis decreases to 6.5 min.[246]

The third method for preparation of coloured analytical forms in the PUF phase is based on chemisorption processes involving the terminal groups of these polymers. In this case, a higher selectivity is to be expected. This technique was used, for example, to determine nitrite ions [180] and free active chlorine [181] in water.

4. Luminescence

A number of studies have been devoted to the use of PUF in luminescence analysis. The key factors influencing the intensity of fluorescence of sorbed molecules such as the thickness of the sample layer, sample humidity, the structure of the polymeric framework of PUF and the sorbate content have been studied in relation to the $[Ru(Phen)_3]Cl_2$ complex, pyrene, rhodamine 3B, rhodamine 6G and butylrhodamine sorbed on PUF.[244, 247] It was found that the polymer framework of PUF has virtually no influence on the fluorescence emission and fluorescence excitation spectra of the sorbates; the spectra of sorbates on different PUF normally do not differ from one another and in most cases, they are similar to the spectra of these substances in aqueous solutions. The limits of detection of compounds with intense fluorescence in the PUF matrix are $n \times 10^{-3}$ μg (the weight of PUF $\simeq$ 0.04–0.07 g) or $n \times 10^{-5}$ μg ml^{-1} for a sample volume of 25–100 ml. The range of linearity of calibrating plots coincides, as a rule, with the initial linear sections of sorption isotherms and holds up to a change in the sorbate concentration by one to two orders of magnitude.

In most cases, compounds that luminesce on the sorbent surface (for example, metal complexes with organic ligands) are obtained by sorption from the solution in which they have been synthesised. A sorption–luminescence method for yttrium determination includes the formation of a complex with 8-hydroxyquinoline, sorption of the complex on PUF and measurement of the luminescence intensity at 510–513 nm (λ_{excit} = 398 nm). The method was applied for determination of yttrium in lanthanum [100] and scandium [101] oxides. In a highly sensitive sorption–luminescence method of selenium determination in soil, the target element is sorbed as 4,5-benzodiazoselenol, which is prepared by the reaction with 2,3-diaminonaphthalene.[248] In a method for determination of Eu in scandium oxide, the mixed-ligand complex of this element with thenoyltrifluoroacetone and 1,10-phenanthroline is sorbed by polyurethane foam and then Eu is determined by luminescence directly in the sorbent, the limit of detection being

1×10^{-6} %.[106] Thallium is sorbed on PUF as the chloride complex, then the sorbate is treated with rivanol, a diamino derivative of acridine, and the fluorescence intensity is measured at 497 nm (λ_{excit} = 367 nm).[51] Only gallium is sorbed together with thallium. The analysis of these elements is not interfered with by the presence of large amounts (1 : 1000) of Cu, Co, Ni, Cd, Zn, Hg, In and La and alkali and alkaline earth metals; the limit of detection is 0.5 μg litre^{-1}.

A method for determination of Cr(III) based on the quenching of fluorescence of rhodamine 6G sorbed on PUF has been described.[249] The limit of detection equals 8 ng ml^{-1} for a sample volume of 25 ml.

A scheme of analysis has been proposed to perform fast screening of water samples for the content of PAH. According to this procedure, PAH are collected on PUF and their total amount is determined by the sorption-luminescence method.[125] Individual PAH are determined in the eluate after desorption of the sorbed impurities by acetonitrile using high-performance liquid chromatography (HPLC) with a fluorescence detector.[25]

5. Atomic-absorption and atomic-emission spectroscopy

The preconcentration of elements by sorption on PUF is often combined with determination in eluates by atomic-absorption spectroscopy (AAS) and atomic-emission spectroscopy with inductively coupled plasma (ICP AES). The flame AAS method was applied to determine platinum[44] and thallium[50] after preconcentration of the elements as halide complexes on PUF followed by desorption on treatment with acetone.

Combination of group preconcentration of elements by sorption on PUF loaded with ammonium pyrrolidinedithiocarbamate (PUF – APDTC),[220, 221, 223] a mixture of hexamethyleneammonium hexamethylenedithiocarbamate with methyltrioctylammonium chloride (MTOA)[224] or on PUF loaded with sodium diethyldithiocarbamate[222] followed by determination of elements by non-flame AAS or ICP AES proved successful. A procedure for determination of As, Bi, Sb, Hg, Sn and Se in natural waters[220] includes collection by sorption on columns with PUF – APDTC, elution of the element pyrrolidinedithiocarbamates with methanol, generation of hydrides directly in a methanol solution by the reaction with $NaBH_4$ and subsequent determination by ICP AES. The limits of detection of elements are, ng ml^{-1}: 0.2 (As), 30 (Bi), 0.03 (Se, Sb and Sn).

In determination of Cd, Co, Cu, Fe, Hg, Ni and Pb in high-purity oxalic acid,[224] trace elements are concentrated under dynamic conditions on columns with PUF – APDTC or PUF – APDTC – MTOA; the degree of recovery of elements is higher than 97%. The components are desorbed by methyl isobutyl ketone (for AAS determination) or 4 M HNO_3 (for ICP AES determination). The limits of detection are 0.1 (Cd), 0.3 (Pb), 1 (Ni), 2 (Co and Cu) ng g^{-1} and 0.1 (Hg) μg g^{-1} for non-flame AAS and 0.05 (Cd), 0.1 (Cu), 0.2 (Ni) and 1 (Pb) μg g^{-1} for ICP AES.

The column version of the solid-phase extraction using PUF loaded with APDTC was used[221] to collect As, Bi, Hg, Sb, Se and Sn impurities in waters of various types. The degree of recovery of elements on passing of 150 ml of a sample (pH ~4.5) at a flow rate of 2 ml min^{-1} through a column was 97% – 100%. After elution with methanol, the concentrate was analysed by ICP AES; the limits of detection were, ng ml^{-1}: 3 (As, Se), 8 (Bi), 0.12 (Hg), 2 (Sb) and 6 (Sn). It should be noted for comparison that the use of non-flame AAS after desorption of the elements with methyl isobutyl ketone decreased the limits of detection of elements down to 0.06 (As and Sb), 0.1 (Bi and Sn), 0.08 (Se) and 0.3 (Hg) ng ml^{-1}.

A method for lead determination in sea food has been proposed;[250] lead is collected on a microcolumn packed with PUF loaded with 2-(2-benzothiazolylazo)-2-cresol, desorbed with 0.1 M HCl and determined by flame AAS. The limit of detection of lead by this method is 1 μg l^{-1}.

A flow-injection system has been used[251] for atomic-absorption determination of zinc in waters and biological materials after preconcentration by sorption on a microcolumn packed with PUF.

6. X-Ray fluorescence spectroscopy

X-Ray fluorescence spectroscopy has been used to determine Ga,[41] Co,[58, 60] Fe, Pd, Pt and Zn,[60] As,[88] Ge,[90] PO_4^{3-} (see Refs 92, 93) methyl- and phenylmercury chloride, inorganic mercury[226] and U.[252] Indirect determination of phosphorus on the basis of molybdenum or antimony after preconcentration on PUF as phosphomolybdate[92] or molybdoantimonylphosphoric acid[93] has fairly low limits of detection (0.1 and 0.02 μg ml^{-1}, respectively). The latter procedure is more selective: large amounts of silicon do not interfere with the determination of phosphorus. The relative standard deviation does not exceed 0.05. In an X-ray fluorescence determination of arsenic[88] and germanium,[90] they are transformed into arsenomolybdate and molybdogermanate, which are sorbed on PUF. The range of concentrations determined in this way is fairly broad: 0.5 – 3.5 and 0.25 – 35 μg ml^{-1}, respectively. Arsenic can be determined in the presence of large amounts of PO_4^{3-} and SiO_4^{2-} (1 : 10) and an equal amount of germanium. The limits of detection are 40 and 70 ng ml^{-1} and the relative standard deviations do not exceed 0.07 and 0.09 for arsenic and germanium, respectively.

Determination of Co, Zn, Pd, Pt, Fe is carried out using sorption of their thiocyanates from acid solutions in the presence of NH_4Cl.[60] The ranges of linearity of the calibrating plots are rather narrow: 1 – 5 (Co, Zn, Fe) and 1 – 10 μg ml^{-1} (Pd, Pt), the corresponding relative standard deviation being not more than 0.05. In sorption – X-ray fluorescence determination of chloride, methyl- and phenylmercury chloride, PUF loaded with sodium diethyldithiocarbamate is used.[226]

7. Neutron activation method

Direct determination of sorbed elements by neutron activation analysis (NAA) was shown to be, in principle, possible in a number of studies.[14, 31, 227] The NAA method with a neutron flux density of 3×10^{13} neutron cm^{-2} s^{-1} (irradiation for 10 min) allows determination of Au, In, Hg and Zn in the polyurethane foam matrix after collection of these elements from thiocyanate media.[14] It was noted that irradiation of PUF for more than an hour results in polymer destruction; irradition in H_2SO_4 leads to complete dissolution. Determination of gold in natural waters after sorption from 6 M HCl on ether-based polyurethane foams has been described.[31] Neutron-activation determination of antimony is preceded by its isolation using PUF loaded with potassium diethyldithiocarbamate.[227]

8. Enzymic methods

In enzymic methods of analysis, PUF are used as polymeric supports for immobilised enzymes. A method for the immobilisation of cholinesterase comprising capture of an enzyme into a starch gel followed by impregnation of the gel into the PUF matrix has been proposed.[253] An analytical system in which an enzymic minireactor is combined with an electrochemical sensor within one unit has been developed[254] to determine toxic substances of the anticholinesterase action (for example, insecticides) in air and in liquid media. As the air or solution sample under analysis is pumped through the minireactor, the inhibitor is collected on the immobilised enzyme and inhibits it. The combination of preconcentration and analytical reaction in one unit with the sensor increases the method sensitivity and shortens the response time. The limit of detection of organophosphorus insecticides by such a system is 0.1 – 4.5 ng ml^{-1}, that for carbamates is 0.5 – 20 ng ml^{-1}.

A method for immobilisation of horse-radish peroxidase[255, 256] and alkaline phosphatase[257] in a chitosan film followed by impregnation into PUF has been developed. This procedure was used to develop highly sensitive test methods for

determination of mercury [255] and organomercury compounds.[256] The oxidation of *o*-dianisidine in the presence of thiourea by hydrogen peroxide is used as the indicator reaction. This procedure provides mercury(II) determination at a level of 1 ng ml^{-1}; the lower limits of determination of methyl-, ethyl- and phenylmercury are 0.008, 0.01 and 25 μmol $litre^{-1}$.

A test procedure for determination of 0.05–10 000 ng ml^{-1} of lead has been described.[257] In the development of this procedure, the inhibitory action of lead on the activity of PUF-immobilised alkaline phosphatase in the hydrolysis of *p*-nitrophenyl phosphate was utilised. It was noted that the key advantages of PUF over polystyrene and chromatographic paper used previously for enzyme immobilisation include a long (1–1.5 years) period of maintenance of enzyme activity; the researchers also noted good metrological characteristics of the developed procedures.

9. Chromatographic methods

The most important applications of PUF in chromatographic methods of analysis include preconcentration and isolation from waters and air of PAH,[110–113, 117, 122, 124] PCB [107, 121, 124, 131, 133, 153] and chlorine- and phosphorus-containing insecticides.[127, 128, 133, 134, 152] After collection on PUF, organic compounds are determined using gas chromatography (GC) and HPLC in combination with various types of detector: flame ionisation (FID), electron capture (ECD), mass-spectrometric (GC/MS technique), N/P-selective and UV and fluorescence detectors. The existing chromatographic methods for the determination of trace amounts of organic compounds consist of several stages: collection of the trace elements on PUF, desorption, evaporation of the solvent and analysis of the concentrate.

Various solvents have been proposed for desorption of compounds from PUF: acetone,[11, 107, 110, 117, 152] hexane,[107, 133, 134, 153] methanol,[117] an acetone–hexane mixture,[133] diethyl ether and petroleum ether.[121] Solvent desorption is carried out in the Sohxlet apparatus for 18–24 h.[107, 113, 115, 116, 118, 130, 132–134, 149] In some cases, samples are treated with ultrasound to intensify the process.[122] Supercritical fluid extraction (SFE), which makes it possible to shorten the desorption time to 10–20 min,[124, 156] and a method based on extraction of impurities with a small amount of an organic solvent after compression of PUF to 10% of its initial volume in a special column can provide alternatives to the prolonged and cumbersome procedure of Sohxlet desorption.[123] In has been shown [123] that 4 ml of dichloroethane or 6 ml of a 10% solution of acetone in hexane is sufficient for quantitative elution of eighteen PAH from a PUF sample with an initial volume of 115 cm^3.

The preconcentration of organic compounds from waters is carried out in a dynamic regime; the flow rate reaches 270 ml min^{-1}. Traces of PAH are collected from water samples having large volumes (4–60 litres) using columns filled with one or several cylindrical inserts of PUF (45 × 45 mm).[109, 110] A water sample heated to 62 ± 2 °C is passed through a column at a flow rate of 250 ± 10 ml min^{-1}. It was noted that pre-heating decreases the loss of PAH caused by co-precipitation on the suspended particles present in water samples.[109] For most of PAH including 3,4-benzopyrene, the degree of recovery amounts to 90%–98% for the model samples prepared from distilled water and 65%–85% for real potable or river water samples.[109, 110] It was demonstrated in relation to 3,4-benzopyrene that PAH samples sorbed on PUF are stable for 7 days when the storage temperature is 4 °C.[109] The PAH are desorbed by successive treatment with acetone and cyclohexane and determined by GC with a FID or by HPLC with a luminescence detector.[110, 111]

The efficiency of PUF as sorbents for the isolation of PCB (2–20 ng $litre^{-1}$) from natural water with a view to subsequent GC determination has been evaluated.[107, 126–128, 135] When large sample volumes (up to 1790 litres) are passed through columns packed with PUF cylinders (3.8 × 2.2 cm) at a flow rate of 250 ml min^{-1} and then elution with acetone or hexane is carried out in a Sohxlet apparatus, 80%–100% of PCB is recovered. The influence of the flow rate on the degree of recovery of organic compounds under dynamic conditions has been studied. It was noted that an increase in the rate from 10 to 100 ml min^{-1} has no influence on the completeness of PCB recovery; however, an increase in the flow rate to 250 ml min^{-1} decreases the degree of recovery to 30%–60%.[128]

Polyurethane foams are used to collect thirteen organochlorine insecticides (DDT, Lindane, Aldrin, *etc.*) and polychlorinated biphenyls by passing water through a (20 × 2 cm) column packed with PUF at a flow rate of 100 ml min^{-1}.[127, 128] The collected compounds were washed out from the column by successive treatment with acetone and hexane and determined by chromatography.

Several types of samplers which allow a flow rate of 800 litres min^{-1} to be reached have been developed for analysis of air.[117, 118, 121, 128, 133–135] The samplers are stainless-steel, glass or plastic tubes filled with cylindrical inserts made of PUF, in some cases, in combination with other sorbents or with glass-fibre filters. Prior to the use, sorbents are subjected to prolonged (up to 24 h) purification by means of various organic solvents and water in the Sohxlet apparatus.[113, 117, 133, 134] A large potential of portable samplers based on combination of PUF with other sorbents such as Tenax CG [121, 135] and XAD-2 [118, 121, 128] for preconcentration of PAH, PCB and chlorine-, phosphorus- and nitrogen-containing insecticides in urban air samples has been demonstrated. For a sampling velocity of 0.1–0.3 m^3 min^{-1}, the recovery of compounds is not less than 75%.[121] After desorption with a diethyl ether–petroleum ether mixture (15 : 85) [111] or 5% diethyl ether in hexane [133] in a Sohxlet apparatus and evaporation of the solvent, the concentrate was analysed by various chromatographic methods: HPLC with UV detector and GC with ECD, PID and N/P-selective detectors. One sampler of this type was used to determine organochlorine compounds in the air above the Arctic.[134] Air samples with a volume from 300–600 m^3 to 2000–4000 m^3 were pumped through a sampler for a period from 8 h to 2–7 days at a flow rate of 750–800 litre min^{-1}. Solid particles were retained on the glass-fibre filter, while the vapours of organochlorine compounds were sorbed in two cylindrical PUF inserts. The impurity components were desorbed by 100–300 ml of hexane for 8 h in a Sohxlet apparatus, then the solvent was partially removed and the concentrations of the impurities were determined using GC with an ECD, GC/MS and HPLC with an UV detector. The Arctic air was found to contain various PCB isomers, DDT and other organochlorine compounds whose concentrations are several pg m^{-3}.

A method developed [113] for determination of PAH in air at the ng m^{-3} level includes the following stages: preconcentration by sorption on PUF for 24–48 h at a flow rate of 0.5 m^3 min^{-1}, successive elution with pentane and a mixture of dichloromethane (30%) with pentane, solvent evaporation from the eluate and analysis of the concentrate by GC/MS or by HPLC with a fluorescence detector.

A procedure for isolation, preconcentration and identification of volatile mutagens present in air has been described.[117] The procedure includes sorption on PUF, elution with methanol or acetone, removal of the solvents, bioassays and analysis of the concentrate by GC/MS or by HPLC with a fluorescence detector.

Eighteen PAH were determined using GC/MS in exhaust gases after preconcentration for 20 min on a PUF-packed column and desorption with a small volume of dichloromethane or 10% of acetone in hexane.[123]

Combination of the desorption of components collected on PUF using supercritical fluid extraction with subsequent determination of these components by the GC/MS technique was reported to be efficient.[124] This combination underlies a scheme for determination and identification of PAH, PCB and n-alkanes present in exhaust gases and the cigarette smoke. The scheme implies preconcentration of organic impurities on PUF followed

by desorption by the CO_2 fluid directly to the separating chromatographic column and allows gas-chromatographic analysis to be carried out over a period of less than an hour.

10. Test methods

The high efficiency of preconcentration by sorption on PUF of many compounds, the intensive colour of the sorbent observed in some cases, the ready availability and low cost of the sorbent are attractive features stipulating the use of PUF in test methods of analysis — simple and cheap methods for detection and determination of substances.[258] A colour change of the sorbent after the reaction indicates the presence of the target component, and the content of the component is found by comparing the intensity of the sorbent colour with the appropriate scale or by measuring the length of the coloured zone or the time it takes for the characteristic colour to appear. The reliability of visual detection can be improved in some cases using portable miniphotometers which record light reflection from solid samples.

The possibility of using PUF in test methods of analysis was first mentioned by Braun and Farag.[218] Determination was preceded by element preconcentration on chromofoams (the term was introduced by Braun [218]), *i.e.*, PUF loaded with photometric reagents. When these foams, as small cubes, are brought in contact with the solution under analysis, the white polymer acquires a colour typical of the given photometric reaction. These reactions are highly sensitive, for example, for sorption in the static regime, tenths (Co,[218] Cu,[214, 218, 233] Cd,[214] Pd,[233] Pb,[218, 219] Cr,[230] Mo [234]) and in some cases, even hundredths (Ag,[211] Ni,[205] Cu,[214] Zn,[218] PO_4 [94]) of a microgram of an impurity can be determined in a sample volume not exceeding 1 – 2 ml. The sensitivity of determination increases by at least an order of magnitude when Co,[218] Cu,[218] Cd,[214] Cr [230] and Mo [234] are sorbed in the dynamic regime. Detection of metals at a level of several nanograms in ml is attained by passing relatively large volumes of a solution (~1 litre) through a chromofoam filled column. The use of these materials ensures higher sensitivity of analysis than the use of impregnated paper or than drop reactions.[205, 214, 218, 219, 230] Chromofoams are also suitable for a semiquantitative determination, which implies either comparison with standard colour scales after sorption in the static regime or measurement of the length of the coloured zone in the column after letting-through the solution under analysis. Usually, the colour intensity of chromofoams is linearly related to the metal concentration in the aqueous solution.

One more way of using these sorbents in test methods of analysis, not associated with the preparation of loaded PUF, is also possible. Pellets of unloaded PUF complete with ampoules containing solutions of reagents have been used as test kits.[105, 163, 165, 172, 180, 181] The reproducibility of the results of visual detection based on a colour scale (s_r) varies in the range of 0.1 – 0.5. Test kits based on PUF for determination of Co, Ni, Fe(III), nitrite ions, free active chlorine, total content of phenols, and anionic and cationic surfactants have passed metrological certification, have been registered as a type of test system [259] and are currently produced in industry. The test systems based on PUF are simple to produce, reliable in operation and suitable for determination of toxic substances in waters of various types including potable and mineral waters, extracts from soils or juices. If necessary, the test form can be retained and analysed in a laboratory using diffuse reflection spectroscopy or, after desorption of compounds, HPLC.[165]

VII. Conclusion

The presented data demonstrate that polyurethane foams are of considerable interest for the analytical chemistry of inorganic and organic compounds. Characteristic features of these sorbents include high efficiency in combination with versatility, chemical and mechanical strength, stability against organic solvents, relatively low cost and ready availability. The unique sorption properties of synthetic polymeric materials are largely due to their cellular membrane-like structure, which allows the molecules being sorbed to penetrate inside the sorbent, and to the combination of various hydrophilic and hydrophobic active sites and reactive terminal groups.

The applications of PUF in analytical chemistry are diverse. These sorbents are used for preconcentration of elements and organic substances from water and air and in spectroscopic, sorption – spectroscopic and chromatographic methods of analysis. The good prospects of using PUF in flow-injection analysis are demonstrated. Other applications of these materials are also noted, including the use as polymer matrices for enzyme immobilisation in enzymic methods of analysis.

Polyurethane foams are of interest not only regarding practical use but also in purely scientific aspects. In our opinion, the scope of application of PUF in analytical chemistry has not been adequately appreciated because most studies are aimed at the solution of applied problems of substance preconcentration and only few publications deal with investigation of physicochemical processes that proceed during sorption. Too little attention is devoted to elucidation of the relationship between sorption parameters and the properties of the sorbed molecules and evaluation of the contributions of intermolecular sorbent – sorbate interactions. Virtually no works are related to the study of physicochemical properties of the polyurethane foams themselves.

The study of heterogeneous chemical reactions involving the PUF surface are of considerable interest. This line of research, which is successfully developing in other fields of chemistry, can provide important results that would allow one to approach the problem of target-directed change of the properties of PUF by surface modification.

One may hope that PUF would be used more and more extensively in hybrid methods of analysis based on the combination of preconcentration by sorption with the subsequent determination in the sorbent matrix using diffuse reflection spectroscopy, luminescence or X-ray fluorescence spectroscopy and in test methods of analysis.

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