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Water and aqueous environments: on-line chemical analysis, problems and solutions

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Contents

I.	Introduction	145
II.	Alternatives to the traditional off-line analysis scheme	145
III.	How can chemical analysis be automated?	146
IV.	Flow analysis as a general approach to the automation of chemical analysis	146
V.	Extension of the analytical potential of flow-injection analysis	147
VI.	Practical use of on-line chemical analysis based on the principles of flow-injection analysis	148
VII.	Sequential injection analysis as the next step in the automation of on-line chemical analysis	149

Abstract. General approaches to the automation of chemical analysis and to the design of systems for on-line monitoring of aqueous environments are considered. The advantages of flow analysis techniques in the development of these systems are substantiated. Merits and demerits of the existing versions of flow analysis, namely flow-injection and sequential injection analysis, as well as continuous flow analysis and combined versions of these two methods, are discussed. The bibliography includes 108 references.

I. Introduction

The chemical control of aqueous environments is needed in many branches of human activity. The most important include the environmental monitoring of natural waters and the monitoring of industrial processes that use water as the operating environment (for example, in thermal and nuclear power engineering). Unfortunately, most researchers still have to consider data obtained in the laboratory analyses of samples taken at intervals. An important drawback of such off-line arrangements of analytical control is the substantial time delay before the information on the monitored object is obtained and, hence, late decisions concerning the intervention into the monitored process for preventing an undesirable development. This is especially important for the monitoring of potentially hazardous engineering processes.

The ecological monitoring of natural waters brings about specific problems, as sampling and sample transportation require more time and labour. This is responsible for errors caused by contamination of samples or degradation of the analytes during sampling, transportation, and storage. When abnormal values are obtained for the parameters under control, verification of the results requires additional time and facilities or may not be possible at all, because one cannot take two identical samples even from the same water area. The selection of the spatial and temporal coordinates of sampling points is largely random. Therefore, the results are scattered and often do not allow one to draw correct conclusions even on the basis of repeated observations.

The need for alternative ways of monitoring the processes taking place in aqueous environments whose composition changes spontaneously is obvious. The purpose of this review is to analyse the general trends in the development of on-line methods for continuous analysis of water environments which appeared recently.

II. Alternatives to the traditional off-line analysis scheme

The search for alternative solutions has resulted in new schemes of chemical analysis. In medicine, '*in situ*' analysis is used most often, *i.e.*, determination of the analyte directly within the analytical control object. This is done by monitoring easily measurable physical parameters: temperature, pressure and flow rate.[1] The '*on site*'[2] plan has found application in the solution of ecology-related analytical problems. This analysis is performed directly on the site where the monitored object is located. Both schemes imply the development of special methods of analysis as applied to the conditions under which they are performed. In the case of the '*in situ*' analysis, these are chemical sensors, while in the case of '*on site*' analysis, they are test methods.

The most versatile scheme is on-line analysis, which implies creation of a continuous sampling line from the monitored environment and installation of continuously functioning analyser(s).[3] In the on-line scheme, the range of applicable methods of analysis is virtually endless. Algorithms for the selection of an adequate analytical method and, correspondingly, the appropriate analyser have been proposed.[4] To date, up to a hundred methods can be used for continuous ecological and in-process monitoring of aqueous environments.[5] Information on the commercially available analysers has been covered in the *Anadata Analyser Encyclopedia*;[6] and a system of priorities has been outlined.

If it is necessary to monitor simultaneously a large number of impurities, high performance liquid chromatography (HPLC) is a convenient choice. However, the instrumental complexity of liquid chromatographs and, hence, their higher cost for lower reliability, and also the necessity of using flammable and toxic

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solvents as eluents hamper broad use of HPLC in the automated systems for continuous in-process monitoring. During the period of vigorous development of HPLC, forecasts were made concerning fast extension of the scope of its application in in-process control, and special liquid chromatographs were manufactured for this purpose (for example, the Optichrom series produced by the Applied Automation company).[5] However, liquid chromatographs, except for ionic ones, have not found wide use in in-process control.[7] Whereas gas chromatography is almost irreplaceable in analysis of hydrocarbon mixtures, in the case of liquid chromatography, there exist alternative solutions. In those rare cases where HPLC is still used for in-process control, conventional laboratory instruments are employed in automated systems. For example, SAMOS (System for the Automatic Measurement of Organic micropollutants in Surface water) designed for the monitoring of organic pollutants in the Rhine collecting area is based on HP 1090 liquid chromatographs.[8–10]

In recent years, rapid separation-free methods of analysis have appeared in the optical and electrochemical technology (for example, those using rapid-scanning spectrophotometers on photodiode lines with computer processing of the spectra).[11] When photodiode lines are used as detectors, a full spectrum composed of 200–1000 points is recorded in several milliseconds.[12,13]

Ion chromatography, which does not require hazardous solvents and operates at much lower pressures, is still used in thermal and nuclear power engineering. Actually, one can hardly propose equally efficient and relatively inexpensive methods for determination of anions.[14–18]

After a period of moderately successful attempts at the development of on-line automated monitoring systems based on HPLC, flow-injection analysis (FIA) has now become the method of choice for the design of such systems.[19]

III. How can chemical analysis be automated?

The problem of automation of chemical analysis involves two aspects: the automation of proper analytical procedures in the traditional off-line chemical analysis and the integrated automation of the analytical control including sampling, sample processing and data collection and display stages. The problem of integrated automation of the in-process monitoring where the composition of the monitored material spontaneously varies includes automation of analytical procedures for particular methods as a part of continuous on-line analysis.

A monograph[20] presents an attempt to describe the general approaches to the automation of laboratory analysis based on electrochemical, colorimetric, spectroscopic, thermal, radiometric (X-ray) and chromatographic analysis and sample preparation procedures involving separation techniques. The technical solutions proposed for any of the above methods and especially for the processing of analytical information, described in the monograph, are now essentially out-of-date. However, everything concerning the general concepts of automation of chemical analysis remains actual.

In solving the problem of automation of proper chemical analysis, two basically different approaches are possible. The first one, robotic, implies the design of mechanical devices that copy the operation of an analytical chemist when performing analyses. These devices are to measure the required amounts of samples and reagent solutions, mix them, fill the measuring cell or take aliquot portions and inject them into the analyser, measure the analytical signal, and so on. The major advantage of this approach is versatility. Almost any chemical analysis technique (for example, laboratory liquid chromatographs operating in the automated mode[10]) can be automated using the robotic approach. However, analysers of this type have a common drawback: high cost and low reliability caused by complexity of mechanical units.[20] The design of these analysers does not comply with an important requirement of automated systems for chemical analysis, in particular, the principle of minimisation of the number of moving parts.[5]

The second approach implies, instead of the direct imitation of the operator's action, its mimicking under conditions most susceptible to automatic control. This approach is embodied in flow analysis.

IV. Flow analysis as a general approach to the automation of chemical analysis

This group of methods opens up the most extensive opportunities for the automation of analysis. They were first implemented as continuous flow analysis (CFA) whose history and key principles have been outlined in certain books.[21,22] The hydraulic flow diagram of CFA is presented in Fig. 1 *a*. The flows of the sample and a solution of a reagent capable of producing an 'analytical form' with the analyte detectable by the flow detector are continuously pumped by a peristaltic pump, mixed in the mixing helix, and routed to the detector. This version is used if the detector cannot catch the analytical signal directly from the analyte. Otherwise, the reagent and the mixing helix are not required. A drawback of this flow chart is the fact that correctness of the detector reading cannot be checked during the measurements. This is due to elimination of the boundary between the consecutive samples of different compositions in hydraulic lines caused by mixing; this precludes the possibility of checking the detector readings due to mixing of the test and reference samples.

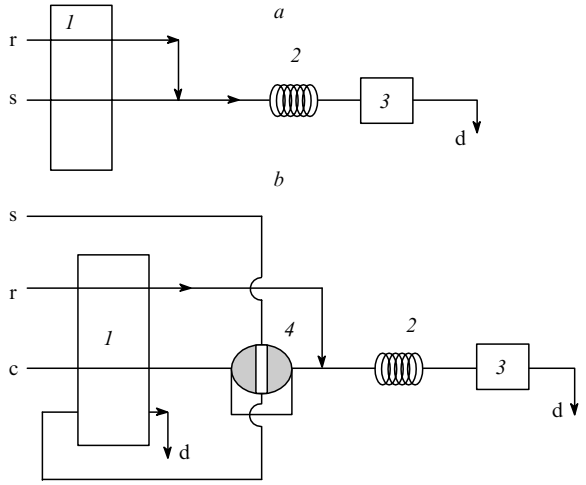


Figure 1. Hydraulic block diagrams of CFA (*a*) and FIA (*b*).
(*1*) Peristaltic pump, (*2*) mixing helix, (*3*) flow detector, (*4*) measuring valve. Inlet lines: s — for the sample, r — for the reagent, c — for the carrier solution; d — for the discharge.

The FIA scheme[23] implies the introduction of discrete batches of the sample into a moving laminar flow of the carrier solution to form a controlled concentration gradient of the analyte (Fig. 1 *b*). The flow of the carrier solution is combined with the flow of the reagent solution in the mixing helix and the mixture enters the flow detector, which records concentration peaks, the peak width being determined by the dispersion of samples as they move along the hydraulic lines. Thus, FIA is the flow analysis with a 'controlled sample dispersion'.[24] The carrier solution, the flow of which carries the test sample, can serve additionally as the correcting medium, which creates conditions (for example, stabilises the pH) needed for the formation of 'analytical forms' of the analyte upon mixing with the sample. The amplitude and the area of the obtained peaks are related to the analyte concentration. The FIA principles and equipment have been described in the literature.[23,25–27] Specific problems of the application of FIA for the continuous on-line process control have been considered.[28–33]

The major advantage of FIA is the possibility to perform almost all known operations included in the sample preparation † — dilution,[35] preconcentration and isolation of the analyte by extraction,[36–42] dialysis [43–47] and sorption [27,41,46,48] in the on-line mode. In addition, quantification can be carried out using almost any of the known detection techniques ranging from simple sensors to mass spectrometers.[19,27,49]

Yet another important advantage of FIA is the possibility of calibrating instruments with a specified scale unit directly under operating conditions,[50–56] which is especially important for monitoring systems. The automated taking into account of the drift of the base line and the possibility of correcting the calibrating curves ensures the reliability of the results.

Flow-injection analysis can be considered as a set of instrumental techniques that ensure the automation of the routine analytical procedures of sample preparation and measuring of the analytical signal for most methods used to quantify the analytes. The indisputable advantages of this approach resulted in a growth of the number of companies engaged in the manufacture of flow-injection analysers for process control. The information on the equipment for FIA can be found in the publication.[57] Flow analysers and automated multichannel systems for the on-line analytical control based on them have now been developed.[58]

To eliminate the loss of information concerning the monitored process during the periods between FIA cycles, a combined flow method joining the advantages of CFA and FIA has been proposed.[59] This approach implies alternation of different modes of operation of a flow analyser according to a specified algorithm. To obtain analytical information on even short-term fluctuations of the sample composition, if spontaneous changes are possible, the analyser operates most of the time in the CFA mode, and to verify the detector readings, the analyser is switched to the FIA mode with periodic supply of reference solutions to the inlet. This provides the opportunity to check the position of the detector base line and the response to a particular analyte concentration. Figure 2 shows the form of the analytical signal recorded with alternation of the CFA and FIA modes. During the time period from 0 to t_1, the analyser operates in the CFA mode with the supply of the test sample to the inlet. At the instant t_1, the analyser is switched to the FIA mode with the same sample being supplied to the inlet, as indicated by equal amplitudes of the peaks and the magnitudes of the continuous signal. At time instant t_2, a standard solution of the analyte starts to be supplied, and at time instant t_3, the analyser is switched again to the CFA mode and the test sample moves through the system.

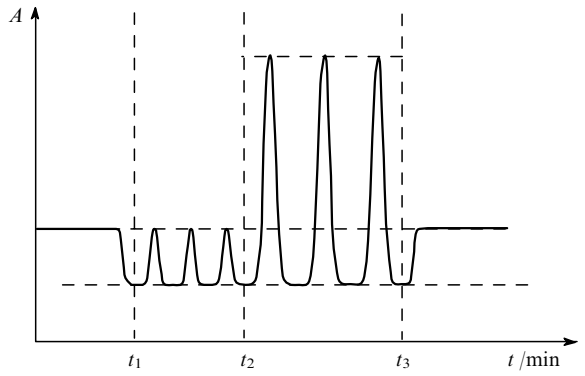


Figure 2. Form of the analytical signal recorded upon consecutive operation of the flow analyser in the CFA and FIA modes.

† It should be noted that in automated on-line monitoring systems, the most critical problems arise at the sample preparation stage.[34]

V. Extension of the analytical potential of flow-injection analysis

Among the advantages of FIA as a versatile method for performing chemical analysis in the on-line mode, worthy of note is the possibility of incorporation of preconcentration and isolation of analytes into the analysis sequence; in some cases, this compensates for the insufficient sensitivity of widely used detectors. The separation and preconcentration methods used in FIA have been surveyed in a collection of papers [28] and in a monograph.[46] The most widely used methods include gas diffusion through porous hydrophobic membranes, extraction and sorption.

In flow analysis, the separation methods based on gas diffusion through a membrane perform two functions in sample preparation.[60] The first one is the isolation of analytes in the aggregative state most convenient for the subsequent determination by flow detectors. Depending on the aggregative states of the source and receiving phases, the analyte can be converted from a gas into a liquid and *vice versa*. Liquid absorption is normally used in FIA and CFA for the analysis of atmospheric air,[46,61] while gas extraction is used more often in vapour analysis of aqueous media.[62] Another study describes [63] the use of membrane gas diffusion cells for the reaction gas extraction in FIA in which the analyte is intentionally transferred into a volatile form (for example, in the determination of NH_4^+ in sewage water).

The second function of gas diffusion methods in FIA is to change deliberately the composition of the test medium (for example, the pH) in order to create the optimal conditions for the formation of 'analytical forms' of the substances to be determined.[64–66]

Liquid extraction, like gas diffusion, is used in FIA not only as a preconcentration method but also for the isolation of substances in the aggregative state most convenient for their subsequent determination. An example is extraction of petroleum products and phenols into hexane or carbon tetrachloride.[67] The use of extraction in FIA has required the development of special flow extraction apparatus. Extraction in segmented flows has gained the widest use.[39–42,68] For this purpose, portions of an extractant are introduced at intervals into the flow of the test solution (after pre-adjustment of the composition of this solution to ensure the optimal conditions for extraction). As a result, the homogeneous flow of the solution is converted into a two-phase segmented flow in which segments of the aqueous solution alternate with segments of the extractant whose length in the capillary tube (about 0.5 mm in diameter) is 1–6 mm. The segmented flow passes through the extraction helix, which intensifies the phase transfer, and enters the separator in which the phases are separated. The organic phase is routed to the flow reactor.

The most severe drawback of these systems is the fact that it is impossible to control the ratio of phase volumes over broad ranges, which stipulates a limitation for the attainable preconcentration factor even when the distribution coefficient in the extraction system used is high.

1. New methods in liquid and gas flow extraction

New possibilities for the flow extraction appeared owing to the chromatographic-membrane mass exchange processes in liquid–liquid and liquid–gas systems.[69] The idea of chromatographic-membrane processes is based on the use of capillary effects in hydrophobic porous media.[70] The mass exchange between two phases differing in polarity takes place in a capillary porous medium from a hydrophobic material containing two types of pores with different sizes. The capillary pressure arising in micropores prevents water and aqueous solutions from getting inside. In turn, the aqueous solutions that enter, according to experimental conditions, the biporous system under a higher pressure fill macropores and prevent non-polar phases from entering the macropores. Thus, the two phases can move independently within the mass exchange space formed by the hydrophobic biporous medium. The diagram of a chromatographic-membrane cell

(CMC), shown in Fig. 3, corresponds to the case where the flows of two phases intersect at right angle. The mass exchange takes place in conformity with the rules of a chromatographic process, as the porous structure of the mass exchange layer in the CMC is similar to the structure of a stationary non-polar packing in an extraction-chromatographic column. The differences are manifested only as an increase in the phase transfer rate compared to that in a conventional chromatographic process (in which one phase is stationary) due to the convective movement of both phases at the interface.

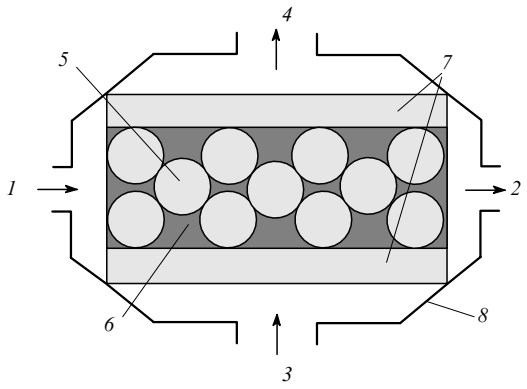


Figure 3. Block diagram of a chromatographic-membrane cell.
(*1*, *2*) Polar liquid inlet and outlet; (*3*, *4*) non-polar liquid or gas inlet and outlet; (*5*) biporous hydrophobic matrix (microporous filler); (*6*) macropore space; (*7*) microporous hydrophobic membranes; (*8*) cell casing.

A flow of a non-polar liquid or a gas is introduced into the mass exchange space and leaves this space through hydrophobic microporous membranes, in which the pore size is close to the size of micropores in the biporous matrix. The material of the membranes and the pore size should ensure the impermeability of the membrane for the aqueous phase under conditions of the mass exchange process.

The chromatographic-membrane liquid or gas extraction is an alternative to not only extraction in segmented flows but also to the isolation by gas diffusion, because it provides intensification of phase transfer both in the liquid – liquid and liquid – gas systems. Instead of the slow diffusion through a porous membrane, the gas-diffusion membrane processes involve the delivery of phases to the interface.

Numerous examples of the use of the chromatographic-membrane liquid and gas extraction in FIA have been reported.[60] A number of combined protocols of sample preparation are possible. For example, for the determination of arsenic, the chromatographic-membrane reaction gas extraction is combined with gas liquid chromatography;[71] petroleum products and phenols are determined in water using an extraction chromatographic column for the preconcentration and isolation of the analytes into the organic phase.[67] After these have been eluted by the extractant, the resulting two-phase flow is separated in a chromatographic-membrane separating vessel.

2. Sorption preconcentration in the flow-injection analysis

Sorption techniques for sample preparation actively compete in FIA with the extraction methods and, in some occasions, the former are even preferred.[27, 46, 48] This is the case where it is necessary to attain the limiting preconcentration factors (for example, to determine beryllium in natural water [72]) or to exclude the use of organic solvents. Sorbents with chelating functional groups have found the most extensive use in FIA.[48] As regards minimising the time required for the sorption preconcentration, sorbents with fibrous structure are most efficient, as they ensure the highest rate of sorption equilibration.[72] In this case, it is expedient to incorporate a high-speed peristaltic pump into the hydraulic circuit for sample filtration through a column containing the sorbent (Fig. 4). When the position of the switching valve corresponds to the route shown by the continuous lines, a mixed flow of the sample and a buffer solution is filtered through a column at the highest permissible rate. Simultaneously, the eluent is mixed with the reagent solution and passes through the flow detector, which records the base line. After the valve has been switched into the position corresponding to the dashed lines, the sample is routed to the discharge and the eluent is fed to the sorption column. At the column outlet, the eluate is mixed with the reagent solution and flows to the detector, which records the analyte peak against the base line obtained in the previous cycle.

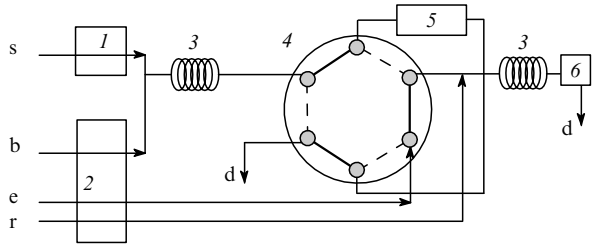


Figure 4. Hydraulic diagram of FIA with sorption preconcentration on a fibrous sorbent.
(*1*) Single-channel high-speed peristaltic pump, (*2*) multichannel peristaltic pump; (*3*) mixing helices, (*4*) six-way switch valve, (*5*) sorption column, (*6*) flow detector.
Inlet lines: s — for the sample, b — for the buffer solution; e — for the eluent; r — for the reagent, d — for the discharge.

VI. Practical use of on-line chemical analysis based on the principles of flow-injection analysis

Most publications devoted to FIA describe procedures of off-line analysis in stationary laboratories. Much fewer papers have been devoted to the applications of FIA in the on-line mode. The attention is focused on the continuous determination of products either formed in the processes of biotechnology (during operation of fermenters) or supplied to the reaction medium. The publications consider both the general aspects of the on-line analytical monitoring of biochemical processes [73–79] and particular issues of continuous monitoring of the concentration of separate components: proteins,[80] enzymes,[81] amino acids,[82] antibiotics,[83, 84] glucose,[85, 86] lactate and so on.

The publications devoted to analysis of various types of water — subsurface, rain, river, sea and potable water — refer mainly to procedural aspects of the off-line determination of particular impurities. The data on flow-injection analysers operating in the on-line mode on real water environments are summarised in Table 1. Most of them provide monitoring of some single parameter of water contamination, *i.e.*, making use of automated single-channel analysers adjusted to determination of one analyte in the on-line mode.

Among interesting, although disputable solutions,‡ worth noting is the SCANNER analyser, which is an example of using FIA for *in situ* control.[100] It is designed for determination of SiO_3^{2-} and S^{2-} in sea water directly from the ship and can operate at depths of up to 2500 m.

To perform automated chemical monitoring of several quality parameters of a water medium in the on-line mode, two systems are possible: (i) the design of *n* independent parallel channels, each

‡ The point that seems disputable is overcoming of sealing problems when working under high pressures, instead of using (designing) a simple and more reliable system for continuous sampling of water from a required depth.

Table 1. Application of FIA for impurity analysis in the aqueous environments of real objects (in the on-line monitoring mode).

Impurity	Object of analysis	Detector	Detection limit /μg litre^{-1}	Range of linearity /μg litre^{-1}	Operation time [a] /day	Ref.
PO_4^{3-}	natural water	photometer, $\lambda = 660$ nm	12 [b]	0 – 1000	–	87
NO_3^-	the same	photometer, $\lambda = 565$ nm	24	0 – 12000	4	88
NO_3^-	hydroponics solutions	photometer, $\lambda = 542$ nm	–	–	–	89
NO_3^-	natural water	photometer, $\lambda = 550$ nm	–	–	7 [c]	90
F^-	the same	ionometric electrode	–	–	7	91
NH_4^+	water from biological treatment plants	photometer, $\lambda = 590$ nm	–	500 – 50 000	–	92
NO_3^-	the same	the same	–	500 – 20 000	–	92
PO_4^{3-}	"	"	–	500 – 30 000	–	92
F^-	natural water	fluorimeter	–	0.2 – 20	–	93
H_2O_2, H_3BO_3	solutions of neutron moderators	amperometric	–	–	–	94
NH_4^+	natural water	photometer, $\lambda = 635$ nm	17	0 – 5000	3	95
NH_4^+	sewage water	the same	600	0 – 40 000	7	96
SO_3^{2-}	KCl brines (up to 18%)	fast-scanning spectrophotometer, $\lambda = 412$ nm	–	0 – 20 000	7	97
Al(III)	natural water	photometer, $\lambda = 538$ nm	< 45	0 – 1000	14	98
V(V) [d]	alkaline solutions of the Sulfoline process	photometer, $\lambda = 550$ nm	–	$(5 – 150) \times 10^4$	–	99

[a] Duration of the continuous autonomous operation. [b] For phosphorus. [c] The total testing time is 2 years of operation. [d] In the presence of excess V(IV).

being tuned for determination of one of *n* monitored parameters, and (ii) the design of a system containing additional units for switching the flows in order to adjust channels for determination of one or another parameter.

The experience of design and operation of an automated system according to the principle of *n* parallel channels to monitor the quality of the outside water from a moving ship [58] has shown that such a system ensures a sufficient reliability when up to 14 parameters are simultaneously determined (Table 2). Therefore, in the design of a ship system for real-time ecological analytical monitoring, an *n*-channel system was preferred over the adjustable system. This provides higher reliability of the equipment due to minimisation of the number of mechanical units [5] and elimination of the necessity of combining units of flow-injection analysers that implement different methods of analysis. Evaluating objectively the potential of FIA, the authors [101] noted that these devices function efficiently in a laboratory but are not always suitable for industrial conditions. The need to use sets of different units for each analytical method and the relative complexity of operation of peristaltic pumps are the general drawbacks of FIA as regards the design of on-line monitoring systems. The former drawback is important for the *n*-channel configuration of a multiparametric control system,[58] which is less favourable for economic reasons than a system with adjustable analysers.

Table 2. List of controlled parameters of water quality and ranges of quantifiable concentrations (RQC) by systems of the flow monitoring of water quality.[58]

Component	RQC /mg dm^{-3}	Component	RQC/mg dm^{-3}
NO_3^-	0.3 – 5.0	SO_4^{2-}	25 – 250
NO_2^-	0.05 – 2.0	Zn^{2+}	0.01 – 0.1 [b]
Cl^-	3 – 3500	Mn^{2+}	0.01 – 0.1 [b]
F^-	0.03 – 7.0	Fe^{3+}	0.05 – 1.0
PO_4^{3-} (see [a])	0.5 – 10.0	dissolved	0.02 – 1.0 [c]
	0.025 – 1.0	petroleum	
Cu^{2+}	0.02 – 1.0	products	
	0.001 – 0.02 [b]	anionic surf-	0.03 – 1.5 [c]
NH_4^+	0.05 – 0.8	actants	
		phenol	0.001 – 0.1 [c]

[a] Calculated for P; [b] with sorption preconcentration; [c] with chromatographic-membrane extraction concentration.

VII. Sequential injection analysis as the next step in the automation of on-line chemical analysis

The search for an alternative to FIA has given rise to a new approach in the flow analysis techniques, namely, sequential injection analysis (SIA).[101]

In flow-injection analysis, the analytical process takes place in a system of tubes along which the sample or calibrating solutions and solutions of reagents move in one direction. After combination of the flows, the sample or the calibration solution is mixed with the reagent, and the flow of the carrier with the reaction products moves toward the detector. Therefore, for inducing the flow along each inlet tube (the sample, the reagent solution, and auxiliary solutions), a separate pump is required. The multichannel peristaltic pump, which is usually employed for this purpose, is actually a set of pumps operating in parallel. In addition, a measuring valve is required for introducing aliquot portions of the sample or a reagent solution into the flow of the carrier.

In the sequential injection analysis, a single liquid line is used, instead of the set of tubes, in which a syringe pump operating according to a definite schedule induces a flow of solutions moving alternately into two directions (Fig. 5). The piston of the syringe pump moves in discrete strokes in order to suck in the wash solution (*1*), the solution of the sample (*2*) and the solution of the reagent (*3*) into the liquid channel composed of the reaction helix, flow detector and the holding helix. The distributive valve ensures the sequential injection of solutions into the channel by switching the valve outlets synchronously with pumping. During the reverse stroke of the piston, the mixed solution of the sample and the reagent passes through the detector to the discharge and the hydraulic line is washed. Among the important advantages of SIA, noteworthy is the option to stop the flow, which allows this method to be used for measuring the rates of chemical reactions.[102] The possibility of stopping the flow is also useful for adjusting the conditions of analysis as regards the time for the formation of the 'analytical forms' of the analyte.

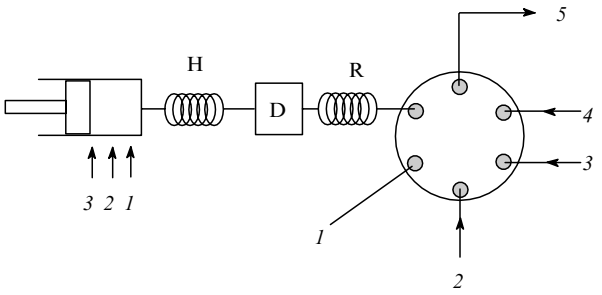


Figure 5. Block diagram of the sequential injection analysis. (*1*) Wash solution, (*2*) a solution of the sample, (*3*) a solution of the reagent, H is the holding helix, R is the reaction helix, D is detector, (*4*) standard solution, (*5*) discharge.

The authors of SIA [101] stipulated the use of a pump having a 'zero time lag' and a 'zero elasticity,' which requires replacement of a peristaltic pump by a computer-controlled plunger pump. The MilliGAT plunger pump,[103] which completely rules out flow pulsation, is the most successful engineering solution. However, peristaltic pumps are also used in some cases.[104]

Sequential injection analysis has a number of advantages over FIA (especially in the on-line mode), in particular, minimisation of the consumption of the reagent solution and a better adaptability to computer control in the case of SIA.[101] Moreover, the SIA version no longer requires the measuring valve (which is considered to be a trouble spot in FIA instruments),[105] the selection of every next solution being accomplished by means of a multiway valve. The authors of the method believe that the replacement of the measuring valve eliminates the problems related to the operation of mechanical units of the analyser; however this is not self-evident. The description of the software for the automation of flow analysis systems in SIA is documented.[106]

The attraction of SIA as a new approach to the automation of chemical analysis is indicated by numerous publications: more than 200 papers, several patents and a review [105] have now been published on this topic.

The discussion of on-line analysis would be incomplete without considering the problem of continuous sampling. According to different estimates, 70% to 85% of malfunctions in on-line analysis systems refer to this stage.[107] The sampling problem is solved rather easily in the case of the in-process control of the aqueous media circulating or occurring in the controlled object under an elevated pressure. Connection of the sampling line requires a choke with a controlled flow rate made of an inert material.

The information on the development and functioning principles of continuous sampling systems (CSS) for natural and sewage water is very limited. The Fathom Oceanology Ltd company (Canada) has designed a CSS having a fluoroplastic hose 8 mm in diameter and a pump for water supply to the ship (with a productivity of up to 40 dm^3 min^{-1} at a ship velocity of up to 12 knots). Similar systems have also been designed by the Japanese companies Morikawa and Progress Trading. Direct measurements of contaminants in a sea water flow are also performed.[108] Determination of nitrates and nitrites was carried out by reverse flow-injection analysis (with injection of reagents); sea water was pumped directly through the tubes of a flow-injection analyser. Later, analyses of sea water for sulfates, phosphates, silicates and a number of metals (cobalt, manganese, copper, iron) have been carried out. Analyses were performed from a drifting ship, *i.e.*, no monitoring of water basins, which requires on-line analysis, was involved.

All the CSS systems mentioned above are meant for taking representative samples into sampling vessels for their subsequent chemical analysis in the laboratory (off-line mode). However, an experience in the design and operation of CSS in combination with a multiparametric system of on-line analysis has been reported.[58] The block diagram of the CSS is shown in Fig. 6. To minimise the time delay between obtaining the data on the sample composition and the real time, a two-step pattern of sample supply to the analyser was chosen. The first step is a main channel with a membrane pump operating for the discharge of the main bulk of water overboard. The main channel includes a unit for splitting of the sample flow, some of the flow being routed to the inlet of analysers. To ensure the sample representativity, polytetrafluoroethylene and stainless steel were chosen as the main structural materials for the CSS. The removal of mechanical impurities was attained by three-step filtration. The design of water intake devices includes coarse filters manufactured from a stainless-steel grid, which separate particles larger than 1 mm. The flow splitting unit installed in the main channel of the CSS includes a fine filter for water with a filter cell made of porous stainless steel for separating particles larger than 0.1 mm. At the inlet of each analyser, except that for petroleum products, fine filters made of porous polytetrafluoroethylene are installed additionally. The filters are expected to protect the hydraulic lines and flow measuring cells of the analysers from plugging with coarse suspensions of either mineral or organic origin, which are always present in natural waters. At the same time, the filters do not influence the chemical composition of the sample.

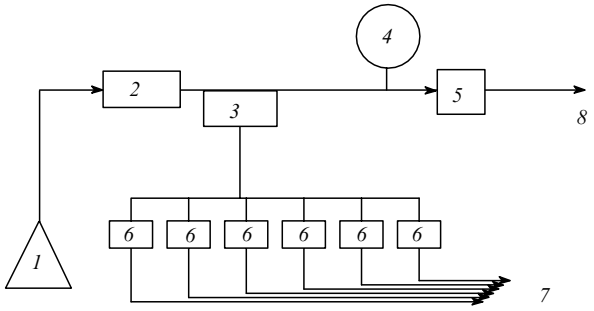


Figure 6. Block diagram of the continuous sampling system for natural water: (*1*) water intake device; (*2*) main pump; (*3*) coarse filter; (*4*) manometer; (*5*) controlled choke; (*6*) fine filters; (*7*) sample inlet channels of the monitoring system; (*8*) discharge line.

The presented block diagram of CSS and the diverse types of flow analysers considered above demonstrate the presence of a methodical and instrumental base for the design of automated on-line chemical analysis systems for the industrial process control and ecological analytical control of aqueous environments.

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