Analytical profile of the methods in reactive polymeric solid phase

Grdinić, Vladimir; Luterotti, Svjetlana

CROATICA CHEMICA ACTA CCACAA **73** (1) 23–56 (2000)

ISSN-0011-1643
CCA-2634

Review

Analytical Profile of the Methods in Reactive Polymeric Solid Phase

*Vladimir Grdinić and Svjetlana Luterotti**

Faculty of Pharmacy and Biochemistry, University of Zagreb, HR-10000 Zagreb, Ante Kovačića 1, Croatia

Received October 12, 1998; revised January 22, 1999; accepted January 26, 1999

This review is aimed at covering the recent advances and the present status of trace analysis methods based on *in situ* measurements in the reactive polymeric solid phase.

Key words: methods on polymeric solid phase, analytical profile, review, trace analysis.

INTRODUCTION

Ion exchange has evolved into a major technique for the separation and enrichment of metal ions at trace levels. The selectivity of the reactive polymeric solid phase, like in chelating exchangers, is often superior to that of conventional ion exchangers. The analytical processes, those essentially heterogeneously phased, provide the use of characteristic reactions of ionic or molecular species distributed throughout solid matrices, in most cases in the form of ion-exchange resins.[1] Solid matrices are materials that, in a reversible manner, exchange their own ions for the ions of the solution and are insoluble in the solvents in which they are used. Consequently, qualitative and quantitative examinations are based on the colouration of beads or particles of polymeric solid phase, produced by the uptake of ionic or molecular species. The analyte detection and determination depend on the nature of the solid phase loading, the equilibria involved in the *e.g.* ion-exchange reactions, and other fundamental processes related to the qualitative and quantitative resin spot test methods.

* Author to whom correspondence should be addressed. (E-mail: sluter@.nana.pharma.hr)

Selective and sensitive procedures for the determination of trace amounts of analytes are obtained by combining the selective enrichment procedure with sensitive detection in the solid phase. Analytes can be determined at trace level because the targeted species are enriched in the small volume of a solid phase. Selective detection might be possible with a solid phase containing an agent of high reactivity to the targeted species. Moreover, solid-phase extraction involves no difficult phase separation caused by mutual solubility of water and organic solvent layer and no interference from particulate matter suspended in aqueous samples because particles are not adsorbed onto the solid phase medium. Analytical methods on polymeric solid carriers were extensively covered during the last decade by a book and several review articles.[1–14]

This review is a continuation of the authors' investigations published in the book entitled »*Analytical Profile of the Resin Spot Test*« in 1990.[1] This book is a comprehensive reference work and contains a wealth of detailed information on the application of resin spot tests[15] to inorganic and organic microchemical analyses. The resin spot test is a generic term applied to a collection of simple, inexpensive and easy-to-use analytical methodologies, facilitated by the reaction with or adsorption by functionalized resins and aimed at detecting analytes by colour development. The resin spot test is limited by the perception of its methodology, qualitative in principle. Some twenty years ago, first reports on quantitative application of resin spot tests appeared under the name of »ion-exchanger colorimetry«.[16] Since then, the quantitative approach has been progressively developed on account of the qualitative one.

This report is aimed at covering the last decade achievements in the methods in the solid phase, which have outgrown the conventional resin spot test. In order to make this article more informative than comprehensive, it is confined only to investigations with an *in situ* measurement as well as to the papers with highly accentuated analytical applications. Several border fields that are not included in this report are those dealing with:

– model investigations and development of selective extractants;
– synthesis and physico-chemical studies of solid carriers and chemical sensors;
– sorption studies of efficient sorbents in view of their sorption capacity and enrichment techniques;
– solid carriers that are not of a polymeric nature;
– application of sorbents in sample pretreatment, separation, and/or SPE with no *in situ* measurements;
– liquid ion exchangers;
– flotation-extraction procedures.

THE NATURE OF ANALYTICAL SYSTEMS

Analyses of traces of constituents demand highly sensitive methods. Since the methods in the solid phase combine the preconcentration of the species of interest on a solid matrix, usually an ion exchanger, and subsequent measurement of the physical phenomenon of the species in the solid phase, they fulfill this task. Procedures are often based on the use of loaded or modified solid phases while the fixed species may be analyte itself if it is a coloured or luminescent species, or the coloured or fluorescent reaction product. Trace metal analyses, for example, need highly sensitive and selective chromogenic reagents, such as coordination reagents, ion association colour reagents, surfactants. For example, Fe^{III} could be selectively retained and separated from other common heavy metal ions by hydroxamate resin.[17] To enhance selectivity and sensitivity as well as to remove the large background caused by the absorption of the solid phase, derivative techniques are also frequently applied.

Methods on polymeric solid carriers should be classified according to:

- measured parameter (UV/Vis absorption, luminescence, diffuse reflectance, current or voltage, photoacoustic measurements, visual colorimetry);
- type of the solid phase (ion exchangers, polystyrene-DVB or dextran-type, modified or non-modified, or some other type of polymeric material);
- analytical significance (quantitative, semiquantitative or qualitative).

Solid Phase

Different commercial ion exchangers and those laboratory prepared can be applied both to microdetection and to determination of trace analytes.[1] Ion-exchange resins are relatively uniform in structure and capacity, and minimize errors during the analytical procedure. Functional groups or anchor groups used in organic ion exchangers vary widely. The selectivity of chelating exchangers is often superior to that of conventional ion exchangers. The widespread application of such special collectors, however, has been frequently hampered by their difficult and expensive syntheses.[18]

An overview of solid supports used for *in situ* measurements is given in Table I. Solid carriers used for *in situ* measurements are recruited from ion exchanger materials, ionic and non-ionic polymers, and are used in the form of spherical beads, granules, membranes, fibrous materials or foams.

A very important position among solid carriers belongs to chelating sorbents provided with either grafted groups or those loaded with appropriate chelating reagents. For example, an iminodiacetic acid resin of styrene/DVB type[19] and hydroxamate acrylic resin[17] or silica[20] belong to the first group. Conventional ion-exchange resins are often used to prepare resinous reagents, *e.g.* with PAN,[21] ECBT,[22] XO,[23] NRS.[24] Immobilization of a chelat-

TABLE I

An overview of recent solid supports for *in situ* measurements

Ion-exchange resins / gels

Exchanger type	Skeleton	Functionality*	Immobilized species/ modified form	Reference(s)
Cationic	Not disclosed		–	58, 109, 114, 120, 143, 149
	Styrene/DVB	$-SO_3^-$, sA, ge/m	–	21, 29, 47, 67, 77–79, 102, 103, 150, 153, 184
			pDAB	183
			PAN	21
			ferrioxamine B	38, 39
			BBK	125
	Acrylic(methacrylic)acid/DVB or cross-linked polyacrylate	$-COO^-$, wA	–	105
	Cross-linked dextran	$-C_3H_6SO_3^-$, sA	–	70–72, 101
		$-CH_2COO^-$, wA	–	100
Anionic	Not disclosed		–	106, 110, 113, 119, 140, 147, 180, 186
			sulphanilic + chromotropic acid	76
	Styrene/DVB	$-CH_2N^+(CH_3)_3$, sB, ge/m	–	29, 47, 48, 54, 55, 57, 60, 66, 74, 104, 107, 108, 111, 115–118, 121, 137, 139, 145, 182, 185, 189
		$-CH_2N^+(CH_3)_3$, sB, ge	antrazochrome	122
			ECBT	22
			XO	23
			TAN-3,6S	123
			TAAF	124
			NRS	24
		$-N(CH_3)_2$, wB	–	47

TABLE I, cont.

	Cross-linked dextran	$-C_2H_4N^+(C_2H_5)_2CH_2CH(OH)CH_3$, sB	–	21, 49, 50, 62, 56, 64, 68, 69, 73, 75, 85, 86, 88, 89, 112, 148, 151, 152, 163, 165, 166
		$-C_2H_4N^+(C_2H_5)_2H$, wB	–	51–53, 63, 84, 87, 90, 91, 93–99, 169, 172
Chelating	Styrene/DVB	$-CH_2N(CH_2COO)_2$, Ch	–	19
	Acrylic(methacrylic)acid/DVB or cross-linked polyacrylate	$-COO^-$, wA, m	–CONHOH, Ch	17

Fibrous exchangers

Exchanger type	Skeleton	Functionality*	Immobilized species/ modified form	Reference(s)
Cationic	Cellulose	$-OPO(OH)_2^-$, sA, f, p	–	59
		$-CH_2OH/-COO^-$, wA, f, p	–	141, 173, 174, 179
			β-cyclodextrin + Pb^{II} acetate	175
		$-CH_2OH/-COO^-$, wA, f	pDAB+CCl_3COOH	34
Anionic	Cellulose	$-O(CH_2)_2N^+(C_2H_5)_3$, B, f	Arsenazo III	36

Inorganic exchangers

Exchanger type	Skeleton	Functionality	Immobilized species/ modified form	Reference(s)
Cationic	Sb-silicate/Sn^{IV} arsenate		pDAB	183

TABLE I, cont.

Polymeric membranes

Skeleton	Functionality*	Immobilized species/ modified form	Reference(s)
Polyethersulfone	$-SO_3^-$, sA	–	132
Cross-linked polyacrylate	$-COO^-$, wA	–	80
Cellulose	$-CH_2COO^-$, wA	carboxymethylcellulose (analyte)	40
	$-CH_2OH/-COO^-$, wA	PAN, dithizone, MTK	35
Cellulose nitrate		–	46, 58, 60, 61, 130, 131, 136, 140
		DNA or DNA/ChE	44
		gelatine	177
Cellulose acetate nitrate		–	146
Cellulose acetate		–	58
Polyamide		–	58, 144
Teflon		–	58
PVC		–	133
		BC	33
		BP	32
Nylon		–	176

Other polymers

Skeleton	Functionality	Immobilized species/ modified form	Reference(s)
Styrene/DVB		–	178, 190
		chloramine T	129
Cross-linked dextran		–	155–160, 164, 168, 171
		hydroxypropyl ether	154
Styrene		antibody IgG	45
		amines (analyte)	41
		GM1 (analyte)	42
Chitin		–	142

TABLE I, cont

Micron-size glass beads

Skeleton	Functionality	Immobilized species/ modified form	Reference(s)
Controlled-pore glass	aminopropyl	3-HPA (substrate)	43

Silica gel

Skeleton	Functionality*	Immobilized species/ modified form	Reference(s)
SiO_2		–	27, 67, 181
		PBHA	20
		C_{18}	27, 65, 84, 92, 93, 97, 161, 162, 99, 167, 190
		XO, Phen	25
		5-BrPADAP	26
		DEPD	27
	$-SO_3^-$, sA	–	27

Foamed plastics

Skeleton	Functionality	Immobilized species/ modified form	Reference(s)
Polyurethane foam		–	28, 29, 67, 126–128
		HMNQO	28
		FMF	31
		PAR	29
		dithizone	30, 31

* Ion exchanger designation: sA – strongly acidic, wA – weakly acidic, Ch – chelating, B – basic; sB – strongly basic, wB – weakly basic, ge – gelatinous, m – macroreticular, f – fibrous, p – paper.

ing agent on ion-exchange resin takes place by an ion-exchange mechanism but interactions between the exchanger matrix and condensed rings of the organic reagent may not be excluded. Due to their favourable sorption capacity and kinetic properties, the sorbents with macroporous structure play an important role. Chelating sorbents with functional groups immobilized by covalent bonds on inorganic polymers, usually silica, have been synthesized by chemical transformation of the matrix, *e.g.* by introduction of PBHA groups,[20] XO and Phen,[25] 5-BrPADAP[26] and DEPD.[27] Despite their high mechanical strength and thermal and chemical stability, the chelating sorbents based on inorganic matrix have a relatively low sorption capacity. Mechanical impregnation of the inert matrix, such as foamed plastics with complexing agents, is also possible. For example, open-cell polyurethane foams have been successfully used after being loaded with HMNQO,[28] PAR[29] or dithizone.[30,31] Non-ionic polymeric inert matrices such as PVC membrane have been successfully impregnated with BP[32] or BC.[33] Fibrous chelating sorbents such as the cellulosic ones are characterised by a large surface area and excellent kinetic properties, which are superior to granular sorbents. Thus, loading of celluloses with pDAB,[34] PAR, dithizone or MTK[35] and Arsenazo III,[36] as well as that of β-cyclodextrin with 5-BrPADAP,[37] have been described.

These considerations apart, one has to be aware of reagent resins prepared by loading with metal complexes.[38,39] Moreover, analyte-[40–42] or substrate-loaded[43–45] carriers may be useful as well.

Microscale Enrichment in the Solid Phase

There are three types of interactions during the detection or determination processes: loading of ion exchanger with: a) analyte, b) reagent, and c) reaction product.[1] The ways of developing the colour in the ion exchanger phase all depend on the nature of the particular sample components, the chromogenic agent, pH and associated factors. Consequently, the preconcentration step in the solid phase may involve enrichment of analyte, followed by addition of the reagent and formation of the reaction product in the solid phase, enrichment of reaction product from the solution, or collection of analyte in the solid phase previously modified with the reagent. For example, the fact that Be^{II} is strongly adsorbed from alkaline solutions on a glass surface by the anion-exchange mechanism has been used for selective enrichment of Be^{II} based on solid phase extraction on glass-fibre filter.[46] Be^{II} adsorbed was eluted with 0.1 M HCl and subsequently determined by solid-phase spectrometry on a cellulose nitrate membrane filter. The degree of adsorption of metal chelates on the ion-exchange resins and membrane filters is dependent on the charge, hydrophobicity and configuration of the compounds. For example, BC, BCS and BPS were found to be useful reagents for the enrichment of copper using Amberlyst A-27 macroreticular resin and BC, DPT and BP for enrichment of copper using the cellulose nitrate membrane filter.[47]

Species in the Solid Phase

Spectral Characteristics

An ion-exchange resin has, in general, only a featureless spectrum in the visible region.[1] On the other hand, coloured ionic species, especially metal complexes adsorbed in a resin phase, sometimes show interesting absorption spectra, especially in anion-exchange resins.

Ion exchanger phase is a special type of solution, which influences the physico-chemical characteristics and behaviour of the retained species in various ways. Metal ions are very often collected on a solid carrier in the form of coloured or fluorescent metal complexes formed with common complexing agents. The anion-exchange mechanism for metal ions may be interpreted in terms of coordination chemistry. For example, high ligand number or polynuclear complexes cannot be formed in ordinary solutions but have been found in anion-exchange resin phases. Metal complexes immobilized in the solid support may be used for detection of organic ligands.[38,39] Vis-spectra of the thin layer and transparent pellet (λ_{max} = 480 and 484 nm, resp.) of reagent-resin suggested the predominance of the tetradentate species of ferrioxamine B, $[Fe(H_2\text{-DFB})]^{2+}$, loaded on Dowex HCR($H^+$) resin. For the system Ru^{III}-HMNQO on polyurethane foam, a well defined absorption peak at 460 nm is assigned to the ligand (Π) $\rightarrow$ metal (d) charge transfer complex.[28] The mixed ligand complex, formed with a chromogenic and an auxiliary (usually masking) agent, also serves as a complexing system for fixation. This provides an increase in selectivity and sensitivity of the SPAS methods and applies, for example, to microdetermination of U^{VI} with PAR in the presence of F^- ion with the formation of anionic ternary complex of the composition 1:1:1.[48]

Hyperchromic effects responsible for enhanced sensitivity of the reaction in the solid phase are usual in SPAS and frequently accompanied by batochromic shifts from the solution to the solid phase. This applies, for example, to PAR, ECR, hydroxamic acids, ECBT or ferrozine complexes.*e.g.* [17,22,49–56] V^{IV} reacts with ECR at pH = 5.0 forming a 1:1 complex fixed on the Sephadex anion exchanger with a significant hyperchromic effect observed in relation to solution at the same pH.[53] Methyl benzoate gives with hydroxylamine benzohydroxamic acid, which reacts with V^V and originates several complexes. The violet species formed in HCl medium is strongly fixed by anionic resins, λ_{max} = 516 nm; in the presence of oxalate a new complex is formed and fixed, V^V-BHA-oxalate (1:1:2), with a batochromic shift to 546 nm and hyperchromic effect.[57] Contrary to this, red cationic Fe^{II}-Phen complex is strongly retained on cation exchangers, showing an absorption spectrum similar to that in solution.[58,59] Co^{III}-PAN absorption spectra in solution and on the membrane filter are similar,[60] whereas Ge^{IV}-Pfn complex collected on the membrane filter appears to be the same species as that formed in the

solution (λ_{max} = 505–508 nm).[61] The same applies to the Be^{II}-CAB complex.[46] For the fluorescent complex Mo^{VI}-CA, peak wavelengths in the emission spectra are different for the immobilized and solvated systems.[62] The maxima of the excitation spectra of the two systems differ as well. However, for W^{VI}-CA[63] and Be^{II}-morin[64] complexes, λ_{max} in the emission spectra are identical for the immobilized and solvated systems whereas the maxima of the excitation spectra in the dextran-type gel phase differ from those in solution. The modification of the fluorescence spectra features has been considered to be resulting from the modification of the surrounding environment and/or of the complex itself by being fixed in the resin phase, whereas the identical emission spectra suggest that the complex is relatively insensitive to its environment. Shifts of λ_{em} from 362 to 370 nm and of λ_{ex} from 398 to 392 nm observed for morestan at C_{18}-silica gel in relation to solution are no doubt due to the change of the environment.[65]

Organic Ligand Dissociation

The distribution equilibria of metal complex ions or large organic ions between an aqueous solution and an ion-exchange resin lie, generally, largely on the side of the exchanger.[1]

When PAR is considered a chromogenic agent, fixation of the respective chelates onto anion-exchange resin is due to the anionic nature of the chelates formed in slightly acidic medium, *e.g.* with Co^{II}, UO_2^{2+}, VO_2^{+} and Cu^{II}.[48,54,55,66,67] This was confirmed by the fact that the Co^{II}-, Cu^{II}- and V^{V}-PAR chelates could not be extracted into non-polar solvents but were successfully extracted into Adogen 464 in toluene. For example, Cu^{II}-PAR 1:1 complex is not necessarily neutral in charge.[55] PAR is considered a terdentate ligand with three donor atoms in the plane: metal is coordinated through pyridinic nitrogen, azo nitrogen further from the heterocyclic ring and the *ortho* hydroxyl group of the reagent. The coordination requirement of the Cu^{II} atom will be fulfilled by unidentate anion, *e.g.* Cl^{-}, $H_2PO_4^{-}$, HPO_4^{2-}. In this way the coordination unsaturated chelate can be extracted into an organic solvent in the presence of an auxiliary ligand or suitable pairing cation only. On the other hand, the *para* hydroxyl group of PAR may deprotonate at working pH; evenmore, chelation and fixation of metal-PAR complex on anion-exchange resin promote the dissociation of *p*-hydroxyl group of PAR.[54,66] The extractability of the $[Co^{III}(PAN)_2]^{+}$ complex on the membrane filter in the form of mixed ligand complex with some anionic ligand is considered to be due to its hydrophobic properties.[60]

In the presence of Sephadex QAE A-25 anion-exchange resin, the anionic 1:1 Be^{II}-morin complex is probably sorbed in the resin.[64] The complex has an anionic nature due to the ionization of morin (pK_{a1} = –1, pK_{a2} = 4.8, pK_{a3} = 7, pK_{a4} = 13) at working pH of 11.50.

pH-Dependence

Accurate regulation of acidity of the reaction medium may be of crucial importance for an analytical method, especially for the efficiency of the fixation process.[1] When considering the effects of acidity, one of the most outstanding features describing the behaviour of ion exchangers is their swelling, which is proportional to the pH over a considerable range. The pH of the medium has a remarkable influence on the formation of the analytical product as well.

PCV was used for determination of Sn^{IV},[68] and Mo^{VI}.[69] It has been noted that the fixation of PCV on ionic gel strongly depends on the medium pH. At pH < 1, the H_4L neutral species is present in the solution and there is no fixation on anionic gel; at pH > 1, yellow H_3L^- species with λ_{max} = 445 nm becomes fixed; at pH = 3–4, the violet species H_2L^{2-} with λ_{max} = 610 nm fixes on anionic gel. The presence of anionic gel displaces the dissociation equilibria: pK_{a2} of H_3L^- species, which is 7.51, turns to 3.6 in the presence of the dextran-type anion-exchange gel.[68] In the presence of Sn^{IV}, an anionic 2:1 complex is formed: the reagent is bound to tin by means of the previously deprotonated 3-OH and 4-OH groups of each PCV molecule. The fixation mechanism possibly requires formation of the complex in solution and its later retention by ion exchange.

Fixation of sulphonamides ST and SM on Sephadex SP C-25 is found to be strongly pH-dependent since they are fixed as monoprotonated species.[70–72] At pH values lower than 2.5, the absorbance for ST decreases due to the increased competition of H^+ ions for the ionic sites on the gel.

The optimum pH value for fixation of the Fe^{II}-Phen complex on cation-exchange filter was within the range of 3 to 5.5. At pH < 3, the absorbance of the complex decreases significantly because, owing to the protonation of the functional groups, the fixation process does not take place. At pH > 5.5, the Na^+ cations compete with the complex in fixation.[59] Reduction of Fe^{III} by ascorbic acid requires acidic medium; at the same time the formation of Fe^{II}-Fz anionic complex and its fixation on the resin are also pH-dependent, pH = 5.0 being the most appropriate.[56]

The hydrolysis of carbaryl in the presence of Sephadex QAE A-25 gel starts at pH = 8.0 and is complete at pH = 11.0.[73] Although not being fixed in the gel, carbaryl shows fluorescence at pH > 8 due to the fixation of its hydrolysis product, 1-naphthol, with fluorescence maxima at 332 and 450 nm, respectively.

An interesting example is the effect of pH regulated by HCl and NaOH on the formation of filterable Fe^{III} species.[74] The effect was investigated using a 0.45 μm cellulose nitrate membrane and remarkable similarities of the theoretical pH dependence of the $Fe(OH)_3$ formation with the adsorption of Fe^{III} onto the membrane filter were observed.

Processes in the Solid Phase

Reaction Mechanisms

By the analyte and reagent reaction, coloured, more or less soluble simple complexes, chelate species, polynuclear complexes, sparingly soluble products, dyestuffs, colloids or adsorbates, splits of matter, decomposition products of reagents, *etc*. could be formed.[1]

BC and analogous chelating agents react with Cu^{I} forming $Cu^{I}L_2$ complexes whereas BP and the analogous chelating agents react with Cu^{II} to form $Cu^{II}L_3$ complexes.[47] In the complexation reaction with *N,N*-donors such as BC and BP, the charge on Cu^{I} and Cu^{II} ions cannot be neutralized and this might lead to an electrostatic repulsion between the complex and the ion-exchange sites of the anion-exchange resins. However, Cu^{I}-BC and Cu^{I}-BCS complexes have been found to be fixed quantitatively on both the strongly and weakly basic anion-exchange resins. It may be assumed that Cu^{I}-BC complex is fixed on the resin as a result of hydrophobic interactions between the complex and the matrices of the resin, whereas for Cu^{I}-BCS complex, fixation due to ion-exchange by the sulphonate groups predominates. Analogously, Fe^{II}-BPS anionic complex is strongly sorbed on the anion exchanger owing to strong electrostatic interactions.[75] With a polystyrene-type anion-exchange resin the complex is even more strongly sorbed because of hydrophobic interactions between the complex and the resin matrix. According to stronger electrostatic repulsion of the anion-exchange resin, the sorption of Cu^{II}-BP complex is much lower than that of Cu^{I}-BC complex. This is probably due to the fact that Cu^{II}-BP complex has an octahedral configuration and two positive charges, whereas Cu^{I}-BC has a tetrahedral configuration with a single positive charge. Furthermore, hydrophobic interactions, due to an overlap between the benzene rings of the complex and the resin matrix would be much more favourable for the complex of tetrahedral than of octahedral configuration. Bulky octahedral configuration of Cu^{II}-BP complex probably reduces the electrostatic and hydrophobic interactions with the cation-exchange resin as well. Its affinity to cation-exchange resin is markedly reduced in comparison with the corresponding Phen complex, probably due to the presence of phenyl groups at positions 4 and 7 of Phen.

When nitrite was applied to the anion exchanger previously modified with a mixture of chromotropic and sulphanilic acid, diazotization of sulphanilic acid and azo coupling of sulphanilic acid diazonium salt with chromotropic acid occurred in the exchanger phase.[76] This resulted in the formation of a coloured reaction product, *p*-sulphophenylazo-1,8-dihydroxy-3,6-naphthalenedisulphonic acid.

The aldazine formed between pDAB and hydrazine is strongly sorbed on the cation exchanger, Dowex 50W-X8(H^+).[77] This may be explained by differ-

ent mechanisms: first, fixing, which is carried out by adsorption, because of the aromatic nature of the solid support and that of the aldazine and/or by ion-exchange process involving the cation exchanger groups; second, aldazine formed might be protonated by cation exchanger and then sorbed on the resin beads; third, hydrazine, which is protonated by the ion exchanger, is sorbed on the resin and then pDAB forms the chromogenic derivative. A further explanation is that pDAB may be sorbed on the resin and then protonation and sorption of the protonated aldazine on the solid support take place. Finally, it might be also possible that the first three mechanisms occur simultaneously.

As regards the 1:1 complex of Mo^{VI} and PCV, which was formed and sorbed on anionic dextran gel,[69] the overall complexation-fixation process may be represented by the following scheme:

$$MoO_2^{2+} + H_3L^- + E^+\text{-}Cl^- \rightleftharpoons E^+\text{-}(MoO_2HL^-) + Cl^- + 2H^+$$

where E^+ denotes the solid ion exchanger matrix with fixed $(CH_2)_2N^+(C_2H_5)_2\text{-}CH_2CH(OH)CH_3$ ion. The distribution ratio of the complex was found to be $(4.9\pm0.2) \times 10^5$ mL g^{-1}. An analogous reaction mechanism on anion-exchange resin was proposed for the system VO_2^+-PAR.[54]

Using the same ion exchanger, Fe^{II}-ferrozine chelate might be quantitatively sorbed.[56] The global process of Fe^{III} reduction by ascorbic acid, complexation and fixation of Fe^{II}-Fz complex can be represented in the following way:

$$C_5H_6O_6 + 2Fe^{3+} + 6L^{2-} + 8E^+\text{-}Cl^- \rightleftharpoons C_5H_4O_6 + (E^+)_8\text{-}\{[FeL_3]^{4-}\}_2 + 8Cl^- + 2H^+$$

A simply constructed electrode with direct incorporation of the appropriate amount of an ion-exchange resin in the carbon paste made the basis for electrochemical detection of Cu^{II} and Cd^{II}.[78,79] This incorporation offers a beneficial alternative for the accumulation of ions, because here one is dealing with cationic resin in the acid form and the preconcentration reaction may be expressed as:

$$2E^-\text{-}H^+ + M^{2+} \rightleftharpoons (E^-)_2\text{-}M^{2+} + 2H^+$$

with E^- representing sulphonic-type ion-exchange resin matrix. The measurement step is performed by applying a potential to the electrode producing reduction of the retained ion:

$$(E^-)_2\text{-}M^{2+} + 2e^- \rightleftharpoons 2E^- + M^0$$

OH^- ions may exert an influence on the mechanism of the reduction process, since the analyte is converted into metallic form, *e.g.* copper. An increase in $[OH^-]$ induces the ions and the exchange groups to compete, thus affecting the reduction process in the electrode-solution interphase.

Sorption / Desorption Processes

Generally, the solid phase colour and its intensity depend on a number of parameters, *e.g.* the specific nature of the colorimetric reaction, choice of the solid carrier, rate of the reaction, concentration of the reagents used, *etc*.[1] The analyte/reagent must reach active centres by their diffusion into the solid matrix. This process is essential and, if it is slow, it is a rate-controlling step in the appearance of colour.

Cu^I in the aqueous solution produces a cationic complex with BC at the surface of the BC-loaded PVC membrane; in the presence of picrate $[Cu^I\text{-}L_2]^+ \cdot (\text{picrate})^-$ ion pair is formed.[33] The colouring rate of the BC-loaded PVC membrane is found to be proportional to the Cu^I concentration, supporting the fact that copper-BC complex is quantitatively formed in the membrane.

In a system consisting of ferrioxamine B-loaded ion-exchange resin and EDTA, two strong ligands, edetate anion and desferrioxamine B, compete for Fe^{III}-ion.[38,39] In the presence of urine matrix, the competition of other ligands for Fe^{III} and that of transition metals for desferrioxamine B may also take place. Namely, ferri edetate is known as a more stable complex than ferrioxamine B in acidic medium. The ratio of $pFe_{[Fe(H_2\text{-}DFB)]^{2+}} / pFe_{[Fe(H_j\text{-}EDTA)]^{j-1}}$ was approximately 0.8, and it seems to be a driving force responsible for decomposition of ferrioxamine B immobilized on the resin. Probable correlation between the tolerance limits for metal ions and the stabilities of corresponding complexes with desferrioxamine B confirms this assumption, regardless of the expected preserving action of the solid phase. The composition of the urine sample influences both the decomposition dynamics of ferrioxamine B on the reagent-resin and the development of analytical signal.

Comparison of kinetic curves for the Cu^{II} uptake by the cation-exchange membrane and an analogous process in ion-exchange resin proved that, at equilibrium, ion-exchange beads in Ca^{2+} form are less effective than those in Na^+ form; the opposite is true for ion-exchange membrane.[80] The curve reversal indicated that processes other than electrostatic attractions play a key role in the uptake of Cu^{II} by the ion-exchange membrane. However, depletion of cuppric ion from the solution was achieved by the use of sodium form of the Amberlite-type acidic resin in a quicker manner than that performed by weakly acidic membrane. The following holds for the exchange constant of the arbitrary metal ion M^{2+} uptake by ion-exchange film in Ca^{2+} form:

$$K_{ex}^{Ca} = [Ca^{2+}][\overline{M}^{2+}] / [\overline{Ca}^{2+}][M^{2+}]$$

The exchange constant value for the uptake of copper ion by Ca^{2+} form of the cation-exchange film was found to be 1.07, whereas the analogous value obtained with Dowex 50 (4% DVB) was 0.84. This speaks in favour of a more efficient exchange process in film than in conventional resin.

Distribution of the Species

Distribution of the species in the solid phase may be defined by the slope of absorbance *vs*. $1/m_r$ function (K):

$$K = \varepsilon_c l_R C_0 V 1000$$

where ε_c is the molar absorptivity of the sample species in the resin phase, l_R is the mean light-path length, C_0 is the initial molar concentration, V is the volume of the sample solution and m_r is the ion exchanger mass. Excellent agreement of theoretical and experimental values of K for the systems V^V-PAR and Fe^{II}-Fz was claimed by the authors.[49,54,56]

QUANTITATIVE AND QUALITATIVE ASPECTS

Methods

Quantitative and Semiquantitative Analysis

Solid-phase spectrometry is based on direct retention of a reaction product in a solid support and subsequent measurement of any appropriate optical property *in situ*. Some synonyms found in earlier literature are: ion-exchanger phase absorptiometry, solid-state spectrometry, ion-exchange(r) spectrophotometry (colorimetry), gel phase absorptiometry. Measurement of the resin phase colour by a spectrophotometer was first suggested by Yoshimura and co-workers through »ion-exchanger colorimetry« as early as in 1976.[16,81,82,1] They found linear relationship between the resin-phase light-absorbance and the sample-component concentration in the initial solution.[83] Since then solid-phase spectrometry has been widely applied and developed.

Solid-phase absorption spectrometry (SPAS) is one of the principal methods of quantitative analysis in the solid phase. SPAS analytical systems generally comprise different solid substrates (ion exchangers or adsorbents), different matrices (*e.g.* air, waters, urine, foods) and different reaction types, such as dye formation, formation of mixed coordination complexes (binary, ternary or bimetallic complexes), redox and catalytic reactions. SPAS is usually performed on ion exchanger beads or on some filtration media. Since solid-phase preconcentration is used in combination with direct spectrometry in the solid phase itself, an improvement in selectivity and detection limit and above all a substantial increase in sensitivity of up

to three to four orders of magnitude is achieved over conventional spectrometric methods in homogeneous solution.[49,77,83,84]

SPAS measurements are performed using ion exchangers or other polymers, usually packed in a cuvette of 1-mm thick layer, or in the form of a membrane or foam, subjected to the measurement of absorbance of light in Vis or UV region. (In this paper SPAS refers to the measurement of absorbance of transmitted light.) Dextran-type ion exchangers are used for determination of metal ions mainly in environmental samples,[49–53,68,69,85–90] phosphate ion,[91] colorant matters in food and cosmetic products,[84,92–99] and sulphonamides and vitamins in pharmaceutical preparations and other samples.[56,70–72,100,101] Unmodified polystyrene/DVB ion-exchange resins are used for determination of metal ions[21,48,54,55,66,102–115] as well as other environmental pollutants such as atmospheric SO_2[116] and sulphite in water[117] and other inorganic and organic analytes.[29,57,77,118–121] Methods on reagent-resins are again mainly directed to the analysis of metal ions.[17,22–24,45,76,122–125] β-cyclodextrin and polyurethane foams are used for determination of metal ions[28,30,37,126,127] and phosphate ion[128] in water, whereas XAD-type reagent-beads are used for the analysis of HCN in air.[129] UV/Vis techniques used with filtration systems may in some cases include that the desired coloured complex in the presence of ionic surfactants is collected onto a membrane filter and then determined directly on it. Either modified or non-modified filtration media have been used primarily for the analysis of metal ions and surfactants;[32,33,35,46,59,61,80,130–136] after immobilization of DNA, nitrocellulose film has been successfully applied for solid-phase enzyme immunoassay.[44] The coloured reaction product may be fixed on the sorbent, which is then collected on a membrane filter in the form of a disc. Alternatively, the insoluble reaction product may directly be collected on a filtration medium. In both cases, solid-phase tristimulus colorimetry (SPTC)[137,138] or diffuse reflectance spectrometric (DRS) determinations on a thin-layer disc have been used. Using non-modified or loaded solid carriers, it is possible to quantify metal ions[20,26,47,58,60,74,139–143] in various samples, synthetic dyes,[144] glucose in full blood,[43] bilirubin[29] and some other analytes[40,145–147] densitometrically.

Coupling of SPAS with FIA leads to even higher sensitivity and selectivity of analysis in comparison with conventional SPAS methods.[9,148–150] An ion-exchange material is usually placed in the flow cell to preconcentrate the analyte; the product of chemical reaction is usually retained on a solid support. Several metal ions[75,148–153] and silicic acid[154] have been determined.

Solid-phase spectrofluorimetry (SPSF) is a method combining the advantages of the fluorescent methods with enrichment of analyte in the solid phase and offering an increased level of selectivity, lower detection limits and improved sensitivity. SPSF has proved advantageous in ultratrace

analysis of intrinsically fluorescent analytes such as organic pollutants,[65,73,155–168] but also of metal ions[62–64,89,169–171] and Br^- [170,172] after being transformed into fluorescent products. Native phosphorescence of some pesticides[173,174] and of nalidixic acid[175] fixed on filter paper has given rise to sensitive transmitted room-temperature solid phase spectrophosphorimetric assays. Among luminescence-based methods, chemiluminometric assaying of choline-related substances in pharmaceutical preparations is also worth noting.[176]

Other methods of quantitative analysis in the solid phase include electrochemical detection of DNA antibodies,[44] Cu^{II} in pharmaceutical products[78] and atmospheric Cd^{II},[79] press-blotting combined with image processing for quantitative immunodetection of peptides,[177] optical beam deflection for ultrasensitive spectrochemical analysis of haemoglobin in a single leukemia WBC[178] and ETAAS of copper.[47] Indicator tubes have been frequently used for visual colorimetric quantitative as well as semiquantitative analysis of metal ions,[19,25,27,28,31,36,80,132,136,137,179,180] phosphate ion,[128] paraquat[181] and aniline.[27]

Qualitative Analysis

The resin spot test, as a special case of batch operation in spot testing, offers the simplest and the most sensitive general method for the qualitative and even quantitative analysis of very small amounts of substances. The majority of such ion-exchange processes are accompanied by chemical reactions, which produce new chemical species or consume the species initially present in the solid phase. Generally, the relevant chemical reactions could be presented as:[1]

$$A_{soln} + y\ RY_{soln} + x\ EX_{solid} \longrightarrow E_xS_a\ (\text{or } E_xS_r,\ E_xS_{a,r})_{solid} + x\ X_{soln} + y\ Y_{soln}$$

where A is the analyte (*e.g.* thiosalicylic acid, $HS–C_6H_4–COOH$), RY is the reagent (*e.g.*, trisodium aquapentacyanoferrate(II), $Na_3[Fe(CN)_5H_2O]$), S_a is the coloured product of the reaction (*e.g.*, $[Fe(CN)_5HS–C_6H_4–COOH]^{3-}$), E is the polymer frame with functional group [*e.g.*, $–N^+(CH_3)_3$], X is the mobile exchangeable ion (*e.g.*, Cl^-) and Y is a part of the reagent RY released by dissociation (*e.g.*, H_2O from $[Fe(CN)_5H_2O]^{3-}$).

Conventional RST on ion-exchange resin beads as well as column spot colorimetry on various supports constitute the basis for detection of metal ions,[28,36,182] organophosphorus insecticides,[34] edetates and glycine in urine,[38,39] and other organic analytes.[41,181,183–186]

Spot reactions for systematic detection of functional groups can likewise be conducted by RST. Systematic approach to microchemical identification of some nitrogen compounds has been suggested for a quick detection of

amines, pyrrole derivatives, amino and hydroxamic acids, nitroso and azo compounds, hydrazine and similar compounds, amide and imide of carboxylic and sulphonic acids, and anilide of carboxylic acid.[187]

Analytical Performances

The selection of a suitable method of analysis is a vital step in the solvation of an analytical problem, but it suffers from many hardships.[1] The performance characteristics of an analytical method used under a given set of experimental conditions are a set of quantitative and experimentally determined values for parameters of fundamental importance in assessing the suitability of the method for any given purpose. A well described procedure has a certain precision, accuracy, detection limit, selectivity, *etc*.

Analytical performances or performance characteristics of analytical methods have been extensively studied by the authors, primarily as a function of sample volume and analytical method. In general, sample volume, for example, has been found responsible not only for the method sensitivity but also for limiting values and linear concentration range, whereas no significant influence on the precision has been observed.

Enhancement of Sensitivity

In general, a sensitive reagent for conventional solution absorptiometry may be also satisfactorily used for the solid phase method, provided that the resulting complex is strongly retained by the solid support.[1,83]

Fixation of the complex on the solid carrier results in a noticeable increase in sensitivity in solid phase as compared with the solution, due to the concentration of the absorbing species by the ion-exchange resin. One of the softwares of sensitisation of colour developing reactions serves for synthesizing new sensitive chromogenic reagents and for improving the existing ones. The complexing systems of mixed ligands provide an increase in selectivity and sensitivity of the SPAS methods. SPAS-FIA is a method that is by a factor of 100 or even 220 more sensitive than a conventional method.[149] Hardware of sensitisation, among other things, includes the use of new methodologies such as thermal lens spectrometry, photoacoustic spectroscopy, long-capillary-cell spectrometry, microscope spectrometry,[188] *etc*., which should be widely used. OBD technique, for example, which is another kind of photothermal metod, has been proved extremely sensitive: the method has the capability to measure weak absorbance of 10^{-4} and provides trace analysis at the 10^2 fg level in a single microparticulate sample.[178]

Moreover, determination sensitivity can be extremely enhanced by employing derivative spectra, because the peaks become sharper and their

magnitude increases remarkably with an increase of the order of differentiation.*e.g.* [102]

Among many effects of surfactants in analytical chemistry, sensitisation and acceleration of colour developing reactions of metal complexes are among the most important issues for the SPAS determinations of trace metal ions, mainly on nitrocellulose filters.*e.g.* [46,61,130–132]

The SPAS sensitivity depends strongly on the measured thin-layer thickness and can be enhanced by using a thicker ion exchanger layer. This is due to the fact that the background attenuance increases only moderately whereas the net absorbance of the sorbed sample increases considerably when the cell length is increased. Despite the fact that the 10-mm path length may be used effectively,[21] there are just a few procedures using a thin layer thicker than 1 mm.

An increase in sample volume leads to the improvement of sensitivity and limiting values. An increase in reagent volume and concentration of coexisting components may also affect sensitivity. The increase in sensitivity achieved by sample volume increase can be expressed as a ratio of the slopes of the respective calibration lines. For example, with an increase of ten and hundred times the sample volume, the sensitivity increases by a factor of eight and thirty-nine[100] and nine and fifty-three,[55] respectively.

Increasing the Selectivity

Selectivity can be used as a criterion for judging the quality of an analytical procedure, particularly if quantification of selectivity is possible.[1]

The effects of foreign species are usually due to preconcentration of coloured species in the solid phase, decomposition of the reagent (ligand), competition of matrix components for the analyte/ligand, and redox reaction of either component. Selectivity has often been improved by masking the metal ions that interfere with common masking agents; interference from Fe^{III} is eliminated by precipitation with thiocyanate and Zeph[134] or with ascorbic acid and Phen,[133] whereas coprecipitation of Nb^{V} with Fe^{III}- quinolin-8-olate at low pH allows removal of matrix elements such as aluminium, alkaline earth and alkali metals.[130]

As far as selectivity is concerned, it should be pointed out that the degree of adsorption of metal chelates on the anion- and cation-exchange resins is dependent on the charge, hydrophobicity and configuration of the compounds, whereas the degree of adsorption of the chelates on a membrane filter is related to the hydrophobic properties of the compounds.*e.g.* [47,49–53,59,63,64,68,75,85,86,88,151,185]

The selectivity of a procedure can be also increased by transformation of species and/or by modification of the resin affinity. Thus, by varying the

type of the exchanger, relative affinity can be modified.[1] Different functional groups of an exchanger show different affinities for different ions. This is especially pronounced in reagent functional groups in resinous reagents.

Derivative spectra offer two advantages over zero-order spectra. First, they avoid the necessity of working at two wavelengths in order to suppress the effect of resin beads packing on the reproducibility of absorbance measurement, *i.e.* to remove large background noise caused by the absorption of the resin itself. Secondly, they eliminate the necessity of a blank, since its first-derivative signal is null at the measurement wavelength. Derivative modes do not enhance selectivity only but lead to better limiting values and recovery as well. The combined use of SPAS [*e.g.* 22,69,71,72,87,88,93,94,101,102,123,132] or SPSF [*e.g.* 73,160,169–171] and derivative techniques has appeared in the last decade, frequently enabling to resolve the mixtures of compounds which are found in low concentrations and which show overlapping spectra after being retained on the same sorbent. Because of the large overlap of the spectra for selective determination of ST in the presence of SM, first-derivative of the spectrum has been taken,[71] whereas simultaneous determination of ST and SM in a mixture can be accomplished using second[101] and fourth-derivative technique.[72]

Selective determinations of synthetic pigments in mixtures were achieved upon ionic natures of SY, QYWS, BB, FY, CM, TT and PR, which may be isolated on anionic Sephadex gel, and non-polar SUD, QYSS, 4-phenylazoaniline and 1-naphthylazo-1-naphthol, which were successfully fixed on C_{18}-silica gel.[84,92–99] Therefore, when dealing with colorant mixtures, the colorants of the same sorption characteristics fix on the same sorbent. The partial overlap of their spectra calls for applying either the derivative spectra[93,94] or partial least squares multivariate calibration procedure[95,98] in order to achieve selective analysis. Another example: benefiting from its cationic nature, thiamin hydrochloride was selectively fixed on Sephadex CM C-25 cation-exchange gel and its intrinsic absorbance was directly measured in the resin phase at 247 and 320 nm.[100] By doing so, both the sensitivity and the tolerance for other vitamins of the B complex were dramatically increased with respect to the analogous procedure in homogeneous solution.

The mixtures of PAHs cannot be resolved by conventional spectrofluorimetry or by synchronous scanning spectrofluorimetry, since the spectral shapes almost completely overlap, which causes difficulties in detection of interference-free signals. Therefore, variable-angle scanning with different $\lambda_{ex}/\lambda_{em}$ has been proposed for the determination of mixtures of PAHs, the spectra of which overlap considerably.[*e.g.* 156] The selection of optimum $\Delta\lambda$ for the synchronous spectra may allow detection of the most serious interfering species and a simultaneous determination of PAHs.[168]

Linearity and Range

The linearity of an analytical method is determined by mathematical treatment of the test results obtained by analysis of samples with analyte concentrations across the claimed range of the method. The treatment is normally the calculation of a regression line by the method of least squares of test results *versus* analyte concentration. In most types of the quantitative resin spot test procedures, calibration is a vital step.[1]

Owing to the characteristics of the analytical system under study, the concentration range obeying Beer's law generally lies within a ppb-to-ppm range. For example, the applicable concentration ranges for determination of 4-phenylazoaniline and FY in mixtures by SPAS were 10.0–100.0 and 3.0–600.0 ppb, resp.[97] Significant influence of sample volume on linearity range has been observed: bigger volume shifts the concentration range to the lower values. For example, for the SPSF method for bromide determination using fluorescein, calibration graphs were found to be rectilinear for 0.2–1.2, 0.1–0.6 and 0.05–0.3 ppb Br^- for 250-, 500- and 1000-mL sample, resp.[172]

Limiting Values and Precision

Basic parameters in trace analyses are the determination and detection limits, *i.e.* the least amount of the analyte that can be determined or qualitatively proved.[1]

Detection limit and quantification limit values have been generally found in the ppb-to-ppm range as well. For example, down to 1 ppm of HCN may be detected in air within one minute,[128] whereas an LOD of 0.15 ppb of iron by SPAS using Phen has been gained.[143] As low as 5 ppb Al^{III} may be detected by visual detection and 3 ppb upon spectrometric determination in water using the ion-pair adsorption film colorimetry.[133] Extremely low detection levels have been achieved by SPSF: LOD values achieved for inorganic ions lie between 0.2 and 0.4 ppb,[170,171] whereas as low as 14 ppt anthracene,[162] 30 ppt BaP, 50 ppt BaA and 80 ppt Pyr in a mixture,[168] 60 ppt fluoranthene and warfarin,[164,166] 100–200 ppt carbaryl and 100 ppt OPP,[73,165] and 150 ppt benomyl and 180 ppt morestan in a mixture,[167] could be detected. For semiquantitative determination of Th^{IV} with Arsenazo III, an LOD of 0.01 ppm has been found.[180]

Limiting values are improved by an increase in the sample volume. For example, LOD value of 80.0 ppb of vitamin B_1 was estimated using the 10-mL sample; however, from 100- and 1000-mL samples, the LOD values as low as 13.5 and 3.0 ppb, resp., have been achieved.[100] An LOD reduction from 11 to 0.91 ppb ascorbic acid was gained by a sample volume increase

from 10 to 100 mL.[56] A 100-fold sample volume increase resulted in LOD drop from 2.70 to 0.067 ppb Cu^{II},[55] and from 0.29 to 0.018 ppb V^{V},[54] with PAR by SPAS.

Moreover, LOD reduced for one to two orders of magnitude has been gained in analysis of some metal ions when spectrofluorimetry in solution has been replaced by spectrofluorimetry in the solid phase: as low as 20 ppt Be^{II} may be detected with morin[64] and 0.3 ppb Mo^{VI} with CA[62] by SPSF. Detection limits for thiabendazole in various fruits and vegetables obtained by different methods including solution spectrofluorimetry, GC, TLC and liquid chromatography range from 5 ppb to 1 ppm.[158] However, the proposed SPSF method for thiabendazole in pears provided one order of magnitude lower LOD over the best result obtained with the aforementioned methods. The same applies to SPAS-FIA analysis of silicic acid in respect to the IC, AAS and ICPS methods.[154] SPSF method for simultaneous determination of OPP and CBL in waters has shown also LOD value lowered for one order of magnitude relative to other methods, except for HPLC.[73] The same LOD improvement factor has been achieved by SPSP analysis of morestan in vegetables *versus* GC with electron capture detection.[173] Contrary to this, the LOD values obtained by SPAS and PAR as reagent for Cu^{II},[55] and for V^{V},[54] have been found comparable to the detection limits of AAS, AFS and ICPS methods although the time required for the analysis by these techniques is shorter than in SPAS. For example, the limiting values obtained by OBD method are up to three and one order of magnitude superior to that of conventional absorption microspectrometry and PAS, respectively.[178]

The SPSF procedures proved to be highly precise. For example, various PAHs and pesticides were determined with an RSD $\leq 1.5\%$ in model systems.[73,155–157,159–165,167,168] Moreover, high precision was achieved in determination of Hg^{II} with thiothenoyltrifluoroacetone on filter membrane by tristimulus colorimetry with an RSD of 0.75%.[138] SPAS determination of copper in water was performed with the precision of 0.04%,[109] and that of Ru^{III} on polyurethane foam with an RSD of $\leq 1.0\%$.[28] ST and SM were determined in the mixture by derivative UV-SPAS with respective RSD values of up to 0.9 and 1.7%.[72,101]

Variability of the solid phase packing contributes significantly to the relative standard deviation values and may be significantly reduced by centrifugation of resin beads prior to SPAS measurement. For example, for V^{V}-PAR system, after centrifugation of the beads in the cell for 2 min at 5000 rpm, RSD was reduced from 7.0% to 1.4%.[54] The precision of the method has been found similar to that of other methods, such as ETAAS, AFS and ICPS.

Accuracy and Recovery

Accuracy of an analytical method is the closeness of the test results obtained by the method to the true value. Accuracy is often expressed as a percent recovery by the assay of known and added amounts of analyte.

Methods in the polymeric solid phase have been found highly accurate in comparison with other methods, for example, AAS,[47,55,69,80,113] ICPS and AAS,[112] reference methods[53,54,56] such as HPLC,[70–72] spectrometry and neutron activation,[124] ICP-MS,[55,75] ^{1}H NMR and homogeneous solution methods,[118] or by the use of reference standards.[87,176] For example, accuracy of UV-SPAS determination of ST of 0.1–0.8%[70–72] and of SM of 1.0%[72] relative to the HPLC method has been evaluated.

Favourable recoveries reported by the authors additionally confirm acceptable accuracy. Together with agreement of the results between SPAS and the reference method within 2.9%, propitious recoveries for ascorbic acid have been found.[56] For example, the recovery of Cu^{I}-BC complex from the solution onto the cation- and anion-exchange resins and cellulose nitrate membrane filter has been found to be almost quantitative,[47] whereas the recovery of the precipitate $(R_4N)_2[Co(SCN)_4]$ was strongly affected by the final sample volume, decreasing with the increasing sample dilution level.[145] Owing to the incomplete fixation of the complex on the Amberlyst A-27 resin, the recovery of Mo^{VI}-Tiron complex has been found to be deteriorated by an increased ionic strength of the medium, *i.e.* by NaCl at a concentration higher than critical.[139]

RECENT SCOPE OF APPLICATIONS

The efficiency of the resin spot test and of the related techniques for analysis of real samples is well reflected in the number of publications.[1] Methods in the reactive polymeric solid phase may be of special value in the fields of inorganic and organic chemistry, pharmacy, medicine, geochemistry, agriculture, metallurgy, environmental chemistry, *etc*.

Recently, most of the methods in solid polymeric carrier have been devoted to solving health protection problems. This includes monitoring of water and air pollution with respect to metal ions and cancer-suspect organic contaminants as well as food-quality control with respect to trace metal ions and additives such as synthetic pigments. In the field of drug control, the methods on the solid support have proven efficient in assaying the active substances in pharmaceutical preparations. Above all, biomedical analyses of body systemic fluids, which make the basis of diagnostic tools, such as biosensor for autoimmune disease diagnosing[44] or detection of haemoglobin in single leukaemia white blood cell, *in vivo*,[178] should be mentioned.

An overview of recent applications is given in Table II.

TABLE II

Recent applications of the methods on the solid phase

Environmental pollution and industrial hygiene

Nature of sample	Analyte	Method code*	Reference(s)
Water (natural, tap, industrial, waste, high purity), air, plants (vegetables, fruits), animal tissues, soil extracts	Inorganic contaminants (metal ions, anions, silica/silicic acid, SO_2, HCN)	SPAS	17, 24, 28, 30, 37, 48–55, 66, 68, 69, 76, 85–91, 104, 106–108, 112, 114–117, 119–122, 126–129, 134, 189, 191
		SPAS-FM	32, 33, 35, 46, 59, 61, 80, 132, 133
		SPAS-FIA	75, 150, 152, 154
		DRS	20, 26, 47, 58, 74, 139, 143
		SPSF	62–64, 89, 169, 170, 172
		VC	19, 25, 31, 36, 179, 180
		SPTC	138
		SPED	79
		ETAAS	47
	PAHs (fluorene, BaP, BaA, Pyr, anthracene, fluoranthene)	SPSF	156, 157, 159, 160, 162, 164, 168
	Pesticides (morestan, CBL, OPP, benomyl, thiabendazole, warfarin, organophosphorus insecticides)	SPSF	65, 73, 155, 158, 161, 163, 165–167
		SPSP	173, 174
		VC	34
	Other organic analytes (humic acid, surfactants, hydrazine)	SPAS	77
		SPAS-FM	135, 136
		DRS	74

Geology and metallurgy

Sample type	Analyte	Method code*	Reference(s)
Minerals, petroleum crudes, ores, alloys	Metal ions	SPAS	22, 23, 49, 50, 53, 54, 85, 87, 105, 106, 111–113, 123–125
		SPAS-FM	130
		SPAS-FIA	148, 152, 153
		DRS	26, 141, 142

TABLE II, cont.

Biomedical analyses

Nature of sample	Analyte	Method code*	Reference(s)
Systemic fluids (blood, plasma, serum, urine, cerebrospinal fluid), hair	Paraquat, diquat	VC	181
	Glucose	DRS	43
	Edetates, glycine	RST	38, 39
	Hydrazine	SPAS	77
	GM1 ganglioside	SPAS	42
	Human pancreatic secretory trypsin inhibitor	SPAS	45
	Antibodies to DNA	SPAS-FM SPED	44 44
	Haemoglobin in leukemia WBC	OBD	178
	Acetoacetate	SPAS	118
	Bilirubin	SPAS	29
	Ascorbic acid	SPAS	56
	Nalidixic acid	SPSP	175
	Metal ions	SPAS SPAS-FM	37, 49 59

Drugs control

Nature of sample	Analyte	Method code*	Reference(s)
Pharmaceutical preparations	Metal ions	SPAS SPED	49, 55, 66 78
	Sulphonamides (ST, SM)	SPAS	70–72, 101
	Synthetic pigments (SUD, SY)	SPAS DRS	84 144
	Choline derivatives (acetylcholine, choline theophyllinate, succinylcholine)	SPC-IP	176
	Ascorbic acid	SPAS RST	56 185
	Thiamin · HCl	SPAS	100
	Nalidixic acid	SPSP	175

TABLE II, cont.

Food and cosmetic products control

Nature of sample	Analyte	Method code*	Reference(s)
Fruit juices, wines, beers, creams, meat	Metal ions	SPAS SPAS-FM SPAS-FIA DRS	49, 66, 68, 87, 103, 125 32, 59 151 60, 140
	Synthetic pigments (SUD, SY, QYSS, QYWS, CM, NAN, TT, PR)	SPAS	84, 92–96, 98, 99
	Aromatic esters	SPAS	57
	Ascorbic acid	SPAS	56

Other applications

Nature of sample	Analyte	Method code*	Reference(s)
Various	FY, 4-phenylazoaniline, CM, NAN	SPAS	97, 99
	Proteoglycans	DRS	146
	Peptides, immunodetection of	SPAS-IP	177
	$Fe^{II/III}$	SPTC	137
	Phosphorus	DRS	147
	Ascorbic acid	SPAS	56

* See: Abbreviations and codes

ABBREVIATIONS AND CODES

AAS – atomic absorption spectrometry; AFS – atomic fluorescence spectrometry; BaA – benzo[*a*]anthracene; BaP – benzo[*a*]pyrene; BB – Brilliant Blue FCF; BBK – Basic Blue K; BC(S) – bathocuproine (disulphonate); BHA – benzohydroxamic acid; BP(S) – bathophenathroline (disulphonate); 5-BrPADAP – 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol]; CA – carminic acid; CAB – Chromazurol B; CBL – carbaryl; ChE – choline esterase; CM – carmoisine; DEPD – *N,N*-diethyl-*p*-phenylenediamine; DFB – desferrioxamine B; DPT – 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine; DRS –diffuse reflectance spectrometry; DVB – divinylbenzene; ECBT – Erio Chrome Black T; ECR – Erio Chrome Cyanine R; EDTA – ethylenediaminetetraacetic acid; ETAAS – electrothermal atomic absorption spectrometry; FMF – 1,2-di-(2-fluorophenyl)-3--mercaptoformazan; FY – Fast Yellow AB; Fz – ferrozine; GC – gas chromatography; HMNQO – 3-hydroxy-2-methyl-1,4-naphthoquinone-4-oxime; HPLC – high performance liquid chromatography; 3-HPA – 3-hydroxyphenylacetic acid; IC – ion chromatography; ICPS – inductively coupled plasma spectrometry; LOD – limit of detection (quantitative); MTK – Michler's thioketone; MS – mass spectrometry; NAN – 1-naphthylazo-1-naphthol; NMR – nuclear magnetic resonance; NRS – Nitroso R Salt; OBD – optical beam deflection; OPP – *o*-phenylphenol; PAH – polycyclic aromatic hydrocarbon; PAN – 1-(2-pyridylazo)-2-naphthol; PAR – 4-(2-pyridylazo)resorcinol; PAS – photoacoustic spectroscopy; PBHA – phenylbenzohydroxamic acid; PCV – Pyrocatechol Violet; pDAB – *p*-dimethylaminobenzaldehyde; Pfn – phenylfluorone; Phen – 1,10-phenathroline; PR – Ponceau 4R; PVC – polyvinyl chloride; Pyr – pyrene; QYSS – Quinoline Yellow Spirit Soluble; QYWS – Quinoline Yellow Water Soluble; RSD – relative standard deviation; RST – resin spot test; SM – sulphametazine; SPAS – solid-phase absorption spectrometry; SPAS-FIA – solid-phase absorption spectrometry – flow injection analyis; SPAS-FM – solid phase absorption spectrometry on filtration medium; SPAS-IP – solid-phase absorption spectrometry – image processing; SPC-IP – solid-phase chemiluminometry – image processing; SPE – solid-phase extraction; SPED – solid-phase electrochemical detection; SPSF – solid-phase spectrofluorimetry; SPSP – solid-phase spectrophosphorimetry; SPTC – solid-phase tristimulus colorimetry; ST – sulphathiazole; SUD – Sudan I; SY – Sunset Yellow FCF; TAAF – 2-(2-thiazolylazo)-5-diethyl-*m*-aminophenol; TAN-3,6S – 1-(2-thiazolylazo)-2-naphthol-3,6-disulphonic acid; TLC – thin-layer chromatography; TT – tartrazine; UV – ultraviolet; VC – visual colorimetry; Vis – visible; WBC – white blood cell; XO – Xylenol Orange; Zeph – Zephiramine.

REFERENCES

1. V. Grdinić, S. Luterotti, and L. Stefanini-Orešić, *Analytical Profile of the Resin Spot Test*, CRC Press, Boca Raton, 1990.
2. K. Yoshimura, *Bunseki* No. 5 (1986) 341–345., ref. *Chem. Abstr.* **105** (1986) 71586t.
3. K. Yamamoto, *Bunseki* No. 1 (1987) 40–46., ref. *Chem. Abstr.* **106** (1987) 167841u.
4. G. D. Brykina, L. S. Krysina, and V. M. Ivanov, *Zh. Anal. Khim*. **43** (1988) 1547–1560.
5. Q. Yang, *Lihua Jianyan, Huaxue Fence* **24** (1988) 55–60.; ref. *Anal. Abstr.* **50** (1988) 10J110.

6. K. Matsuhisa and K. Aomura, *Kenkyu Hobun – Asahikawa Kogyo Koto Senmon Gakko* **25** (1988) 43–57.; ref. *Chem Abstr.* **109** (1988) 65976m.
7. G. Zhang, W. Yang, and H. Shi, *Fenxi Shiyanshi* **8** (1989) 86–104.; ref. *Anal. Abstr.* **52** (1990) 1J41.
8. F. Capitán, L. F. Capitán-Vallvey, M. C. Valencia, J. M. Bosque Sendra, F. Molina, and I. de Orbe, *Analusis* **19** (1991) 177–179.
9. K. Yoshimura and S. Matsuoka, *Lab. Rob. Autom*. **5** (1993) 231–244.; ref. *Chem. Abstr.* **120** (1994) 288716e.
10. Y. Zheng and A. Tong, *Photometric Analysis, Fenxi Shiyanshi* **12** (1993) 80–109.; ref. *Chem. Abstr.* **120** (1994) 314474w.
11. G. D. Brykina, D. Yu. Marchenko, and O. A. Shpigun, *J. Anal. Chem.* (Transl. of *Zh. Anal. Khim.*) **50** (1995) 440–446.
12. H. Waki, *Nippon Ion Kokan Gakkaishi* **7** (1996) 66–79.; ref. *Chem. Abstr.* **126** (1997) 98487g.
13. K. Ohashi and H. Imura, *Bunseki* No. 3 (1997) 215–223.; ref. *Chem. Abstr.* **126** (1997) 301088x.
14. L. F. Capitán-Vallvey, R. Avidad Castañeda, and M. D. Fernández Ramos, *Solid State Spectrophotometry: A Review,* in: *Recent Research Developments in Pure and Applied Analytical Chemistry*, Transworld Research Network, Trivandrum, India 1998, Vol. 1, pp. 149–171.
15. M. Fujimoto, *Bull. Chem. Soc. Jpn*. **27** (1954) 48–50.
16. K. Yoshimura, H. Waki, and S. Ohashi, *Talanta* **23** (1976) 449–454.
17. C.-Y. Liu, H.-T. Chang, and L.-J. Uang, *Fresenius' Z. Anal. Chem*. **328** (1987) 61–63.
18. P. Burba, *Fresenius' J. Anal. Chem.* **341** (1991) 709–715.
19. L. Zabel and R. Rath, Ger. (East) DD 241,961 (Cl. G01N31/22), 07. Jan. 1987, Appl. 281,981, 23. Oct. 1985.; ref. *Chem. Abstr.* **107** (1987) 249203x.
20. Yu. V. Kholin and I. V. Khristenko, *Zh. Prikl. Khim. (St. Peterburg)* **70** (1997) 939–942.
21. K. Yoshimura and H. Waki, *Talanta* **34** (1987) 239–242.
22. M. I. Shtokalo, E. E. Kostenko, and I. Z. Zhuk, *Zh. Anal. Khim*. **46** (1991) 1093–1097.
23. G. D. Brykina, G. G. Lebedeva, and G. F. Agapova, *Zh. Anal. Khim*. **45** (1990) 1838–1842.
24. M. D. Petit Dominguez, M. T. Sevilla Escribano, J. M. Pinilla Macias, and L. H. Hernandez, *Microchem J.* **42** (1990) 323–330.
25. E. I. Morosanova, N. M. Kuz'min, and Yu. A. Zolotov, *Fresenius' J. Anal. Chem*. **357** (1997) 853–859.
26. V. M. Ivanov, S. A. Morozko, and S. Massud, *Zh. Anal. Khim*. **50** (1995) 1280–1287.
27. D. Yu. Marchenko, I. A. Morozkin, E. I. Morosanova, N. M. Kuz'min, and Yu. A. Zolotov, *J. Anal. Chem.* (Transl. of *Zh. Anal. Khim.*) **52** (1997) 1167–1170.
28. M. S. El-Shahawi and M. Almehdi, *J. Chromatogr. A* **697** (1995) 185–190.
29. G. D. Brykina, V. V. Rybalka, S. G. Dmitrienko, and O. A. Shpigun, *Zh. Anal. Khim*. **49** (1994) 178–183.
30. M. N. Abbas, N. B. El-Assy, and S. Abdel-Moniem, *Anal. Lett*. **22** (1989) 2575–2585.
31. M. S. El-Shahawi and R. S. Al-Mehrezi, *Talanta* **44** (1997) 483–489.
32. T. Saito, *J. AOAC Int*. **77** (1994) 1031–1035.

33. T. Saito, *Talanta* **41** (1994) 811–815.
34. H. S. Rathore, I. Ali, and A. Kumar, *Int. J. Environ. Anal. Chem.* **35** (1989) 199–206.
35. A. T. Pilipenko, A. V. Terletskaya, and T. A. Bogoslovskaya, *Khim. Tekhnol. Vody* **14** (1992) 412–417.
36. P. Burba, *Fresenius' Z. Anal. Chem*. **334** (1989) 357–358.
37. R. Li, L. Mao, X. Su, L. Liu, and H. Shen, *Fenxi Huaxue* **25** (1997) 175–177.; ref. *Chem. Abstr.* **126** (1997) 301161r.
38. S. Luterotti, *Analusis* **19** (1991) 107–110.
39. S. Luterotti, unpublished results, 1990.
40. H. H. Chen, *J. Appl. Polym. Sci*. **37** (1989) 365–370.
41. A. Shah, S. S. Rahman, V. de Biasi, and P. Camilleri, *Anal. Commun*. **34** (1997) 325–328.
42. G. Kirschner, M. Bassan, M. P. Facco, G. Ferrari, and L. Callegaro, *J. Pharm. Biomed. Anal*. **10** (1992) 163–166.
43. R. Q. Thompson, H. R. Patel, and C. Andreadis, *Anal. Lett*. **27** (1994) 1201–1214.
44. S. S. Babkina, E. P. Medyantseva, H. C. Budnikov, and M. P. Tyshlek, *Anal. Chem*. **68** (1996) 3827–3831.
45. M. Kurobe, M. Kohno, N. Yoshida, and K. Hayashi, *J. Clin. Biochem. Nutr.* **5** (1988) 173–181.
46. I. Nukatsuka, T. Ohba, H. Ishida, H. Satoh, K. Ohzeki, and R. Ishida, *Analyst* **117** (1992) 1513–1517.
47. K. Ohzeki, M. Minorikawa, F. Yokota, I. Nukatsuka, and R. Ishida, *Analyst* **115** (1990) 23–28.
48. J. M. Bosque Sendra, M. C. Valencia, and L. F. Capitán-Vallvey, *Int. J. Environ. Anal. Chem.* **38** (1990) 551–559.
49. M. L. Fernandez-de Córdova, A. Ruiz-Medina, and A. Molina-Diaz, *Fresenius' J. Anal. Chem*. **357** (1997) 44–49.
50. M. I. Pascual-Reguera, A. Molina-Diaz, N. Ramos-Martos, and L. F. Capitán-Vallvey, *Anal. Lett*. **24** (1991) 2245–2261.
51. M. C. Valencia, S. Boudra, and J. M. Bosque-Sendra, *Analyst* **118** (1993) 1333–1336.
52. J. M. Bosque-Sendra, M. C. Valencia, and S. Boudra, *Anal. Lett*. **27** (1994) 1579–1594.
53. S. Boudra, J. M. Bosque-Sendra, and M. C. Valencia, *Talanta* **42** (1995) 1525–1532.
54. M. L. Fernández-de Córdova, A. Molina-Díaz, M. I. Pascual-Reguera, and L. F. Capitán-Vallvey, *Talanta* **42** (1995) 1057–1065.
55. M. L. Fernández-de Córdova, A. Molina-Díaz, M. I. Pascual-Reguera, and L. F. Capitán-Vallvey, *Fresenius' Z. Anal. Chem*. **349** (1994) 722–727.
56. P. Ortega Barrales, M. L. Fernández de Córdova, and A. Molina Díaz, *Anal. Chim. Acta* **360** (1998) 143–152.
57. M. C. Valencia, J. Garcia, and L. F. Capitán-Vallvey, *Anal Lett*. **23** (1990) 1095–1105.
58. A. T. Pilipenko, A. V. Terletskaya, and T. A. Bogoslovskaya, *Zh. Anal. Khim*. **45** (1990) 1624–1629.
59. F. Capitán Garcia, R. Checa, R. Avidad, and L. F. Capitán-Vallvey, *Talanta* **42** (1995) 711–715.
60. K. Ohzeki, C. Toki, R. Ishida, and T. Saitoh, *Analyst* **112** (1987) 1689–1695.

61. I. Nukatsuka, K. Takahashi, K. Ohzeki, and R. Ishida, *Analyst* **114** (1989) 1473–1478.
62. J. L. Vilchez, G. Sánchez-Palencia, R. Blanc, R. Avidad, and A. Navalón, *Anal. Lett*. **27** (1994) 2355–2368.
63. F. Capitán, J. P. de Gracia, A. Navalón, L. F. Capitán-Vallvey, and J. L. Vilchez, *Analyst* **115** (1990) 849–854.
64. F. Capitán, E. Manzano, A. Navalón, J. L. Vilchez, and L. F. Capitán-Vallvey, *Analyst* **114** (1989) 969–973.
65. J. L. Vilchez, R. Avidad, J. Rohand, A. Navalón, and L. F. Capitán-Vallvey, *Anal. Chim. Acta* **282** (1993) 445–449.
66. M. L. Fernández-de Córdova, A. Molina-Diaz, M. I. Pascual-Reguera, and L. F. Capitán-Vallvey, *Anal. Lett*. **25** (1992) 1961–1980.
67. V. M. Ivanov and S. Massud, *Vestn. Mosk. Univ., Ser. 2: Khim*. **35** (1994) 350–356.
68. M. C. Valencia, D. Gimeno, and L. F. Capitán-Vallvey, *Anal. Lett*. **26** (1993) 1211–1226.
69. A. Molina-Diaz, M. I. Pascual-Reguera, E. Liñán-Veganzones, M. L. Fernández de Córdova, and L. F. Capitán-Vallvey, *Talanta* **43** (1996) 185–191.
70. L. F. Capitán-Vallvey, I. de Orbe, M. C. Valencia, and J. J. Berzas-Nevado, *Talanta* **41** (1994) 1327–1333.
71. L. F. Capitán-Vallvey, I. de Orbe, M. C. Valencia, and J. J. Berzas-Nevado, *Mikrochim. Acta* **111** (1993) 223–229.
72. L. F. Capitán-Vallvey, I. de Orbe, M. C. Valencia, and J. J. Berzas-Nevado, *Anal. Chim. Acta* **282** (1993) 75–80.
73. L. F. Capitán-Vallvey, J. Rohand, A. Navalón, R. Avidad, and J. L. Vilchez, *Talanta* **40** (1993) 1695–1701.
74. K. Ohzeki, M. Tatehana, I. Nukatsuka, and R. Ishida, *Analyst* **116** (1991) 199–205.
75. U. Hase and K. Yoshimura, *Analyst* **117** (1992) 1501–1506.
76. D. Yu. Marchenko, G. D. Brykina, and O. A. Shpigun, *J. Anal. Chem*. (Transl. of *Zh. Anal. Khim.*) **52** (1997) 17–21.
77. P. Ortega-Barrales, A. Molina-Díaz, M. I. Pascual-Reguera, and L. F. Capitán-Vallvey, *Anal. Chim. Acta* **353** (1997) 115–122.
78. L. Hernández, P. Hernández, M. H. Blanco, and M. Sanchez, *Analyst* **113** (1988) 41–43.
79. L. Hernández, J. M. Melguizo, M. H. Blanco, and P. Hernández, *Analyst* **114** (1989) 397–399.
80. C. M. Hill, K. W. Street, W. H. Philipp, and S. P. Tanner, *Anal. Lett*. **27** (1994) 2589–2599.
81. K. Yoshimura, H. Waki, and S. Ohashi, *Kagaku No Ryoiki* **31** (1977) 885–895., ref. *Chem. Abstr.* **88** (1978) 98547y.
82. K. Yoshimura, H. Waki, and S. Ohashi, *Kagaku, Zokan (Kyoto)* No. 78 (1978) 95–105., ref. *Chem. Abstr.* **90** (1979) 161537d.
83. K. Yoshimura and H. Waki, *Talanta* **32** (1985) 345–352.
84. L. F. Capitán-Vallvey, M. D. Fernández, I. de Orbe, and R. Avidad, *Analyst* **120** (1995) 2421–2424.
85. A. Molina-Diaz, J. J. Vida-Sagrista, and M. I. Pascual-Reguera, *Int. J. Environ. Anal. Chem.* **45** (1991) 219–228.
86. F. Capitán, J. M. Roman Navarro, and L. F. Capitán-Vallvey, *Anal. Lett*. **24** (1991) 1201–1217.

87. M. C. Valencia, S. Boudra, and J. M. Bosque-Sendra, *Anal. Chim. Acta* **327** (1996) 73–82.
88. M. I. Pascual-Reguera, A. Molina-Diaz, M. C. Pacheco-Castillo, M. C. Anguita-Fernández, M. L. Fernández-de Córdova, and L. F. Capitán-Vallvey, *Mikrochim. Acta* **112** (1994) 225–235.
89. H. Waki, S. Noda, and M. Yamashita, *React. Polym. Ion Exch. Sorbents* **7** (1988) 227–237.
90. J. M. Bosque Sendra, M. C. Valencia, and S. Boudra, *Fresenius' J. Anal. Chem*. **360** (1998) 31–37.
91. J. M. Bosque Sendra, C. Merida, and L. F. Capitán-Vallvey, *Analusis* **18** (1990) 531–535.
92. L. F. Capitán-Vallvey, I. de Orbe, S. López-Rodríguez, and R. Avidad, *Mikrochim. Acta* **117** (1995) 129–135.
93. F. Capitán, L. F. Capitán-Vallvey, M. D. Fernández, I. de Orbe, and R. Avidad, *Anal. Chim. Acta* **331** (1996) 141–148.
94. L. F. Capitán-Vallvey, N. Navas Iglesias, I. de Orbe Payá, and R. Avidad Castañeda, *Talanta* **43** (1996) 1457–1463.
95. L. F. Capitán-Vallvey, M. D. Fernández, I. de Orbe, J. L. Vilchez, and R. Avidad, *Analyst* **122** (1997) 351–354.
96. L. F. Capitán-Vallvey, I. de Orbe Paya, N. Navas Iglesias, M. D. Fernandez Ramos, and R. Avidad Castaneda, *Quim. Anal. (Barcelona)* **13** (1994) 196–199.
97. L. F. Capitán-Vallvey, M. D. Fernandez Ramos, I. de Orbe Paya, and R. Avidad Castaneda, *Quim. Anal. (Barcelona)* **16** (1997) 41–46.; ref. *Chem. Abstr.* **126** (1997) 344487u.
98. L. F. Capitán-Vallvey, M. D. Fernández, I. de Orbe, and R. Avidad, *Talanta* **47** (1998) 861–868.
99. L. F. Capitán-Vallvey, M. D. Fernández Ramos, I. de Orbe Paya, and R. Avidad Castañeda, *Quim. Anal. (Barcelona)* **17** (1998) 29–34.
100. P. Ortega-Barrales, M. L. Fernández-de Córdova, and A. Molina-Díaz, *Anal. Chem*. **70** (1998) 271–275.
101. L. F. Capitán-Vallvey, I. de Orbe, M. C. Valencia, and J. J. Berzas Nevado, *Quim. Anal. (Barcelona)* **12** (1993) 141–145.
102. H. Ishii, *Fresenius' Z. Anal. Chem*. **319** (1984) 23–28.
103. S. Yang and G. Wei, *Yingyang Xuebao* **11** (1989) 77–81.; ref. *Anal. Abstr.* **51** (1989) 10F13.
104. L. F. Capitán-Vallvey, M. C. Valencia, and I. de Orbe, *Microchem. J*. **40** (1989) 166–174.
105. J. He and S. Su, *Yankuang Ceshi* **8** (1989) 106–108.; ref. *Anal. Abstr.* **52** (1990) 7B95.
106. Q. Yang, X. Liu, and M. Rao, *Lihua Jianyian, Huaxue Fence* **23** (1987) 196–197.; ref. *Anal. Abstr.* **50** (1988) 3H103.
107. L. F. Capitán-Vallvey, J. M. Bosque Sendra, and M. C. Valencia, *Analusis* **17** (1989) 601–604.
108. G. Zhang, Z. Zhang, J. Ma, and H. Shi, *Fenxi Huaxue* **18** (1990) 695–699.; ref. *Anal. Abstr.* **53** (1991) 10H76.
109. G. Zhang, Z. Zhang, J. Ma, and H. Shi, *Fenxi Shiyanshi* **10** (1991) 10–12.; ref. *Anal. Abstr.* **54** (1992) 6H84.
110. T. M. Nikolaeva and A. I. Lazarev, *Zavod. Lab*. **58** (1992) 10–13.
111. G. D. Brykina, G. G. Lebedeva, and O. A. Shpigun, *Zavod. Lab*. **59** (1993) 4–7.

112. A. Molina-Diaz, J. M. Herrador-Mariscal, M. I. Pascual-Reguera, and L. F. Capitán-Vallvey, *Talanta* **40** (1993) 1059–1066.
113. Z. Gao, *Fenxi Huaxue* **23** (1995) 76–78.; ref. *Anal. Abstr.* **57** (1995) 7D37.
114. G. Zhang and H. Shi, *Lizi Jiaohuan Yu Xifu* **6** (1990) 189–194.; ref. *Chem. Abstr.* **114** (1991) 234732q.
115. R. Yi, S. Tien, and Y. Wang, *Lanzhou Daxue Xuebao*, *Ziran Kexueban* **25** (1989) 145–147.; ref. *Chem. Abstr.* **112** (1990) 185437v.
116. J. M. Bosque-Sendra, F. Molina, and E. Lopez, *Analyst* **116** (1991) 871–874.
117. J. M. Bosque Sendra, F. Molina, and M. Nechar, *J. AOAC Int*. **77** (1994) 1224–1229.
118. F. Molina, M. C. Valencia, J. De la Torre, and L. F. Capitán-Vallvey, *J. Pharm. Biomed. Anal.* **7** (1989) 843–850.
119. G. Bing, Y. Ren, Y. Song, and H. Li, *Fenxi Huaxue* **21** (1993) 325–327.; ref. *Chem. Abstr.* **118** (1993) 240341k.
120. G. D. Brykina, D. Yu. Marchenko, and O. A. Shpigun, *Vestn. Mosk. Univ., Ser. 2: Khim*. **34** (1993) 590–594.
121. L. F. Capitán-Vallvey, M. C. Valencia, and J. M. Bosque Sendra, *Analyst* **113** (1988) 419–422.
122. G. D. Brykina and I. P. Smirnov, *Vestn. Mosk. Univ., Ser. 2: Khim.* **32** (1991) 270–273.
123. G. D. Brykina, T. E. Didenko, and G. F. Agapova, *Zh. Anal. Khim*. **43** (1988) 2195–2199.
124. G. D. Brykina, G. F. Agapova, V. F. Kalinina, and L. S.Krysina, *Zh. Anal. Khim*. **43** (1988) 1461–1465.
125. M. I. Shtokalo, E. E. Kostenko, and I. Zhuk, *Zh. Anal. Khim*. **47** (1992) 1827–1832.
126. Y. A. Gawargious, M. N. Abbas, and H. N. A. Hassan, *Anal. Lett.* **21** (1988) 1477–1486.
127. M. N. Abbas, N. B. El-Assy, and Sh. Abdel-Moniem, *Anal. Lett*. **22** (1989) 1555–1565.
128. A. B. Farag, M. N. Abbas, N. B. Al-Assy, and H. Ezz El Din, *Anal. Lett*. **22** (1989) 1765–1777.
129. A. E. Bentley and J. F. Alder, *Anal. Chim. Acta* **222** (1989) 63–73.
130. I. Nukatsuka, T. Munakata, K. Ohzeki, and R. Ishida, *Analyst* **118** (1993) 1071–1075.
131. I. Nukatsuka, T. Miura, K. Ohzeki, and R. Ishida, *Anal. Chim. Acta* **248** (1991) 529–533.
132. I. Nukatsuka, A. Nishimura, and K. Ohzeki, *Anal. Chim. Acta* **304** (1995) 243–247.
133. E. Kaneko, H. Tanno, and T. Yotsuyanagi, *Mikrochim. Acta* **III** (1981) 333–340.
134. I. Nukatsuka, R. Satoh, Y. Wada, and K. Ohzeki, *Anal. Sci*. **12** (1996) 669–671.
135. A. T. Pilipenko, A. V. Terletskaya, and T. A. Bogoslovskaya, *Khim. Tekhnol. Vody* **15** (1993) 113–120.
136. A. T. Pilipenko, A. V. Terletskaya, and T. A. Bogoslovskaya*, Izobreteniya* No. 47 (1992) 159.; ref. *Chem. Abstr.* **121** (1994) 136636m.
137. F. Yokota and S. Abe, *Anal. Commun*. **34** (1997) 111–112.
138. F. Yokota and S. Abe, *Bunseki Kagaku* **46** (1997) 689–693.; ref. *Anal. Abstr.* **60** (1998) 4H64.
139. M. M. A. Shriadah, M. Kataoka, and K. Ohzeki, *Analyst* **110** (1985) 125–129.

140. K. Ohzeki, I. Nukatsuka, K. Ichimura, F. Kumagai, and M. Kogawa, *Microchem. J.* **49** (1994) 256–264.
141. Z. Zhao, C. Hu, J. Jin, P. Qian, and Z. Wang, *Fenxi Ceshi Xuebao* **16** (1997) 10–12.; ref. *Chem. Abstr.* **128** (1998) 9852y.
142. Z. Zhao, F. Li, and C. Hu, *Fenxi Shiyanshi* **16** (1997) 36–39.; ref. *Chem. Abstr.* **128** (1998) 9850w.
143. A. T. Pilipenko, A. V. Terletskaya, and T. A. Bogoslovskaya, *Khim. Tekhnol. Vody* **11** (1989) 716–719.
144. Y. Song, J. Xu, C. Bing, and Y. Ren, *Guangpuxue Yu Guangpu Fenxi* **17** (1997) 116–119.; ref. *Chem. Abstr.* **127** (1997) 210446s.
145. K. Ohzeki and M. Yamagishi, *Analyst* **110** (1985) 1517–1519.
146. M. Lammi and M. Tammi, *Anal. Biochem*. **168** (1988) 352–357.
147. G. D. Bing, Y. L. Ren, Y. R. Song, and H. Li, *Guangpuxue Yu Guangpu Fenxi* **14** (1994) 115–118.; ref. *Anal. Abstr.* **56** (1994) 11F33.
148. K. Yoshimura, *Bunseki Kagaku* **36** (1987) 656–661.; ref. *Anal. Abstr.* **50** (1988) 3B164.
149. K. Yoshimura, *Anal. Chem*. **59** (1987) 2922–2924.
150. K. Yoshimura, *Analyst* **113** (1988) 471–474.
151. L. F. Capitán-Vallvey, M. C. Valencia, and G. Mirón, *Anal. Chim. Acta* **289** (1994) 365–370.
152. K. Yoshimura, Y. Inokura, and U. Hase, *Anal. Chim. Acta* **268** (1992) 225–233.
153. K. Yoshimura and T. Taketatsu, *Fresenius' Z. Anal. Chem*. **328** (1987) 553–556.
154. K. Yoshimura and U. Hase, *Analyst* **116** (1991) 835–840.
155. F. Capitán, E. Alonso, R. Avidad, L. F. Capitán-Vallvey, and J. L. Vilchez, *Anal. Chem*. **65** (1993) 1336–1339.
156. L. F. Capitán-Vallvey, M. del Olmo, R. Avidad, A. Navalón, I de Orbe, and J. L. Vilchez, *Anal. Chim. Acta* **302** (1995) 193–200.
157. L. F. Capitán-Vallvey, M. del Olmo Iruela, R. Avidad Castañeda, and J. L. Vilchez Quero, *An. Quim*. **90** (1994) 125–129.
158. L. F. Capitán-Vallvey, R. Avidad, and J. L. Vilchez, *J. AOAC Int*. **77** (1994) 1651–1654.
159. L. F. Capitán-Vallvey, M. del Olmo Iruela, R. Avidad Castañeda, and J. L. Vilchez Quero, *Anal. Lett*. **26** (1993) 2443–2454.
160. L. F. Capitán-Vallvey, R. Avidad Castañeda, M. del Olmo Iruela, and J. L. Vilchez Quero, *Mikrochim. Acta* **112** (1993) 55–62.
161. J. L. Vilchez, L. F. Capitán-Vallvey, J. Rohand, A. Navalón, and R. Avidad, *Analyst* **120** (1995) 1609–1611.
162. L. F. Capitán-Vallvey, E. J. Alonso, R. Avidad, M. Del Olmo, and J. L. Vilchez, *Anal. Sci*. **9** (1993) 117–120.
163. J. L. Vilchez, A. Navalon, R. Avidad, J. Rohand, and L. F. Capitán-Vallvey, *Fresenius' J. Anal. Chem*. **345** (1993) 716–719.
164. J. L. Vilchez Quero, M. del Olmo Iruela, R. Avidad, and L. F. Capitán-Vallvey, *Quim. Anal. (Barcelona)* **13** (1994) 22–25.
165. J. L. Vilchez, R. Avidad, A. Navalon, J. Rohand, and L. F. Capitán-Vallvey, *Int. J. Environ. Anal. Chem*. **53** (1993) 139–149.
166. J. L. Vilchez Quero, J. Rohand, A. Navalon Monton, R. Avidad Castaneda, and L. F. Capitán-Vallvey, *Fresenius' J. Anal. Chem*. **354** (1996) 470–473.
167. J. L. Vilchez, A. Navalon, J. Rohand, R. Avidad, and L. F. Capitán-Vallvey, *J. Fluoresc*. **5** (1995) 225–229.

168. J. L. Vilchez, M. del Olmo, R. Avidad, and L. F. Capitán-Vallvey, *Analyst* **119** (1994) 1211–1214.
169. F. Capitán, G. Sánchez-Palencia, A. Navalón, L. F. Capitán-Vallvey, and J. L. Vilchez, *Anal. Chim. Acta* **259** (1992) 345–353.
170. F. Capitán, A. Navalon, E. Manzano, J. P. de Gracia, L. F. Capitán-Vallvey, and J. L. Vilchez, *Analusis* **19** (1991) 132–133.
171. F. Capitán, E. Manzano, A. Navalon, J. L. Vilchez, and L. F. Capitán-Vallvey, *Talanta* **39** (1992) 21–27.
172. F. Capitán, L. F. Capitán-Vallvey, and J. L. Vilchez, *Quim. Anal. (Barcelona)* **10** (1991) 21–29.
173. L. F. Capitán-Vallvey, M. Kalil Deheidel, and R. Avidad, *Anal. Lett*. **31** (1998) 2767–2789.
174. L. F. Capitán-Vallvey, M. Kalil Deheidel, and R. Avidad, *Fresenius' J. Anal. Chem*. **362** (1998) 307–312.
175. L. F. Capitán-Vallvey, F. Ojeda, M. del Olmo, R. Avidad, A. Navalon, and T. Vodinh, *Appl. Spectrosc*. **52** (1998) 101–105.
176. S. Luterotti and D. Maysinger, *J. Pharm. Biomed. Anal.* **12** (1994) 1083–1090.
177. P. J. Van der Sluis, C. W. Pool, and A. A. Sluiter, *J. Immunol. Methods* **104** (1987) 65–71.
178. J. Wu, T. Kitamori, and T. Sawada, *Anal. Chem*. **63** (1991) 217–219.
179. J. Zhao, Z. Yang, and Q. Li, *Huanjing Baohu (Beijing)* No. 9 (1995) 27–28.; ref. *Chem. Abstr.* **124** (1996) 277180g.
180. O. P. Shvoeva, V. P. Dedkova, and S. B. Savvin, *Zavod. Lab*. **62** (1996) 13–15.
181. B. H. Woollen and J. D. Mahler, *Clin. Chim. Acta* **167** (1987) 225–229.
182. R. Kuroda and N. Matsumoto, *Fresenius' Z. Anal. Chem*. **327** (1987) 360.
183. M. Ajmal, A. Mohammad, and S. Anwar, *Chem. Environ. Res*. **1** (1992) 459–461.
184. T. Hasan, *Anal. Lett*. **21** (1988) 633–640.
185. S. Z. Qureshi, A. Saeed, and T. Hasan, *Anal. Lett*. **22** (1989) 1927–1937.
186. P. M. Qureshi, S. B. Singh, and I. A. Khan, *Ann. Chim. (Rome)* **79** (1989) 73–79.
187. V. Grdinić and L. Stefanini Orešić, *Acta Pharm. Jugosl*. **37** (1987) 115–121.
188. I. Shinno, *Kobutsugaku Zasshi* **22** (1993) 21–30.; ref. *Chem. Abstr.* **119** (1993) 237485a.
189. V. K. Ososkov, A. M. Zhelezko, and M. E. Kornelli, *Khim. Tekhnol. Vody* **12** (1990) 528–530.
190. W. Frenzel, *GIT Fachz. Lab*. **40** (1996) 713–714.; ref. *Anal. Abstr.* **59** (1997) 1D5.
191. A. T. Pilipenko, A. V. Terletskaya, and T. A. Bogoslovskaya, *Khim. Tekhnol. Vody* **12** (1990) 723–726.

SAŽETAK

Analitički profil metoda na reaktivnoj polimernoj čvrstoj fazi

Vladimir Grdinić i Svjetlana Luterotti

Ovim preglednim radom dan je prikaz novijih dostignuća i sadašnjeg stanja metoda analize tragova koje se temelje na mjerenju *in situ* na reaktivnoj polimernoj čvrstoj fazi.