Recent trends in solid phase spectrometry : 2003-2009. A Review

Matsuoka, Shiro
Department of Environmental Science, Faculty of Science, Niigata University

Yoshimura, Kazuhisa
Department of Chemistry, Faculty of Sciences, Kyushu University

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Recent trends in solid phase spectrometry: 2003-2009
A Review

Shiro Matsuoka[1] and Kazuhisa Yoshimura[2]*

[1]Department of Environmental Science, Faculty of Science, Niigata University, Ikarashi, Niigata 950-2181

[2]Department of Chemistry, Faculty of Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

Abstract

Around 100 papers published from 2003 to the present are reviewed concerning analytical methods for the direct light measurement of a solid phase, in which a target colored or fluorescent analyte is concentrated. Recent attention has been paid to the development of flow injection-solid phase spectrometry as a simple and inexpensive tool for routine analysis of organic compounds or pharmaceuticals. Due to some improvements in flow injection analysis, such as sequential injection and Lab-on-a-Valve, it is possible not only to reduce the reagent consumption but to devise fully automatic and miniaturized systems with minimal maintenance needs. This may have the potential of becoming one of the green analytical methods. Flow injection-solid phase spectrometry is expected to be applied to the speciation of trace chemical components (e.g., specific determination of trace metal ions in different oxidation states) in real samples in the environment.

Keywords: solid phase spectrometry; flow injection-solid phase spectrometry; flow-through optosensor; sequential injection analysis; inorganic analysis; organic analysis; speciation

Contents

1. Introduction

Spectrophotometry has been most commonly used for quantitative analysis of chemical components in solution, due to the continuous development of instrumentation. The simple and easy operation procedures are also important factors. However, the biggest drawback is its sensitivity. To enhance the sensitivity of spectrophotometry and make the most of its advantages, solid phase spectrometry (SPS) has been developed and applied to the determination of trace analytes in various water samples. This method is based on the direct measurement of the light attenuation of adsorbent particles (or the light intensity of the emitted light from adsorbent particles) packed in an optical cell, in which the target analyte in samples are concentrated as a colored (or fluorescent) chemical component [1, 2]. Because the concentration of the target analyte and the direct light measurement of a solid phase are simultaneously carried out without elution, SPS is more sensitive than the conventional corresponding solution method: over a few hundred times greater sensitivity can easily be achieved without using any expensive apparatus. Although the color development procedures for SPS are usually similar to those for conventional solution spectrophotometry, the selectivity can also be greatly improved when the interaction between a target chemical species and a solid phase is quite different from that between co-existing ions and the adsorbent. Ionic strength, pH, the content of organic solvent, and selection of the adsorbent are the important keys to higher selectivity.

SPS has employed two different procedures: batch and flow methods. Because of a fairly large background attenuance of the solid phase, which is due to a surface reflection and/or a diffuse reflection of the solid layer, the sensitivity enhancement by making the light path of the solid particle layer longer is difficult (in many cases the light measurements are carried out within 1 to 2 mm in light path length). It is also slightly time-consuming and requires above average skill to pack the solid particles into a cell when employing the batch method.

An on–line measurement of light attenuation or light emission by the adsorbed species in the flow-through cell makes it possible both to reduce the sample solution volume considerably and to simplify the respective procedures for the derivatization of the analyte and filling the solid particles into the cell.   Some research groups have dealt with developing this batch SPS method into new flow analysis methods under their own separate concepts [3-6].   In this review, all of these methods are called "Flow injection-solid phase spectrometry" (FI-SPS).

Due to the remarkable progress in the recent flow analysis system or the spectrophotometric analysis including the apparatus, the applicability of the analytical method related to SPS has been expanded to various chemical species in a great variety of samples.   Since the first report on SPS had appeared in 1976, many reports on SPS or a flow method related to SPS have been published.   The development of those methods over these three decades has already been summarized in some papers.   The latest review paper on SPS was given by Capitan-Vallvey *et al*., entitled "Solid-phase spectrometric assays" [7].   For the flow method based on SPS, the studies published up to 2004 were reviewed in detail by Miró *et al.* as "Flow-through sorptive preconcentration with direct optosensing at solid surfaces for trace-ion analysis" [6]. In this article, practical applications of analytical methods related to SPS or those for the direct optosensing of a solid phase in which the target analyte is retained are selected and reviewed among those reported from 2003 to the present.

Bead injection (BI) spectrometry [8], in which the disposal of the adsorbent beads and the injection of new sorbent beads into the flow-through cell are carried out after each analytical cycle, is a very powerful method for widening the applicability of FI-SPS.   The BI concept, first proposed by Ruzicka *et al.*, was introduced to use together with sequential injection analysis (SIA) [9].   At an early stage in this technique, a jet ring cell [10] was used for the optical sensing of solid particles collected inside it.   A commercially available flow-through cell could possibly be applied to the

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BI technique [11, 12].   In order to downscale the volume of sample and reagent solutions, this BI concept was then also applied to a lab-on-valve device [13].   The recent achievements in this method have been thoroughly introduced in 2007 and 2008 as "Recent developments in automatic solid-phase extraction with renewable surfaces exploiting flow-based approaches" [14], "How flow-injection analysis (FIA) over the past 25 years has changed our way of performing chemical analyses" [15] and "Lab-on-valve: a useful tool in biochemical analysis" [16].   For this reason, a detailed introduction to this method was not provided, but some papers are reviewed in this article.

2. Instrumental aspects of light measurements

2.1 Absorptiometry

In measuring the light attenuation by a solid phase, the biggest problem is that a relatively small net absorbance, caused by the colored species adsorbed on the solid phase, has to be measured under a fairly large background attenuance of the solid phase. As mentioned above, this large background attenuance, which is characteristic of the light measurements of a solid phase, is due to a surface reflection or a diffuse reflection from the solid layer.   For example, if the attenuance of a 1-cm thick cross-linked polystyrene-type ion exchanger packed into a quartz cell is measured against air as the reference, the light attenuance is about 3 in absorbance units even at 700 nm, at which there is no light absorption by the ion-exchange resin.   This means that the very low absorption of light passing through the resin phase, which is above or near the limit of detection of a common spectrophotometer for quantitative light measurements, has to be measured.

The analytical performance of the methods considered in this article is listed in Table 1.   In the case of batch SPS method, the light path length of a solid particle layer in the cell is 1 to 2 mm; there is only one report applying a 5-mm light path for

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absorptiometry. Inevitably, 50 to 1000 cm^3 sample solutions had to be used for trace analysis to compensate for the shorter light path of solid particle layers. Although novelty in the light measurement techniques could not be found in these papers, some interesting results on the applicability of multicomponent analysis to improve the selectivity and analytical performance [17], a prevalidation method to evaluate the validity or reliability of the SPS method [18], a newly synthesized chromogenic reagent [19] and specific determination of different oxidation states [20] are described. Quite recently, a 0.06 cm^3 portion of a cation exchanger was used to concentrate the target Cr(VI) in a 20 cm^3 water sample, and resin beads were introduced in a flow cell of 1.5-mm diameter and having a 10-mm light path length. Three lenses were used for forcusing the incident light beam and for recovering light scattered by the solid phase in the cell. The sensitivity was higher by a factor of 277 compared with that of the solution method, and the detection limit was 0.014 µg dm^{-3} [21].

In the case of FI-SPS using a micro flow-through cell, light attenuation by the cell also accompanies the background light attenuation of the solid phase. The use of respective optical fibers for incident light radiation and for collection of the light transmitted through the solid phase has attracted increasing interest for this purpose. If the cross-sectional area of the luminous flux of the fibers for incident light beam radiation is smaller than that of the flow-through cell, the light attenuance by the cell can be negligible. When the optical fiber is set as close to the solid particle layer as possible, a considerable amount of the light scattered by the solid particle layer can also be recovered [22]. In focusing the transmitted light on a photomultiplier or on a grating for photo diode array detection, the selection of the proper accumulation time for the transducer is very effective for the reduction of background light attenuance by the solid phase.

2.2 Fluorometry

In the case of fluorescent light measurement emitted from the solid phase in the

cell, utilizing a longer light path cell is not effective because the deeper part of the solid particles in the cell cannot be irradiated by the excitation light beam.   To increase the excitation light beam intensity is also unsuitable for sensitivity enhancement because the scattered or reflected excitation light enters the emission light detector even if it is located perpendicular to the excitation light beam, which results in a serious emission background error.   However, because the sensitivity of fluorometry is inherently higher than that of absorptiometry, a solid phase light path of 1 to 1.5 mm is sufficient for trace analysis, and the measurement of emitted light from the solid phase can be easily accomplished in a way similar to that with solution spectrometry.   As shown in Table 1, about 90 % of the recent papers on SPS or FI-SPS is concerned with fluorometry or phosphorimetry probably because of not only the simplicity of these methods but also the incompatibility of the sensitivity with the troublesome light measurements of solid phase absorptiometry.

   Compared with solid phase absorptiometry, the applicability of solid phase spectrofluorometry, especially for the metal ion determination, has been limited because the number of fluorogenic reagents selective for a specific metal ion was small. However, many researchers have tried to develop this method for analysis of organic compounds such as pesticides, carcinogenic polycyclic aromatic hydrocarbons, and pharmaceuticals.

   As with solid phase absorptiometry, there are not many reports on novel techniques for light measurement for solid phase spectrofluorometry in recent papers.   Although implementations of the FI-SPS system with photochemically induced fluorescence are reported [23-27], the light measurement systems are not specialized. Fernandez-Sanchez et al. tried to apply an optosensing system consisting of a homemade flow cell, two bifurcated optical fibers to irradiate the excitation light beam and to collect the fluorescence emissions from the solid phases and an intensified charge coupled device (ICCD) as a multichannel detector for simultaneous determination of

four kinds of polycyclic aromatic hydrocarbons [28]. In comparison of the analytical performance of this optosensing system with that of the usual FI-SPS, however, the sensitivity of this optosensing system is worse, though the analysis time is one-fourth of that of the corresponding FI-SPS.

To simplify the optosensing system, optical filters for excitation and emission light were respectively used together with a light source and a fiber-optic fluorometric detector for the fluorometric SIA optosensing of paracetamol [29] but the strong spectral interference of acetylsalicylic acid with paracetamol could not be reduced by those filters.

2.3 Phosphorimetry

Under a specific condition, a phosphorescence from a chemical component can be observed even at room temperature. This long-lived emission is called as room temperature phosphorescence (RTP). The RTP methods were extended to the measurement of RTP from the solid phase have also been reported [30-39]. When comparing the RTP method with fluorometry, the RTP method has some advantages over fluorometry; the short lived background luminescence or scattered light can be easily discriminated because of the long-lived emission of the analyte species, and very good separation of the maximum wavelength of phosphorescence from that of the excitation spectra due to Stoke's shifts is achieved [40].

The optosensing system for RTP from the solid phase is not very different from that for solid phase spectrofluorometry except for choosing the respective proper gate and delay times for the light detector to isolate the RTP signal.

To observe the RTP in solution (or from the solid phase in the flow-through cell), the existence of a high concentration of heavy atom salts such as thallium nitrate or iodide, which is thought to play an important role in facilitating the energy transition from excitation singlet state to excitation triplet state of the phosphorescent species, is

very effective. Oxygen scavengers such as sodium sulfite also have to be added [30-32, 34, 35]. The RTP based on the use of a heavy atom is called heavy atom induced–RTP (HAI-RTP) [30, 31, 36]. In spite of the advantages of the RTP method over fluorometry, not many reports on the application of RTP have been published. The main reason is the lack of an RTP system selective for a specific chemical component. In order to solve this problem, an RTP-FI-SPS method based on energy transfer (ET) is also proposed. In this method, both a phosphorescent molecule insensitive to an analyte and a colored chemical species are concentrated on-line in the solid phase in the flow-through cell. The colored chemical species, such as chromogenic reagents or a colored complex, has to be selective and sensitive to the analyte. Moreover, not only the light absorbance of this colored chemical species has to be proportional to the analyte concentration but also the absorption spectra have to partly overlap the RTP emission spectra of the phosphorescent molecule for ET. In this ET-RTP method, a determination method based on the ET-RTP- FI-SPS for trace orthophosphate was reported by Sanz-Medel *et al*. [32]. Orthophosphate ions in sample solutions are introduced into the flow system as a molybdenum blue species, and this colored species is then concentrated in the XAD-4 resin phase in the flow-through cell in which erythrosine B has been previously fixed. Because the emission peak of erythrosine B is around 670 nm, which is in the wavelength range of the molybdenum blue species, the ET from erythrosine B to the molybdenum blue species occurs and a decrease in the RTP with increasing orthophosphate concentration is observed. The sensitivity of this method is high (the detection limit of this method is 0.5 μg dm^{-3}) with selectivity as good that of the solution method.

2.4 Reflectometry

Recently, many kinds of disk type sorbents have become available, and some attempts to use these membrane discs as the location for both the concentration of target colored chemicals and the direct measurement of the intensity of reflected incident light

at the surface of the membrane disc have been carried out. The analytical method using the attenuation of intensities between the incident light and the reflected light, which is correlated with the amount of target chemical species concentrated on the membrane disk, is known as solid-phase reflectometry.

Fritz and co-workers have proposed their original method for the rapid determination of the targeted chemical components in a solution by colorimetric solid-phase extraction (C-SPE)-diffuse reflectance spectroscopy [41-46]. By using a syringe to which the holder for a membrane disc impregnated with a coloring reagent was attached, the target analyte in a sample solution was passed through and extracted on the membrane disc as a colored species. After being removed from the holder, the membrane disc concentrated with the target colored species was used for the diffusion reflectance measurement. The relationship between the reflectance and the concentration of the target colored species absorbed in the membrane surface was expressed by the Kubelka–Munk function. Because the reflectance spectra can be measured by a portable reflectance spectrometer, and also all the procedures are very easy to perform and can be completed within a few minutes, this method can be applicable for an on-site analysis.

On-line concentration of target colored chemicals at the surface of the membrane disc has also been carried out. Recent reports on this technique have been published by Miró and Estela [47-49]. They used a laboratory-made flow-through sandwich cell for disk-based solid phase preconcentration and reflectance measurement. Bifurcated optical fibers, of which one leg is for introducing the incident light beam radiation and the other is for the collection of the reflected light, were also utilized. In comparison with the FI-SPS or FI-SPS using the adsorbent beads packed in the flow-through cell,

smaller particle sizes of adsorbent beads (8-12 μm) tightly bound within a PTFE support of the membrane disk are used. Although these small adsorbents will give rise to a great back pressure and cannot be applied to a flow system, the advantages of this reflectometry are due to such a small particle size, because of the high specific surface area; these small adsorbent beads show a higher capacity per unit weight and a higher adsorption rate for the analyte species [50]. On the other hand, the light path length of a solid phase of 0.5 mm causes the sensitivity of this reflectometry to be inferior to that of FI-SPS.

2.5 Fourier transform infrared spectroscopy

Infrared radiation (IR) has been widely used for the fundamental studies of molecular structures. However, due to the very strong absorbance of water in the mid-IR, a shorter light path length has to be applied. The low absorptivities of analytes in the mid-IR range are also obstacles to a higher sensitivity. For these reasons, there are not very many mid-IR spectroscopy reports for analytical purposes. The combination with SPS is expected to be a very effective way to enhance the sensitivity.

Recently, an attenuated total reflection (ATR) [51] based flow-through sensor has been reported for solid-phase extraction and infrared detection in the SIA system [52]. In this method, commercially available sorbent beads, LiChrolut EN (a polystyrene-divinylbenzene-based polymer) was used as the adsorbent for caffeine. A small amount (~5 mg) of the adsorbent was packed into a diamond ATR flow cell. By using a 3 cm^3 sample solution, the LOD was 5.2 mg dm^{-3} and the sample throughput was about 4 samples h^{-1}.

Similarly, Armenta and Lendl reported the combination of FI-SPS and FT-IR [53].

Their target was also caffeine, but they employed C_{18} silica beads as the adsorbent. By using a 1.5 cm^3 sample solution, the LOD was 2.6 mg dm^{-3} and the sample throughput was about 10 samples h^{-1}.

2.6 Other methods

An attempt to measure the chemiluminescence from a solid phase in the flow-through cell was made for the determination of salicylic acid [54]. The chemiluminescence emitted from the reaction product of salicylic acid with permanganate retained in the QAE-Sephadex anion exchanger phase packed into a flow-through cell was measured with a home-made luminometer. The flow-through cell was placed in front of the side-on photomultiplier tube together with a piece of mirror to reflect the luminescent light emitted in the opposite direction of the photomultiplier tube. Although the salicylic acid concentration at the μg cm^{-3} level in a pharmaceutical preparation can be determined, the sensitivity is not very high probably because of the MnO_4^- elution from the gel phase due to the higher concentration of the sulfuric acid carrier solution.

Analytical methods based on lanthanide–sensitized luminescence are also found in recent papers. Although some lanthanide ions have typical emission bands originating from f-f electron transitions in the visible region, these electron transitions are forbidden and the intensities are usually very low. In the case of a complex between a lanthanide ion and an organic ligand, however, these typical emissions are often considerably enhanced when the organic ligand absorbs the light at its excitation wavelength. Due to the absorbed energy, the ligand is excited to the excitation triplet state through the excitation singlet state, and then the intermolecular transition to the excitation state of the lanthanide ion occurs, followed by deactivation by the radiative process. Molina-Diaz *et al.* selected terbium for this purpose [33]. In the case of orbifloxacin analysis, CM-Sephadex C-25 was used as an adsorbent for the cationic Tb(III)-orbifloxacin complex because the best R.S.D. was obtained; however the reason

was not given. The sensitivity was 20 times higher than the corresponding solution method.

In the case of *p*-aminobenzoic acid determination, a QAE-Sephadex A-25 anion exchanger is utilized as the adsorbent for the Tb(III)-*p*-aminobenzoate complex [35]. To increase the sampling frequency, a small volume of sample solution (100 mm^3) and a higher concentration of NaCl carrier solution (1 mol dm^{-3}) are applied; however, the sensitivity of this flow sensor method is worse than that of the solid surface RTP or the solution method using time-resolved lanthanide-sensitized luminescence.

Photoacoustic spectroscopy (PAS) is also applicable to SPS [55]. The PAS signal intensity is directly proportional to the light absorption by the analyte, and therefore, the sensitivity is expected to be easily enhanced by amplifying the PAS signal with electronic devices and by using powerful light sources. The PAS signal generated by the light absorption of a complex between Pd(II) and 3-[2'-thiazolylazo]-2,6-diaminopyridine (2,6-TADAP) adsorbed on a cation-exchange resin in a PAS cell was measured by a commercially available piezoelectric device. However, the LOD for Pd(II) was 4 µg dm^{-3} and the sensitivity was not much high than that for other SPS methods using highly sensitive coloring regents.

3. Selection of adsorbent

As already reported, the selection of the adsorbent strongly depends on the nature of the chromogenic or fluorogenic reagent and/or the corresponding species of target element. For a charged species, an ion-exchange resin (for the light absorption measurement in the visible region) or a cross-linked dextran gel-type ion exchanger was used. Because of the strong interaction between aromatic rings, the distribution ratio (*D*) of target chemical species containing aromatic rings for the polystyrene-type ion-exchange resin is usually higher than that for the gel-type ion exchanger. Morales

et al. used a DEAE-Sephadex anion exchanger for the adsorbent of 5-(4-sulphophenylazo)-8-aminoquinoline (SPA) so that it would function as a chelating resin for Cu(II) in the sample solution [19]. For this purpose, the polystyrene-type ion-exchange resin seemed to be suitable, but they selected to use the gel type because of easier diffusion of the ligand in the ion exchanger phase.

For the concentration of neutral species, a C_{18} silica gel or an Amberlite XAD resin are often used due to the hydrophobic interaction between the target analyte and hydrocarbons. In the case of absorptiometry, applying the XAD resin as an adsorbent is difficult because of its poor transparency when the content of organic solvent in solution is lower. Many fluorescent impurities due to the aromatic rings in the structure will also cause a serious background noise in the emission measurement. In spite of these disadvantages, XAD resin having various cross linkages is utilized for solid phase spectrofluorometry [28, 56-58] or solid phase phosphorimetry [30-32, 34] probably because of the very strong interactions with the analyte than with C_{18} silica gel. A silica gel modified with macromolecular quaternary ammonium salt was also used for SPS because it has no light absorption in the visible region and better kinetic property [59].

A β-cyclodextrin polymer (β-CDP) was applied to SPS [60]. This β-CDP can be prepared using β-cyclodextrin and epichlorohydrin and its background light absorption in the visible region is about one-half of that of the anion-exchange resin.

Nylon powder was also applied to the fluorescent optosensor for neutral species. Piccirilli and Escandar successfully used nylon powder packed in the flow-through cell both for the thiabendazole concentration and the direct fluorescence measurement [61]. However, the particular advantages of nylon powder over other adsorbents such as C_{18} silica gel could not be found from this thiabendazole analysis.

The applications of molecularly imprinted polymers (MIPs) for FI-SPS are reported. MIPs are polymers formed with a template molecule. If the template

molecules can be removed from the polymer after the polymerization, selective binding sites (recognition sites) to the template molecule are formed in the polymer matrix. Fernandez-Gutierrez *et al.* applied MIPs selective for monoamine naphthalenes (1-naphthylamine and 2-naphthylamine) for their respective or total determinations [62]. The synthesized polymer using naphthalene as a template molecule was ground and sieved to obtain the particles of 80 to 120 μm in diameter before use. Because of the similar $\pi-\pi$ interactions or the formation of hydrogen bonding between MIPs and the analyte, the selectivity for 1-naphthylamine and 2-naphthylamine is not very high. The interference from 1-naphthalenemethylamine, which is also adsorbed on these MIPs, is serious and could not be eliminated. On the other hand, 1-naphthol and 2-naphthol, which are considered as most relevant potential interferents and actually adsorbed on MIPs did not cause serious interference at the wavelength where 1-naphthylamine and 2-naphthylamine are measured.

In the case of a water soluble template molecule, a molecular imprinted sol-gel was also applied. For the determination of nafcillin in a milk-based product, HAI-RTP from a nafcillin imprinted sol-gel in the flow-through cell was measured [36]. Although most of the α-lactamic- and anthracycline-based antibiotics did not interfere, only ampicillin caused an error when its molar ratio to nafcillin was more than 5.

MIPs containing iodine as a heavy atom [37, 38] or the MIPs introduced on the surface of Mn-doped ZnS quantum dots [39] were also applied to HAI-RTP for the determination of fluoranthene or pentachlorophenol, respectively.

In the case of solid-phase reflectometry or C-SPE-diffuse reflectance spectroscopy, the adsorbent disc has to be absolutely white and not glossy. A sufficient physical strength is also required even if the membrane is thin. A

polystyrene–divinylbenzene disc (e.g., 3M Empore SDB-XC membrane) [41], nylon membranes [44], anion exchange membrane (3M Empore TM Anion Exchange-SR membrane) [46], and octadecyl-chemically modified silica (C_{18}) disc [47] were applied. A monolithic disc prepared by a ring-opening metathesis polymerization was also evaluated for the C-SPE-diffuse reflectance spectroscopy [45]. However, their performances were not totally superior to those of the adsorbent discs which have been always used.

As mentioned above, strong interaction between the analyte and the solid phase is effective for SPS. However, in the case of flow methods using a solid phase packed in the flow-through cell, too strong interactions, especially hydrophobic ones between the analyte and the adsorbent, make the elution of the analyte species from the solid phase very difficult. Although aqueous solutions containing a very high concentration of organic solvent [47, 48, 58, 63] or pure solvent [56, 64] such as alcohol or acetone are used as the desorbing agent solution, small bubbles, which will have a great effect on the solid phase light measurements, are easily generated inside the tube. In some cases, complete elution cannot be done even if such kinds of desorbing agent solution are used. BI spectrometry is very effective for this kind of analyte. In this method, the disposal of the adsorbent beads and the injection of new sorbent beads into the flow-through cell are carried out after each analytical cycle. Because the fresh adsorbent beads can always be used for both the retention and the optical sensing of analyte, this is applicable to target analytes which are strongly adsorbed on the solid phase and when the regeneration of the solid phase is difficult or the matrix species in samples are irreversibly adsorbed and lower the adsorption capacity of the adsorbent beads. Many kinds of adsorbent beads for the selective adsorption of target analytes such as Alizarin

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Red S or Zincon-loaded anion exchanger (QAE-Sephadex A-25), protein G-coated Sepharose 4B beads and Cytodex microcarrier beads on which mouse embryonic fibroblasts are grown were applied to BI spectrometry for V(V) [11] or Cu and Zn [12], immunoglobulins [65] and intercellular H_2O_2 [66], respectively.

4. Application

Here, some papers relating to real sample analyses or those including outstanding features will be discussed (Table 1).

4.1 Inorganic chemical components

The batch methods of SPS were developed for some inorganic compounds. A PAN-immobilized cation exchanger was employed for the determination of heavy metals in pharmaceutical samples and the prevalidation concept has been introduced into SPS [17]. A PAN-immobilized cation-exchange resin was also used for the determination of Cu(II), Cd(II) and Zn(II) determination [67], but in this case, solid phase derivative spectrophotometry was applied.

C-SPE-diffuse reflection spectrometry was applied for the determination of Ag(I) in drinking water [41]. A polystyrene–divinylbenzene disc (3M Empore SDB-XC) impregnated with 5-(p-dimethylaminobenzylidene)rhodanine (DMABR) was used for the analyte concentration. Because of the very strong hydrophobicity, the complex formation between Ag(I) in solution and DMABR did not occur at the membrane surface. The addition of a semi-volatile alcohol, such as 1,2-decanediol, or a nonionic surfactant to the DMABR impregnated membrane very effectively increased the hydrophilicity of the DMABR impregnated membrane surface. This method was also used for the determination of iodine [42-44], Cu(II), Ni(II), Fe(III) and Cr(VI) [41],

Mo(VI) [68], and V(V) [69].

For total Hg(II) determination, 1,3-di-(4-nitrodiazoamino)-benzene impregnated β-CDP was applied [60]. The selectivity of this SPS method for Hg(II) is greatly improved over that of the corresponding solution method due to the β-CDP shielding effect.

Trace amounts of vanadium were determined by SPS using 2,3-dichloro-6(3-carboxy-2-hydroxynaphthylazo)quinoxanine as the chromogenic agent and Dowex 1-X8 as the concentration/detection medium. When using a 1 dm^3 sample, the detection limit was as low as 9 ng dm^{-3} [70].

Moliner et al. improved the detection limit for ammonia achieved by Berthelot reaction by use of C_{18} solid-phase extraction coupled with diffuse reflectance spectroscopy. For the determination of occupational exposure to ammonia in air, the sampling time could be significantly shortened due to its high sensitivity [71].

A sol-gel silica entrapped with a pH-sensitive luminescent indicator (mercurochrome) was used for pH optosensing based on the detection of pH-induced reversible changes in the mercurochrome fluorescent emission and in the light reflected by the sensing phase. The applicability of the proposed optode was successfully demonstrated for pH determination in different drinking water samples [72].

FI-SPS has been reported for the flow analysis of Cd(II) [73], Zn(II) [63], Cr(III) [74], Fe(II) [75], sulfide [47, 49] and monophosphate [32]. For the FI-SPS method for sulfide, a plug-in spectrophotometer furnished with a light emitting diode assures the miniaturization of the overall flow analyzer, with the reading adaptable to real-time monitoring schemes [49]. FI-SPS of Cr(VI) has been applied to investigate the reduction rate of Cr(VI) in river waters present at μg dm^{-3} or sub-μg dm^{-3} levels. At a

fixed pH, the Cr(VI) reduction could be expressed as a pseudo-first order reaction. The reduction rates were constant in the low pH range, while they were proportional to [H^+] in the pH range above 4.5.   By using the extrapolated reduction rate, the half-life of Cr(VI) was estimated to be about 400 days under the pH conditions of natural water. The Cr(VI) reduction is very slow even in the presence of dissolved organic matter, and therefore, they concluded that the predominant species in natural water under oxic conditions should be Cr(VI) [76].

A tubular microcolumn packed with C_{18} silica beads was applied to a flow-through cell of the FI-SPS [6, 77].   On-line extraction and pre-concentration of the chemical components (nitrite, nitrate, sulfite, ammonium, phosphate, Fe(II), Fe(III), Cr(VI), Ni(II) and phenol) as non-polar complexes and light attenuation measurement of the C_{18} particle layer in the microcolumn were simultaneously carried out [77].   In the case of a commonly used black flow-through cell for FI-SPS, such as a Hellma 138-OS/QS cell or 178.010-OS/QS cell, changes in the shape of the end of solid particle layer, from where the target analyte is concentrated, often affect the sensitivity and reproducibility.   However, the tubular microcolumn is free from such problems.   In order to reduce the background attenuance, due to the light scattering through the C_{18} packed microcolumn, both the light source and light-detector (photodiode) were placed close to the microcolumn.

4.2 Organic compounds

As shown in Table 1, fluorometry is widely used for the analysis of organic compounds. The fluorescence of the analyte (e.g. aromatic hydrocarbons) or the photochemically derivatized fluorescence of a non-fluorescent analyte is measured after the concentration of analyte into an appropriate adsorbent such as C_{18} silica beads [78,

79], an XAD resin [80, 81] and an ion-exchanger [35] packed in the flow-through cell. However, if the emission spectra (or the absorption spectra) of the analyte are partly overlapped with those of the co-existent organic compounds, a separation method of the analyte, a multi-component analytical method [82] or a statistical treatment of the analytical data [12,34] may be required. Manera *et al.* proposed an FI-SPS system based on both diffuse reflectance spectroscopy and multivariate regression modeling for the simultaneous determination of nitrophenols [48]. A schematic multicommuted flow analysis system [83, 84] is shown in Fig. 1. Multicommutation refers to flow systems in which solenoid valves are controlled by means of a personal computer. The advantages of this method over conventional FIA are to enable the automation of the analytical procedures, to lower both reagent and sample consumption and to reduce waste generation. In an alkaline solution, target nitrophenol derivatives are dissociated and adsorbed on the anion exchange membrane disc in a laboratory-made flow-through optrode cell. After every reflectometric measurement, the desorption of the target analyte and the conditioning of the adsorbent surface are carried out by the respective introductions of a solution of 80 % (v/v) methanol-0.2 mol dm^{-3} HCl and a 0.01 mol dm^{-3} NaOH solution.

For a mixture of analytes, a continuous flow methodology based on the implementation of on-line solid phase extraction, preconcentration, and mutual separation of analytes at a surface of adsorbent beads placed in the flow-through cell, with spectroscopic detection [78, 79]. The systems were controlled for automatic analysis by personal computers. One example is shown in Fig. 2 [85]. Although the sensitivity is not very high because the analytes were eluted and then diluted, mutual interferences could be decreased. However, such systems may be applicable only to

relatively simple mixtures.

4.2.1 Food

FI-SPS is also applicable to the analysis of organic or inorganic chemical components in food samples.

Capitan-Vallvey and co-workers successfully carried out the on-line separation of analytes in a binary mixture in a flow-through cell (Hellma 138-QS) packed with the appropriate adsorbent. The light absorption caused by one analyte with a shorter retention time could be first separately measured, while the other is transiently retained in the upper part of the solid particle layer in the flow cell where the incident light did not enter. The selection of adsorbents, the height of the adsorbent beads in the flow-through cell, pH, the concentration of organic solvent and flow-rate are important parameters for good resolution as well as a higher sensitivity. The proposed FI-SPS system was used for the simultaneous determinations of butylated hydroxyanisole (BHA) and n-propyl gallate (n-PG) [86], butylated hydroxytoluene (BHT) / *n*-PG and BHT / BHA in food and cosmetics samples [87], saccharin (1,2-benzisothiazol-3(2H)-one-1,1-dioxide) (SA) and aspartame (N-L-α-aspartyl-Lphenylalanine-1-methyl ester) (AS) in sweets and drinks [88], and Acesulfame-K (6-methyl-1,2,3-oxathiazin-4(3H)-one-2,2-dioxide) (AK) in tabletop sweeteners [89]. Their FI-SPS system was also used for the determination of AS in low-calorie foods and dietary products [90] and SA in low-calorie foods, but without separation [91].

Methyl (*E*)-2-{2-[6-(2-cyanophenoxy)-pyrimidin-4-yloxy]phenyl}-3-methoxy acrylate (azoxystrobin) residues in grapes, musts and wines were determined by FI-SPS [23]. After the extraction of azoxystrobin from the sample matrix, a 1.5-cm^3 sample solution containing azoxystrobin is introduced into the multicommuted flow analysis system. Because azoxystrobin is non-fluorescent, on-line UV radiation to convert this

pesticide into fluorescent species is carried out prior to the on-line concentration of this fluorescent species in the QAE-Sephadex anion-exchanger phase.

Diphenylamine residues in apple and pear can also be determined by FI-SPS [64]. The extracted diphenylamine residues are concentrated on-line on the C_{18} silica beads in the flow-through cell, and the fluorescence due to the concentrated diphenylamine residues is measured.

The HAI-RTP method and lanthanide-sensitized luminescence method were applied to the screening of tetracyclines in water and bovine milk [34] and the nafcillin determination in milk-based product [36], respectively. In the case of the HAI-RTP method for tetracyclines, iodide as a heavy atom and Na_2SO_3 as an oxygen scavenger were respectively added to the system. On-line monitoring of the RTP from nafcillin concentrated on the molecularly imprinted sol-gel for the selective adsorption of nafcillin in the flow-through cell was carried out. In the latter case, europium as a lanthanide, Na_2SO_3 as an oxygen scavenger and Amberlite XAD-4 as an adsorbent for Eu(III)- tetracycline complex were used.

As mentioned in section 2.5, ATR based flow-through sensor [52] and FTIR based flow-through sensor [53] were used for caffeine determination in soft drinks, respectively.

4.2.2 Contaminant and pesticides

Many FI-SPS methods have been reported for the analysis of pesticides [25, 85, 92-95]. To increase the selectivity, the stepwise elution method was employed as mentioned above.

Contaminants in drinking waters such as monoamine naphthalenes were determined by employing a chemometric-assisted molecularly imprinted

polymer-fluorescence optosensing system [82]. *p*-Aminophenol is also a pollutant in the environment, and an optical fiber reflectance sensor based on immobilized bis-8-hydroxyquinoline was developed [80]. Pentachlorophenol, a pesticide contaminant in water, was determined by employing the molecular imprinting technique and room temperature phosphorescence from Mn-doped ZnS powders [39].

High selectivity for fluoranthene, an indicator of PAHs, was achieved by employing the molecular imprinting technique [37, 38]. For the selective determination of benzo(α)pyrene, an air-borne contaminant, in water samples, the Amberlite XAD solid surface phosphorescence was observed using a pulsed excitation source: a delay time of 1.1 ms after the flash and a gate time of 5 ms were selected [96].

A rapid and simple method for the determination of formaldehyde in drinking water by C-SPE-diffuse reflection spectrometry was also reported using Purpald (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole) as a sensitive and selective chromogenic reagent for aldehydes [46]. A sample solution was collected into a syringe by passing through a reagent cartridge containing NaOH and Purpald. The reaction product of formaldehyde and Purpald in an alkaline medium was then oxidized by the air in the syringe. The purple oxidation product was concentrated on the anion exchange membrane disc in an extraction cartridge by passing the solution in the syringe through the extraction cartridge and then used for the diffuse reflectance spectroscopy. The time required for complete determination of one sample solution was less than 3 min.

4.2.3 Pharmaceuticals and biological samples

Development and prevalidation of a method for phenol determination for monitoring in pharmaceutical preparations was carried out by the batch method of SPS

[12]. Simple mixtures of pharmaceuticals were also determined by FI-SPS with stepwise elution [26, 27, 78, 79, 81, 97-99].

Fernández de Córdova *et al.* proposed an FI-SPS implemented with photochemically-induced fluorescence for the simultaneous determination of binary mixtures of sulfamethoxazole (SMX) and sulfanilamide (SA) or sulfathiazole (STZ) and SA [18]. The FIA system utilized in their proposed method is shown in Fig. 3. A minicolumn packed with QAE-Sephadex anion exchange gel (PC) was used for the separation of SA from SMX or STZ. Sample solutions injected into the flow system are first passed through the PC, and the SA is not retained on the adsorbent at pH 8. On the other hand, SA can be strongly adsorbed on the QAE-Sephadex at a pH higher than 11. Therefore, the solution containing SA is then merged with a 10^{-3} mol dm^{-3} NaOH solution (pH 11) after passing through the PC in order to concentrate the sulfanilamide in the solution into QAE-Sephadex in FC followed by the fluorescent measurements of its native fluorescence. Non-fluorescent analytes of SMX and STZ have to be photochemically derivatized into fluorescent species for the determination, and for this purpose, PR is then turned on and SV_1 and SV_2 simultaneously are switched to select the acetate and H_2SO_4 solutions because the optimum pH for the elution of SMX and STZ from PC, the photochemical derivatization of SMX and STZ and the sorption of the respective photochemically derivatized species on the adsorbent in FC is 2 to 4. The method was applied to pharmaceuticals, milk and human urine.

A combined approach based on solid-phase optosensing and multicommutation principles was applied to develop a method for the simultaneous analysis of naproxen and salicylic acid in biological fluids [79]. The coupling of sequential injection analysis (SIA) and solid-phase lanthanide-sensitized luminescence as a detection

technique made it possible to determine salicylic acid in pharmaceuticals [99]. The detection limit was 45 μg dm^{-3}, and the sampling frequency was 30 samples per hour.

Because propranolol is on the list of forbidden substances in the world of sports, FI-SPS for propranolol was developed and applied to urine samples [58]. A sample solution containing isolated propranolol from a sample matrix was inserted into the carrier solution stream. At pH 6, propranolol can be concentrated on Amberlite XAD-7, and the fluorescence from the solid phase in the flow-through cell was continuously monitored. The detection limit of this method was 0.2 μg dm^{-3} and about 20 samples could be determined within 1 h.

4.3 Speciation

One of the advantages of SPS is its very high sensitivity, which is comparable to those of atomic spectrometries such as inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS). In natural water, elements are sometimes present as some chemical species, different in chemical and biochemical reactivity and toxicity. Therefore, it is necessary to differentiate them. One typical speciation is related to chromium. For the determination of Cr(VI), the concentration of sub-μg dm^{-3} levels was effectively determined by FI-SPS using diphenylcarbazide (DPC) as a chromogenic agent. A novel on-line oxidation method of ultra-trace Cr(III) dissolved in natural water has also been developed using a flow electrolysis cell (Fig. 4) [74]. With an applied potential of 1.35 V (*vs*. Ag/AgCl), Cr(III) was quantitatively oxidized to Cr(VI) at room temperature using a flow-through electrolysis cell. Using an aqueous sample volume of 7.1 cm^3, the detection limit of the proposed method was 0.014 μg dm^{-3} (3σ, $n = 7$).

Sample dilution using an on-line electrochemical cell did not affect the sensitivity of the FI-SPS system because the target species were accumulated on the resin packed in the detection cell after the on-line oxidation.

2,3-Dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline was used for speciation of iron(II) and (III) by the batch SPS [20]. Iron(III) was determined by difference measurements after reduction of iron(III) to iron(II) with hydroxylammonium chloride. The detection limit for a 100 cm^3 sample and 0.5 g of the ion exchanger was 0.3 μg dm^{-3}.

The specific determination of iodine species was achieved by C-SPE-diffuse reflection spectrometry using poly(vinylpyrrolidone) (PVP) [43]. The solution chemistry of iodine is complicate and I_2, I^-, I_3^- and HOI are considered to be the predominant species present in a solution at a pH lower than 7. Among these iodine species, it was found that only I_2 could be extracted by the PVP impregnated membrane surface. If I^-, I_3^- and HOI can be completely oxidized to I_2, the total concentration of the iodine species can be obtained. Sample pre-treatment with Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) to oxidize these iodine species was used in this study. From the difference between the concentrations obtained with or without the Oxone pretreatment, the concentrations of I_2 and the total concentration of I^-, I_3^- and HOI can be calculated.

5. Conclusion

As shown in Table 1, recent application of SPS or FI-SPS has expanded to organic chemical components rather than to inorganic metal ions. The main reason is the great demands for more simple and higher sensitive analytical methods for organic chemicals in various samples. FI-SPS is suitable for this purpose. SPS or FI-SPS for organic chemical components can be more simple than that for inorganic chemical

components, because organic chemical components can be determined utilizing their characteristic light absorption or fluorescent properties in some cases and therefore the target analytes at low concentration can easily be determined if an appropriate adsorbent is applied.   To use the solid phase in a flow-through cell as a medium not only for on-line concentration but also on-line separation of analytes in the mixture makes it possible to broaden the applicability of FI-SPS.   In the case of a simple binary mixture, expensive HPLC systems may no longer be needed.   The application of the derivative techniques or multivariate calibration method to solid phase is also very useful for more complex mixtures.   Owing to the recent improvements in FIA such as SI and Lab-on-Valve, it is possible to reduce both the sample volume and the reagent consumption in an FI-SPS system.   Especially in the case of BI in a Lab-on-valve format, it is possible to reduce the consumption of valuable biological samples and also to automate complicated analytical procedures, and therefore, this method is very effective for biomolecular assays such as Enzyme-Linked Immunosorbent Assay (ELISA).

On the other hand, SPS is much more effective for the speciation of dissolved components with different oxidation states and/or existent chemical forms in water than the analytical methods such as ICP-AES or ICP-MS.   It is inevitable for the enhancement of sensitivity applicable to real samples to use a fairly large amount of water samples such as 10 cm^3 and the resulting longer analytical time such as 20 min. However, the significance of establishing speciation methods for trace metal ions in environmental samples has been widely recognized especially in the fields of environmental sciences and geochemistry.   The development of FI-SPS in the future may produce much important information on the geochemical cycles of trace metals in nature.

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Figure Captions

Fig. 1.   Schematic flow analysis diagram for disk-based preconcentration and optosensing determination of nitro-substituted phenols in waters.   C: carrier; R1: eluent; R2: membrane conditioning solution; S: sample; W: waste; HC: holding coil. The positions ON and OFF of the solenoid valves were on the left and on the right side of each syringe, respectively.   The inset shows the exploded view of the flow-through optrode (reproduced from [34] by permission of Elsevier, Ltd.).

Fig. 2.   Effect of the height (h) of the solid phase column above the irradiated area on the detection profiles [58]: (a) 41.3 mg of C_{18} (h = 0 mm): (b) 47.2 mg of C_{18} (h = 10 mm): (c) 58.0 mg of C_{18} (h = 20 mm).   Carrier: 20% MeOH; eluent: 65% MeOH; [thiabendazole] = 30 μg dm^{-3}; [benomyl] = 1000 μg dm^{-3}; sample volume: 0.6 cm^3 (reproduced from [58] by permission of the American Chemical Society).

Fig. 3. Schematic flow analysis diagram for the determination of binary mixtures of sulfamethoxazole (SMX) and sulfanilamide (SA) or sulfathiazole (STZ) and SA.   S: sample (buffered with 0.025 mol dm^{-3} NH_4Cl/NH_3, pH 8.0); C: 10^{-6} mol dm^{-3} NaOH solution (pH 8.0); E: 0.03 mol mol dm^{-3} CH_3COOH/CH_3COONa buffer solution (pH 4.0); A: 10^{-3} mol dm^{-3} NaOH solution (pH 11.0); B: 6.64×10^{-3} mol dm^{-3} H_2SO_4 solution (pH2.0); IV: injection valve; SV_1 and SV_2: selection valves; PC: minicolumn (packed with QAE-Sephadex A-25); PR: photoreactor (75 cm); FC: flow cell (packed with QAE-Sephadex A-25); SF: spectrofluorometer; W: waste (reproduced from [18] by permission of Elsevier, Ltd.).

Fig. 4. Schematic illustration of the flow electrolysis cell for the online oxidation of Cr(III). (A) Glassy carbon rod for electrical contact with the Pt-mesh working electrode, (B) counter electrode wound around the Vycor glass tube, (C) counter solution (0.1 mol dm^{-3}) KCl, (D) reference electrode (Ag/AgCl, satd. KCl), (E) Vycor glass tube to separate the sample solution and counter solution, (F) sample flow, (G) Pt-mesh working electrode packed into the Vycor glass tube, (H) Teflon cell block (reproduced from [49] by permission of the Japan Society of Analytical Chemistry).

Fig 1
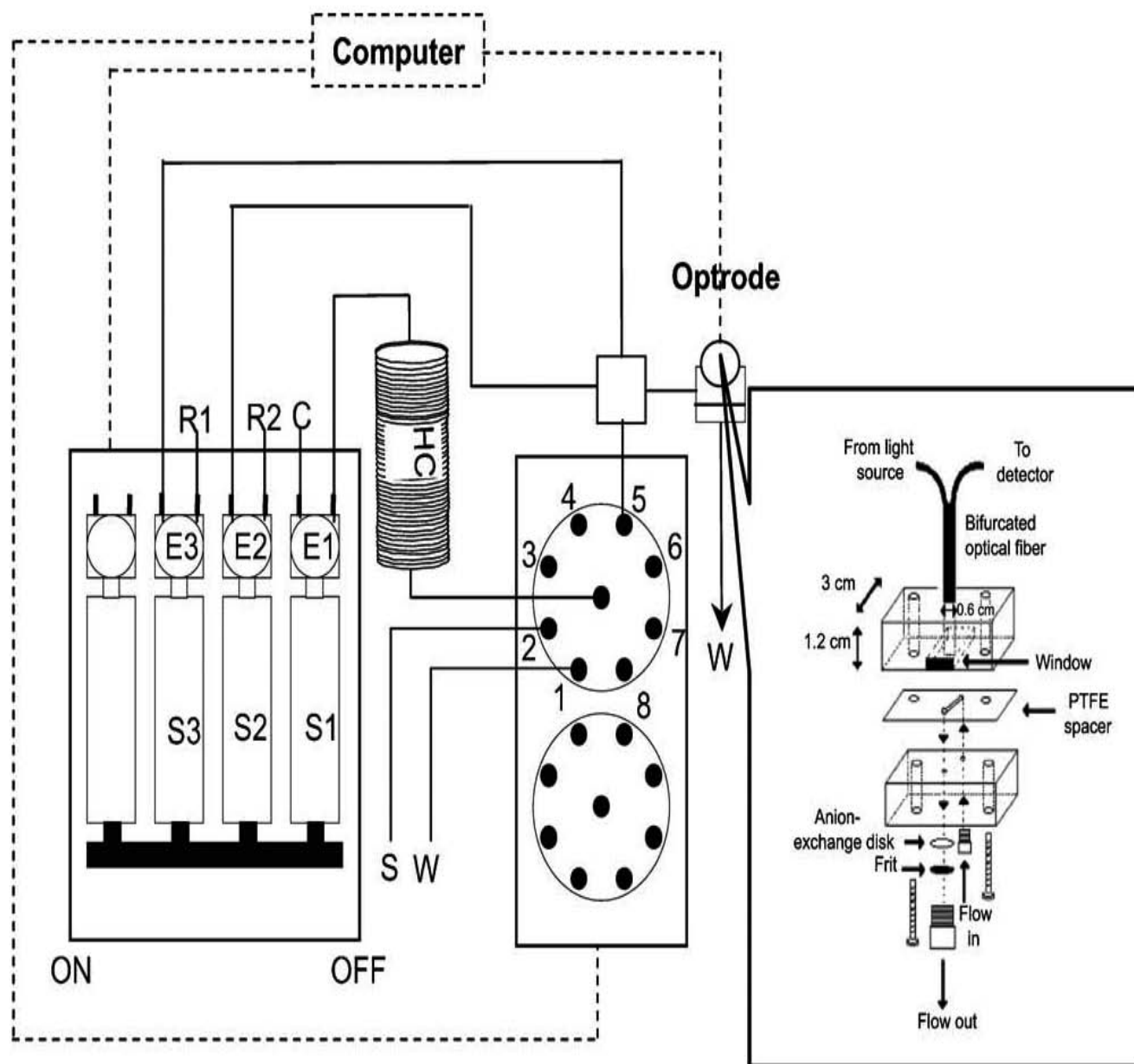
Fig 2
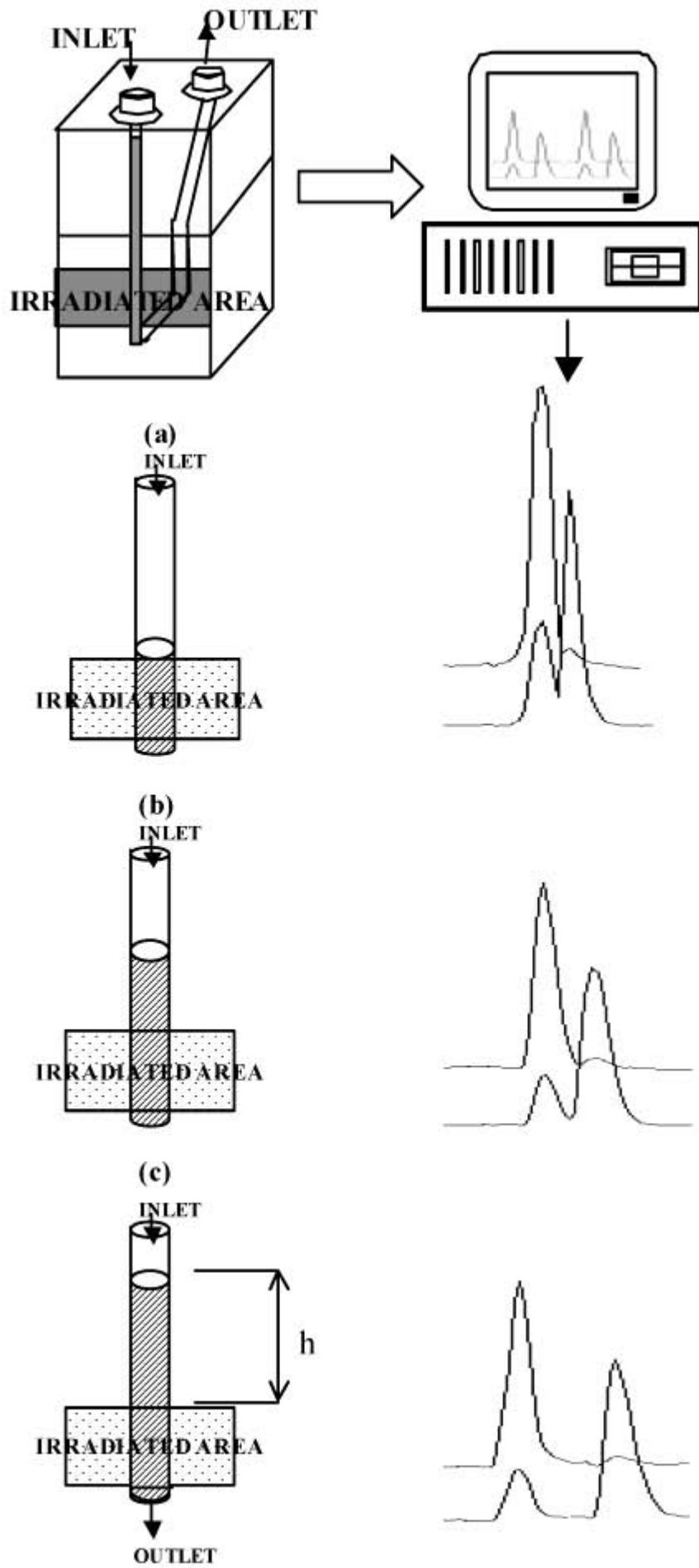
Fig 3
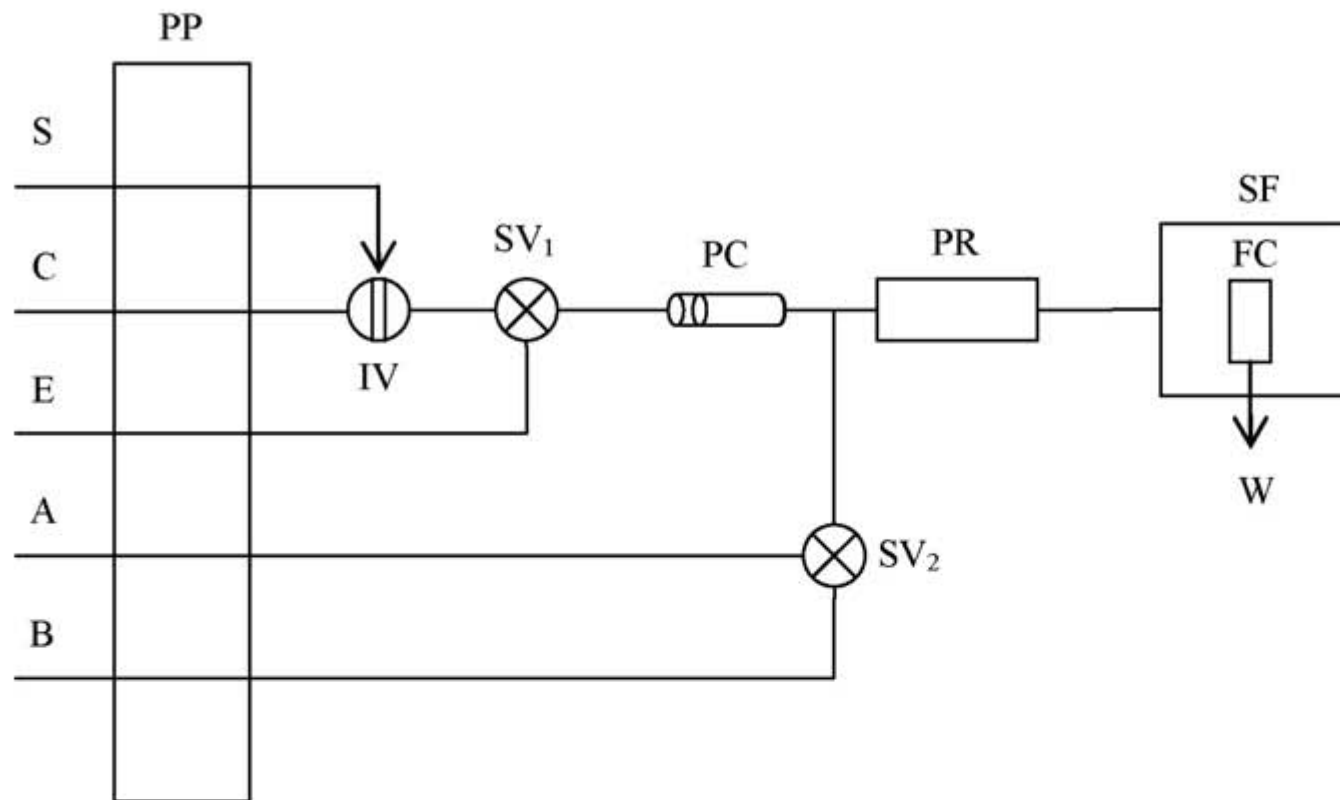
Fig 4
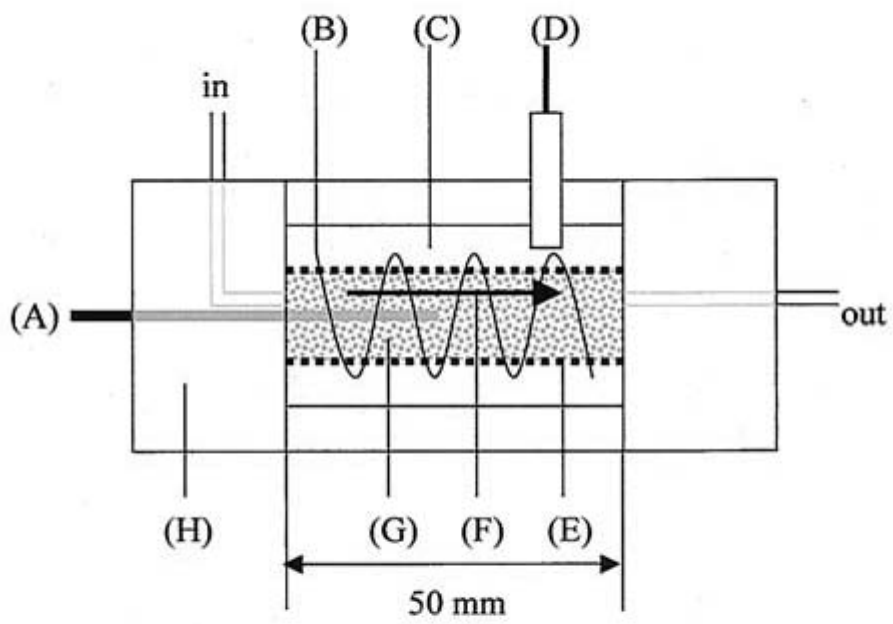
Table 1. Summary of solid phase spectrometry (2003-2009)

Analyte	Detection	Coloring or Fluorescent Reagent	Adsorbent	Optical Path Length (mm)	Excitation Wavelength (nm)	Analytical Wavelength (nm)	Ref
Batch method							
Zn, Pb, Cd, Cu, Co, Ni	absorptiometry	PAN (immobilized on cation-exchange resin)	AG 50W-X2-H$^+$ (150–300 μm)	1	-	554, 565, 625	17
phenol	absorptiometry	4-aminoantipyrine	Dowex 1-X4	1	-	495	18
Cu	absorptiometry	5-(4-sulphophenylazo)-8-amino-quinoline	DEAE-Sephadex A-25	1	-	605	19
Fe(II), (III)	absorptiometry	2,3-dichloro-6-(3-carboxy-2-hydroxyl-1-naphthylazo)quinoxaline	Ion-exchange resin	5	-	743	20
Cr(VI)	absorptiometry	1,5-diphenylcarbazide	Dowex 50W-X2	10		550	21
Ag(I)	reflectometry	DMABR (5-(p-dimethylaminobenzylidene rhodanine)	Empore SDB-XC extraction disk	-		540, 580	41
iodine	reflectometry	poly(vinylpyrrolidone)	Empore SDB-XC extraction disk	-		440	42
iodine		poly(vinylpyrrolidone) and Oxon				440	
Ag(I)		DMABR				540, 580	

Analyte	Method	Reagent	Support			λ (nm)	Ref.
Cu(II)		Zn-dithiocarbamate				420	
Ni(II)		Nioxime (cyclohexane-1,2-dioxime)				540	
Cr(VI)		dichromate				350, 450	
Fe(III)		SNAZOS (8-hydroxyquinoline-5-sulfonic acid)				620	
iodine (speciation)	reflectometry	poly(vinylpyrrolidone) and Oxon	Empore SDB-XC extraction disk	-		440	43
iodine	reflectometry	poly(vinylpyrrolidone)	Nylon membrane (0.45 μm)	-	-	400	44
formaldehyde	reflectometry	Purpald (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole)	EmporeTM Anion exchange-SR	-	-	700	46
Pd(II)	PAS[7]	2,6 TADAP (3-[2'-thiazolylazo]-2,6 diaminopyridine)	Dowex 50W-X4	1	-	625-640	55
phosphate	absorptiometry	molybdoantimonophosphoric acid	Silica gel modified with macromolecular quaternary ammonium	1	-	700	59
total Hg(II)	absorptiometry	1,3-di-(4-nitrodiazoamino)-benzene	β-cyclodextrin polymer	2	-	445, 545	60
Cd, Cu, Zn	absorptiometry	PAN	Dowex 50W-X2	1	-	557, 566, 574.5	67

Analyte	Method	Reagent	Support				Ref
Mo(VI)	reflectometry	Phenylhydrazine	Amberlite XAD-16	-	-	554.05	68
V(V)	reflectometry	PAN and H_2O_2	Amberlite XAD-16	-	-	589.4	69
V(V)	absorptiometry	2,3-dichloro-6(3-carboxy-2-hydroxynaphthylazo)quinoxaline	Dowex 1-X8	1	-	606	70
NH_4^+/NH_3	reflectometry	nitroprusside, HClO, thymol	C_{18} bonded membrane	-	-	690	71
H^+	reflectometry	mercurochrome	silica gel	1.5	473	550	72
					473	473	
Al	reflectometry pulse luminescence	lumogallion	silica gel powder glass plate	-	-	530	100
						520	

Flow method

Inorganic chemical components

Analyte	Method	Reagent	Support				Ref
V(V)	fluorometry	Alizarin Red S	QAE-Sephadex A-25	1.5	521	617	11
Cu(II), Zn(II)	absorptiometry	Zincon	QAE-Sephadex A-25	1.5		627	12
sulfide	reflectometry	methylene blue	C_{18} disk	-	-	666	47
sulfide	reflectometry	*N,N'*-dimethyl-*p*-phenylenediamine	C_{18} silica gel disk	-	-	666	49

Zn	fluorometry	*p*-(tosylamino)quinoline	C_{18} silica gel	1.5	377	495	63
Cd	fluorometry	8-hydroxyquinoline-5-sulfonic acid	QAE-Sephadex A-25	1.5	360	520	73
Cr(III), Total-Cr	absorptiometry	diphenylcarbazide	AG 50W-X2	3-5	-	550	74
Fe^{2+}	absorptiometry	1-(2-thiazolylazo)-2-naphthol	TAN immobiized C_{18} silica gel	1	-	780	75
Cr(VI)	absorptiometry	diphenylcarbazide	AG 50W-X2	3-5	-	550	76
nitrite	absorptiometry	Shinn reaction	C_{18} silica gel	2	-	-	77
nitrate		Shinn reaction + reduction to nitrite by cadmium-filled microcolumn					
sulfite		5,5'-dithiobis-(2-nitrobenzoic acid)					
ammonium,		Indophenol blue					
phosphate		Molybdenum blue					
Fe(II)		Ferrozine					
Fe(III)		Ferrozine + reduction to Fe(II) by hydroxylamine					
Cr(VI)		1,5-diphenylcarbazide					
Ni(II)		dimethylglyoxime					
phenol		4-aminoantipyrine					

Organic chemical components

azoxystrobin	photochemically	UV light	QAE-Sephadex	1.5	374	467	23

residues	induced fluorescence		A-25				
metsulfuron methyl	Photochemically induced fluorescence	photoproduct by UV irradiation	C_{18} silica gel	1.5	323	378	24
thiabezole **metsulfuron methyl**	fluorometry	analyte itself photoproduct by UV irradiation	C_{18} silica gel	1.5	296 323	347 378	25
sulfamethoxazole **sulfanilamide** **sulfathizole**	fluorometry	photoproduct by UV irradiation	QAE-Sephadex A-25	1.5	258	354	26
reserpine	fluorometry	photoproduct by UV irradiation	C_{18} silica gel	1.5	394	489	27
polycyclic aromatic hydrocarbons[1]	fluorometry	analytes themselves	Amberlite XAD-4	1.5	355, 390	382-540	28
paracetamol	fluorometry	Nitroso compound formed by the derivatization reaction between paracetamol and $NaNO_3$	QAE-Sephadex A-25	1.5	325	430	29
1-naphthaleneacetic acid	HAI-RTP[8]	Tl^+ and SO_3^{2-}	Amberlite XAD-7	1.5	292	490	30
naphazoline	HAI-RTP	KI and Na_2SO_3	Amberlite XAD-7	1.5	290	520	31

orthophosphate	energy transfer-RTP	erythrosine B and phosphormolybdenum blue	Amberlite XAD-4	1.5	525	675	32
orbifloxacin	lanthanide-sensitized luminescence	telbium(III)	CM-Sephadex C-25	1.5	275	545	33
tetracyclines[2]	RTP	europeum(III)	Amberlite XAD-4	1.5	394	617	34
p-aminobenzoic acid	lanthanide-sensitized luminescence	telbium(III)	QAE-Sephadex A-25	1.5	290	546	35
nafcillin	HAI-RTP	KI and Na_2SO_3	Molecularly imprinted sol-gel particles	1.5	283	505	36
fluoranthene	RTP	analyte itself	polyurethane	1.5	365	550	37
fluoranthene	RTP	analyte itself	polyurethane	1.5	365	550	38
pentachlorophenol	RTP	analyte itself	Mn-doped ZnS	quantum dots (1 cm × 1 cm)	316	600	39
nitrophenol derivatives	reflectometry	analytes themselves	Anion-exchange membrane disk	-	-	435 for 4-NP and 2,4-NP 415 for 2-NP	48
caffein	ATR-FT-IR[9]	analyte itself	LiChrolut EN	-		1800-1000 cm^{-1}	52

						(integrated)	
caffein	FT-IR	analyte itself	C_{18} silica gel	0.045	-	1550-1566 cm^{-1} (integrated)	53
salicylic acid	Chemi-luminescence	MnO_4^- in H_2SO_4	QAE-Sephadex A-25	1.0	-	-	54
benzo[α]pyrene	fluorometry	analyte itself	Amberlite XAD-4	1.5	392	406	56
polycyclic aromatic hydrocarbons	fluorometry	analytes themselves	Amberlite XAD-4	1.5	355	370-550	57
propranolol	fluorometry	analyte itself	Amberlite XAD-7	1.5	300	338	58
thiabendazole	fluorometry	analyte itself	Nylon powder	1.5	300	340	61
monoamine naphthalenes[3)]	fluorometry	-	Molecularly imprinted polymers	1.5	333 (1-NA) 347 (2-NA) 342 (total)	421 (1-NA) 411 (2-NA) 415 (total)	62
diphenylamine residues	fluorometry	analytes themselves	C_{18} silica gel	1.5	291	372	64
immunoglobulins	absorptiometry	analyte itself	Protein G-coated Sepharose 4B	6.3	-	280	65
intercellular H_2O_2	fluorometry absorptiometry	dichlorofluorescein diacetate	Cytodex microcarrier beads on which	0.8	470	530 470	66

			mouse embryonic fibroblasts were grown				
vitamin B2	fluorometry	analytes themselves	C$_{18}$ silica gel	1.5	294	305	78
vitamin B6					450	519	
naproxen	fluorometry	analytes themselves	C$_{18}$ silica gel	1.5	233	354	79
salicylic acid					299	407	
p-aminophenol	reflectance	2,2'-(1,4-phenylenedivinylene)bis-8-hydroxyquinoline	Amberlite XAD-7	-	-	647	80
2-naphthoxyacetic acid	fluorescence phosphorescence	analyte itself	Amberlite XAD-7 silica gel	1.5	328 276	348 516	81
1-naphthylamine	fluorometry	analytes themselves	molecularly imprinted polymer	1.5	333	421	82
2-naphthylamine					347	411	
1-naphthalene-methylamine							
benomyl	fluorometry	analytes tehmselves	C$_{18}$ silica gel	1.5	293	398	85
thiabendazole					305	358	
BHA	absorptiometry	analytes themselves	C$_{18}$ silica gel	1	-	288	86
n-PG[4)]						272	
BHT[5)]	absorptiometry	analytes themselves	C$_{18}$ silica gel	1	-	274	87
n-PG						272	
BHT						274	
BHA						288	

saccharin	absorptiometry	analyte itself	Sephadex G-25	1	-	210	88
aspartame						205	
aspartame	absorptiometry	analyte itself	DEAE Sephadex A-25	1	-	205	89
acesulfame-K						226	
saccharin	absorptiometry	analyte itself	Sephadex G-25	1	-	217	90
aspartame	absorptiometry	analyte itself	CM-Sephadex C-25	1	-	219	91
bitertanol	fluorometry	analyte itself	C_{18} silica gel	1.5	261	236	92
fuberidazole	fluorometry	analytes themselves	C_{18} silica gel	1.5	314	356	93
carbaryl					281	336	
benomyl					293	398	
carbendazin	solid surface phosprescence	analytes themselves	C_{18} silica gel	-	-	-	94
carbofuran							
benomyl							
linuron[6]	fluorometry	photoproduct by UV irradiation	C_{18} silica gel	1.5	324	418	95
benzo(α)pyrene	fluorescence	analytes themselves	Amberlite XAD	1.5	390	690	96
piroxicam	absorptiometry	analytes themselves	C_{18} silica gel	1	-	285	97
pyridoxine						334	
paracetamol	absorptiometry	analytes themselves	C_{18} silica gel	1	-	275	98
caffeine							
propyphenazone							
salicylic acid	lanthanide-sensitized	Tb-sensitized luminescence	QAE-Sephadex A-25	1.5	300	505	99

	luminescence						
labetalol	fluorometry	analyte itself	C_{18} silica gel	1.5	330	420	101

[1]anthracene (ANT), fluoranthene (FLT), benzo[α]pyrene (BaP) and benzo[β]fluoranthene (BbF); [2]tetracycline (TC), oxytetracycline (OTC), chlortetracycline (CTC) and doxycycline (DTC); [3]1-naphthylamine (1-NA) and 2-naphthylamine (2-NA); [4]butylated hydroxyanisole (BHA) and n-propyl gallate (n-PG); [5]butylated hydroxytoluene (BHT); [6]3-(3,4-dichlorophenyl)-1-methyl-1-methoxyurea (linuron); [7]Photoacoustic spectroscopy; [8]HAI-RTP: heavy atom induced-room temperature phosphorescence; [9]Attenuated total reflection Fourier transform infrared spectroscopy (ATF-FT-IR)

Table 1 (continued)

Sample Volume (cm³)	Sampling frequency (hr⁻¹)	Detection limit (µg dm⁻³)	Precision (%) (concentration in µg dm⁻³)	Outstanding Features	Drawbacks	Ref.
Batch method						
200	-	1.2-4.1	0.68 to 4.15 (59 to 207)	Multicomponent analysis	Relatively large sample volume	17
50	-	11	0.85 to 11.27 (94)	Prevalidation method to evaluate the validity or reliability of the SPS method		18
200	-	6.1	1.1 and 2.0 (50)	Elimination of the interferences of Ag(I) and Au(II) using derivative spectrophotometry	Strong interferences by Fe^{3+}, tartrate, EDTA and citrate	19
100	-	0.28	1.65 (12.0)	Good selectivity	Change in the recovery of Fe in real water samples due to the matrix effect	20
20	-	0.014	< 5 (0.61-4.72)			21
2-10		-	-	Addition of 1,2-decanediol or nonionic surfactant to increase the hydrophilicity of the DMABR-impregnated membrane surface	Interferences by SCN^-, Br^- and I^-.	41

10	-	50	-	PVP impregnated membrane selective to I_2	Sample pre-treatment with Oxone to oxidize iodine species	42
10	-	-	-			43
9.0	-	10	-	Negligible depletion (ND) concept		44
1.0	-	80	-	Complex formation (formaldehyde-Purpald) and the oxidation of this complex inside a syringe.		46
1-10	-	4000	< 5		Lack of sensitivity due to the insufficient power radiometric light source	55
5-100	-	1.9 (as P)	-	Specific determination of orthophosphate, total polyphosphate and phosphoric acid esters		59
100	-	0.024	2.4 (50)	Greatly improved sensitivity	Strong interference by Ag(I)	60
200	-	0.5 (Cd) 0.9 (Cu) 0.4 (Zn)	2.0 (40) (Cd) 1.6 (40) (Cu) 2.0 (40) (Zn)	Derivative spectrophotometry; Sample pre-treatment to eliminate Co and Ni by using dimethylglyoxime and the addition of KI or KF as a masking agent for Hg and Fe		67
1.0	-	200	3.3 (9600)		Lower sensitivity; Interference by V(V)	68

10	-	10	2.8			69
1000	-	0.009	1.4 (1.5)	Improved sensitivity and reproducibility by centrifugation	Severe interferences by Ni, Co and Cu	70
10		10	9	Applicable to air samples	Intereference by methylamine	71
-	-	pH 3 to 8	< 4	Ratiometric approach for optical sensing		72
10	-	30 70 8	-	Composit silica film with anion-exchange properties produced by sol-gel method; Suppression of Cu and Fe(II) interferences by the addition of 1,10-phenaqnthroline		100

Flow method

Inorganic chemical components

0.8	18	0.45	4.22 (50)	Bead injection using a commercially available flow-through cell	Severe interferences by Fe^{3+} and Al^{3+}	11
1.0	15-16	29 (Cu(II)) 40 (Zn(II))	4.55 (1000) (Cu) 4.48 (1000) (Zn)	Cu analysis at pH 5.9 and Zn analysis at pH 11	Severe interferences by Co(II), Ni(II), Be(II), Mn(II), Fe(III) and Al(III) for Zn analysis.	12

					Advantages	Disadvantages	Ref.
2.9		8	2.9	0.7 (50)	Low consumption of reagents due to multisyringe flow analysis system	Lower sensitivity and injection throughput relative to those of previously reported FI-SPS	47
5		5	4.6	2.1 (500)	Plug-in spectrophotometer for the miniaturization of the overall flow analyzer, adaptable to real-time monitoring		49
0.7		20	0.9	1.8 (50)	Good selectivity	Only 10-fold sensitivity increase	63
0.9		16	0.5	1.9 (25)		Fairly strong interferences by Al, Fe(II) and Zn	73
7.9		3-4	0.014	1	On-line oxidation method of Cr(III) using a flow electrolysis cell		74
0.625		25	15	4	Greener procedure based on FI-SPS		75
7.9		4	0.009	4.4 (0.18)	Kinetic study on Cr(VI) reduction in natural water		76
5.0		-	0.5 (nitrite) 2 (nitrate) 2 (sulfite) 1 (ammonium) 3 (phosphate) 1 (Fe(II))	1.5-3.3	Tubular microcolumn packed with C_{18} silica beads as a flow-through cell; On-line concentration and sensing of non-polar chemical components		77

5 (Fe(III))						
2 (Cr(VI))						
80 (Ni)						
1 (phenol)						

Organic chemical componer

1.5	28-33	2.4 to 15.9	1.5 to 2.6 (100 to 1500)	Photochemically induced fluorescence; Multicommutation system	Sample treatment with C_{18} cartridge	23
1	34-36	0.14	3.3 (75)	Low detection limit (very sensitive for metsulfuron methyl)	Somewhat severe interferences by other pesticides such as Aldicarb or aminicarb	24
2.1	12	2.5 (TBZ)[10] 3.3 (MET)	1.1 2.4	Mutual separation; Strongly fluorescent photoproduct from MET on-line generated in micellar by UV irradiation		25
0.9	13	8.1 (SM)[11] 2.9 (SA) 5.7 (ST)	1.1 2.8 1.8	Chromatographic separation and detection		26
0.8	43	0.05	1.5 (2)	Mutual separation	Strong intereferences by mefenamic acid and diclofenac	27
0.5	72	1,4-6.4	3.5-7.9 (50)	Multichannel ICCD detector as	Slightly better detection limits than that	28

				optical transducers	obtained with a photomultiplier	
1.5	6	2000	2.5 (20)	Sequential injection analysis; Cut filters to simplify the optsensing system	Strong interference by acetylsalicylic acid	29
2	-	1.2	3 (50)	About 200 nm separation between the wavelengths for excitation and emission	Only 10 times higher sensitivity than that of the conventional solution method	30
2	-	0.0094	2.32 (0.4)	Comparison among MS-RTP, solution method of HAI-RTP and sensor method	Low sensitivity of flow-through optosensor method relative to that of the HAI-RTP method	31
1	-	0.5	1.2 (20)	Higher sensitivity		32
1	10	3.3	2.81 (100)	Sequential injection analysis	Strong interference by Fe^{3+}	33
1	-	0.026 (TC)[12] 0.041 (OTC) 0.035 (DCT) 0.17 (CTC)	3 (21 to 23)	Direct screening system for tetracyclines	Interference by Fe^{3+}	34
0.1	22	60	1.2	Sampling frequency of 22 h^{-1}	Very strong interferences by Zn^{2+} and Fe^{2+}; Lower sensitivity than that of the solid surface RTP or the method using time-resolved lanthanide-sensitized luminescence	35
0.150	4-6	2400	< 5			36
2	9	-	-	Combination of the RTP and the		37

					iodinated molecularly imprinting techniques		
-		-	23	2.8 (100)	Combination of the RTP and the iodinated molecularly imprinting techniques		38
5		9	0.035	3 (10)	Molecularly imprinting techniques		39
4		-	0.69 (2-NP)[13] 0.42 (4-NP) 0.37 (2.4-NP)	0.9 (2) (2-NP) 2.8 (0.3) (4-NP) 1.9 (0.4) (2.4-NP)	Multivariate least-square regression; Better sensitivity and lower detection limit	Low recovery	48
3		4	5.2	4 (50000)	Elimination of the interference by sucrose using the difference in transient retention between caffeine and sucrose		52
1.5	5	10	2.6	4.1 (25000)			53
0.7		60	300	3.1 (8)	Multicommutation system	Low sensitivity	54
4		-	0.003	5.1 (0.050)			56
0.5		-			Artificial neural networks		57
2		20	1.3	2.4 (150)			58
1.5		14-18	2.8	0.9 (64)	Nylon powder as the adsorbent	Gradual deterioration of the adsorptive properties of nylon; Lower sensitivity than that of the previous reported method using C_{18} as the adsorbent	61

2	5	26 (1-NA)[3] 50 (1-NA) 45 (simaltaneous)	< 3.2	Molecularly imprinted polymer for selective adsorption of monoamine naphthalenes as optosensor	Lower sensitivity; Lower reproducibility (86.4 to113 %)	62
0.5-1.5	12	60	2.2-2.4 (1000)	Multicommutation system	Low recoveries of the target chemical components in real samples	64
0.02	18	5000	-	Maicro-affinity chromatography; Sample volume of 20 mm^3	10 times lower LOD than that of μBIS	65
-	-	-	-	μBI spectrometry; Simultaneous monitoring of fluorescence and absorbance for intercellular H$_2$O$_2$ determination; Normalization of the fluorescence data in a Lab-on valve format by cell density measurement		66
0.7	10	3 (Vitamin B2) 45 (Vitamin B6)	< 2 (45) < 2 (45)	Multicommution system; Stepwise determination by elution/automatic analysis		78
2.4	8	0.3 (NAX)[14] 1.3 (SA)	< 2	Multicommution system; Stepwise determination by elution/automatic analysis		79

10		10	20	4.4 (1100)	Detected as an indophenol dye in the presence of an oxidant	Unable to use the solid repeatedly	80
2		15	2	2.8 (125)	$TlNO_3$ as a heavy atom and Na_2SO_3 as an oxygen scavenger		81
2		-	12 23 20	-	Simultaneous determination using partial least-squares		82
3.2		10	0.08 (BNM)[15] 4.6 (TBZ)	0.6 (10) 0.7 (300)	Stepwise desorption	Severe interferences by fuberidazole for TBZ analysis and by o-phenylphenol and α-naphthol for BNM analysis	85
1.0		9	700 (BHA) 900 (n-PG)	1.7 (BHA) 1.7 (n-PG)	On-line separation in a binary mixture in a flow-through cell	Inferior resolution to that of other methods such as HPLC	86
1.0		9	2500 (BHT) 2000 (n-PG) 2100 (BHT) 1800 (BHA)	1.4 (BHT) 0.8 (n-PG) 1.3 (BHT) 1.0 (BHA)	On-line separation of analyte in a binary mixture in a flow-through cell	Lower sensitivities	87
1.2		10	300 (saccharin) 1400 (aspartame)	1.0 (8000) (saccharin) 1.0 (10000) (aspartame)	C_{18} packed minicolumn to separate aspartame form saccharin in the mixture		88
0.625		24	5650 (aspartame) 10000 (Acesulfame-K)	3.4 (50000) (aspartame) 0.6 (50000)			89

			(Acesulfame-K)			
0.800	20	200	0.78	On-line separation in a binary mixture in a flow-through cell	Severe interference by Cyclamate	90
1,5	24	750	0.55	Sampling frequency of 24 h^{-1}		91
1	20	14	1.8 (150)	Stepwise determination by elution	Severe interferences by carbofurane and carbaryl	92
2.1	8	0.09 (FBZ)[16] 6 (CBR) 9 (BNM)	< 2	Stepwise determination by elution		93
2	-	15 (CBD)[17] 68 (CF) 35 (BNM)	3.5 3.2 2.4	On-line solid-phase separation		94
	15	130	0.8 (3500)	Sensitivity enhancement by the addition of a surfactant	Strong interferences by Fe(III), fuberidazole, thiabendazole, neburon and isoproturon.	95
4	-	12	4	Pulsed excitation source with a delay time of 1.1 ms after flash and the gate time of 5 ms		96
1.3	-	1200 (PC)[18] 270 (PX)	3.0 (24000) 1.2 (6000)	Multicommutation principles; On-line solid-phase separation	Severe interferences by thiamine and saccharin for pyridoxine analysis	97

0.2		11	7500 (PCT)[19] 650 (CF) 1900 (PFZ)	3.5 3.7 3.8	Concentration followed by successive separation in the flow-through cell using precolumn		98
1		14	45	2.7 (500)	Sequential injection analysis; Solid-phase lanthanide-sensitized luminescence		99
1.5		7	3.3	3.4 (100)	Sequential injection analysis		101

[10]thiabezole (TBZ), metsulfuron methyl (MET); [11]Ssulfanilamide (SA), sulfamethoxazole (SMX), sulfathiazole (STZ); [12]tetracycline (TC), oxytetracycline (OTC), chlortetracycline (CTC), doxycycline (DTC); [13]2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-NP); [14]salicylic acid (SA), naproxen (NPX); [15]benomyl (BNM), thiabendazole (TBZ); [16]fuberidazole (FBZ), carbaryl (CBL); [17]carbendazim (CBZ), carbofuran (CF); [18]Pyridoxine chlorhydrate (PC), Piroxicam (PX); [19] paracetamol (PCT), propyphenazone (PFZ);