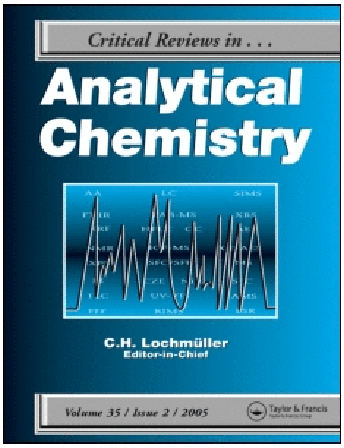

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Flow Injection Techniques in Aquatic Environmental Analysis: Recent Applications and Technological Advances

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This article critically examines the application of flow injection (FI) technology in aquatic environmental analysis. A survey of the important advances in FI technology in the past 5 years (2000–2004) is presented along with critical technological design factors and development issues including automation, preconcentration, speciation, and advanced detection methodologies. Modern environmental applications are also discussed and future perspectives on the directions of FI technology in relation to aquatic environmental analysis are considered.

Keywords automation, environmental analysis, flow injection, preconcentration, sample introduction, sequential injection

A pioneering paper in 1975 by Ruzicka and Hansen (1) introduced the concept of flow injection (FI) in routine analysis. Eleven years and over 800 articles later, the same authors published a comprehensive review describing new developments in FI technology (2). Since that review, there have been over 13,000 publications and several books (3–9) covering FI and its wide range of applications in the fields of biological, chemical, pharmaceutical, environmental, and process analysis. The second generation of FI, termed sequential injection (SI), was established in 1990 by Ruzicka and Marshall (10) with applications and advantages discussed in numerous reviews and trends articles (11–22).

Flow injection systems have many characteristic features, which include low sample and reagent consumption, rapid analysis time, and the incorporation of on-line matrix separation and preconcentration phases (23–26), and can accommodate sensitive and selective derivatization reactions to convert analytes into detectable species (1, 2). Environmental samples often require on-line sample treatment, such as filtration for the determination of biologically or particulate reactive species (e.g., phosphate and trace metals) and photooxidation or acidic peroxydisulfate digestion for biologically important species (e.g., DOC and total Fe). These are all easily incorporated into FI manifolds, as is the detection of the various forms of phosphorus in order to study nutrient budgets and elucidate further details about their biogeochemical cycling in aquatic ecosystems (27, 28). Coupled to their inherent robust design and the ability to be easily deployed in the field, FI monitors are therefore ideally suited for in situ analysis in complex environmental matrices.

This article critically examines the role of FI in aquatic environmental analysis from 2000 to 2004. During this period, important advances in FI technology emerged, including more sophisticated on-line sample treatment, advanced detection methodologies, and improvements in automation, instrument control, data acquisition and portability. This is not to detract from the importance of previous FI developments and studies reported in a number of informative reviews (2, 29–40). The first section of this article presents the theory and key principles of FI, followed by a discussion of important design

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criteria and fabrication issues. The next section reviews recent advances in FI technology, including detection methodologies and the coupling of FI with other analytical techniques. The final section discusses future trends in FI-based analytical methodologies.

THEORY AND PRINCIPLES

Flow injection is a powerful tool enabling contamination-free manipulation of solutions and rapid and reproducible mixing of sample and reagents in close proximity to the detector. Flow injection instrumentation can be configured as robust, compact, and reliable analytical systems that are field deployable, promoting in situ analysis and high resolution monitoring. Reproducibility (typical RSDs of 1% to 5%), high sample throughput (20–300 h^{-1}), and accuracy are the other hallmarks of FI.

Flow injection manifolds commonly consist of narrow bore (0.5–0.8 mm) PTFE tubing and fittings, peristaltic pumps for reagent and sample transport, rotary sample injection valves, a flow through cell, and an appropriate detector (Figure 1a). Flow injection systems are readily automated and can incorporate on-line sample treatment (e.g., solid-phase columns for sample preconcentration and matrix removal). The injection of a precise sample volume into a moving carrier or reagent stream (without the addition of air) results in minimal, but continuous, reproducible sample dispersion (Figure 1b) which results in good precision (typically <2% RSD). The reaction zone then passes through a detector where changes in a physicochemical parameter (e.g., absorbance) result in a transient signal (often recorded as peak height or area), which is proportional to analyte concentration.

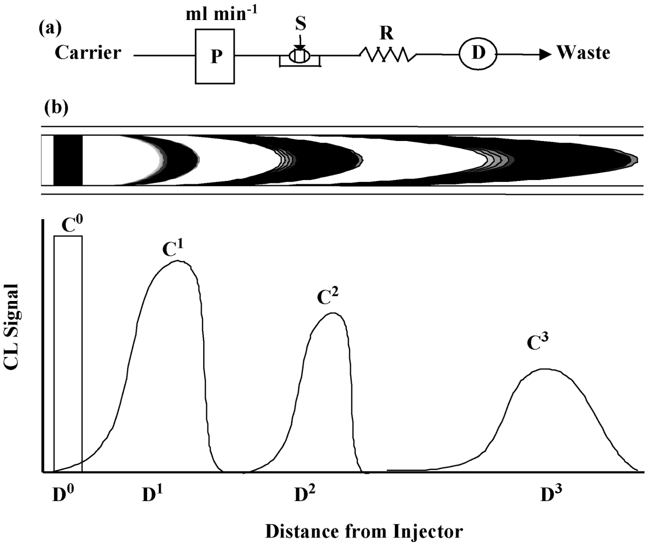

FIG. 1. (a) Schematic of single channel FI manifold: P, pump; S, sample injection valve; R, reagent mixing coil; D, detector incorporating flow cell. (b) Dispersion in FI. The injected sample zone undergoes progressive dispersion as it moves along the FI line. This is reflected in a reduced height but broader peak. C^n, the concentration at distance D^n from the injector. The peak shape is a schematic representation to only illustrate dispersion.

The injected sample forms a well-defined conical (parabolic) profile due to the laminar flow that occurs when typical FI flow rates and narrow bore tubing are used. Control of the degree of dispersion is a central tenet of FI and results in excellent reproducibility coupled with short residence times that, due to the nonequilibrium conditions at the detector, are characteristic of FI (4). The extent of dispersion can be characterized by the dispersion coefficient (D), which is related to peak height (usually at the detector) (6). At the signal maximum:

$$D = Co/Cg \qquad [1]$$

where Co = analyte concentration prior to dispersion and Cg = concentration in the dispersed sample zone on the dispersed concentration gradient at time *t* (commonly at detection).

Dispersion is caused primarily by convection, although molecular diffusion is also a factor, and can be controlled by varying flow rates, reactor geometry, and sample volume. The dispersion coefficient is critically dependent on the volume injected, with small volume changes potentially producing large alterations in signal.

The reproducible dispersion and dilution, which occurs where confluent streams merge, facilitates on-line physical and chemical treatment (e.g., reagent addition, derivatization reactions, and dialysis). The versatility of FI is enhanced by the ability to use commutation, which is the switching of zones between different streams.

When using FI, sample and reagent consumption is low, typically 5–500 μL (reduced to nanoliters in microfluidic systems). These are attractive features where samples are limited in volume (e.g., biological fluids), and they enable accommodation of gas diffusion and ion exchange reactions and in vivo assays (41). Production of waste and the use of expensive and possibly toxic reagents are also minimized, promoting environmentally responsible chemical analysis. Flow-based methods also include the stopped flow technique, which can be used for the identification of unstable transient species, and the use of catalytic methods.

Sequential injection (SI) is a related technique developed in the late 1980s in order to meet the demand for increased versatility and automation. It is a syringe-based system that involves the sequential aspiration (via a multiposition valve with dedicated ports) of aliquots of sample and reagents to form a stack of well-defined zones in a holding coil. Reversal of the flow then directs the zones toward the detector, resulting in zone penetration and mixing of sample and reagents to produce a detectable species. Sequential injection has improved versatility compared with FI systems, enabling alteration of the methodology through easily achieved software control of the dedicated multiposition valve ports, therefore avoiding the need to redesign and reengineer the manifold for different applications.

TABLE 1
Criteria for the design and development of FI instrumentation for environmental monitoring

Design criteria
Detection methodology
Sensitivity and selectivity
Overall cost, simplicity/complexity of design
Robustness, reliability
Sample throughput
Portability, miniaturization
Speciation and interfering matrix removal capabilities
Automation, data acquisition
Low power/reagent consumption
In situ calibration
Data processing and transfer
Sample presentation issues (e.g., filtration, biofouling, sensitivity)

DESIGN CRITERIA AND FABRICATION

Table 1 lists a number of critical design criteria that should be considered when designing and developing FI instrumentation for environmental monitoring. These are especially true for the development of field-based and submersible systems where microfabrication, portability, analytical response, sensitivity, selectivity, biofouling, and power consumption issues are of concern. Selected criteria are discussed in greater detail below.

Molecular spectroscopic detection (e.g., spectrophotometry, chemiluminescence, infra-red (IR), and fluorescence) is the most commonly used and provides rapid determination of chemical parameters in environmental matrices. Flow injection instrumentation incorporating miniature diode array detectors benefits from enhanced spectral acquisition and signal processing, but requires more sophisticated hardware and software (36). Most of the known electroanalytical techniques (e.g., potentiometry, pulsed amperometry, voltammetry, coulometry, and conductometry) are suitable for detection in FI.

Flame atomic absorption spectrometry (FAAS) techniques are also commonly used and often are accompanied by a continuous flow separation or preconcentration step to increase the overall sensitivity (37). Other more sensitive atomic spectrometric techniques used include inductively coupled plasma-mass spectrometry (ICP-MS), electrothermal atomic absorption spectrometry (ETAAS), and inductively coupled plasma-atomic emission spectrometry (HG-ICP-AES). Detection methodologies are discussed with regard to specific applications in the Techniques and Applications section below. Broader coverage of FI detection methodologies can be found in earlier reviews (11, 25, 37, 42–44).

The recent advent of microfabrication (not necessarily nanotechnology) allows the replacement of traditional bulky laboratory techniques and has led to significant advances in the development of miniaturized FI systems. This innovative microfabricated technology has been an important improvement compared with traditional approaches, especially in terms of field use and overall portability. Although not widely used as yet, it has the potential to become the method of choice. It provides significant advantages for environmental process investigations (e.g., metal speciation and bioavailability, and high temporal and spatial resolution mapping). Moreover, microfabricated devices allow for the use of smaller sample volumes (microliters) as compared with the milliliter volumes used in traditional laboratory techniques, and lower overall power consumption.

TECHNIQUES AND APPLICATIONS

Table 2 gives examples of recent environmental applications of FI, which have been selected to provide representative coverage of analytes, FI techniques, and aquatic matrices. Further details of performance criteria for key groups of analytes (2000–2004) are given below.

Metals/Cations

The coupling of FI with ICP-MS has also proved valuable in the determination of trace elements in natural waters. Willie et al. (45), for example, used ICP-MS with FI on-line separation and preconcentration for the determination of Cu, Ni, Zn, Co, Pb, Cd, and Fe in seawater. On-line separation and removal of Ca, Na, and Mg was achieved by optimizing sample loading time, loading pH, selective pH washing of the iminodiacetate-base resin, and configuration of an extra valve in the FI system. These steps were necessary to minimize interferences and to permit calibration using the isotope dilution technique.

A novel way of exploiting FI/SI on-line ion exchange preconcentration for the detection of Ni(II) in environmental samples by ETAAS was described by Wang and Hansen in 2000 (46). This system (Figure 2) incorporated a renewable microcolumn (loaded with an SP Sephadex C-25 cation exchange resin) integrated within a micro FI system. Instead of eluting the retained analyte from the beads as is normally done, the authors devised a technique to transport the bead content directly into the graphite tube of the ETAAS, where the beads were pyrolysized and atomized. This novel technique eliminated the buildup of back pressure encountered in conventional ion exchange procedures. This system achieved a detection limit of 9 ng/L^{-1} with a sampling frequency of 12 h^{-1}.

Flow injection has also been very useful in the determination of dissolved mercury in environmental samples. Tseng et al. for example, developed a dissolved elemental mercury analyzer (DEMA) for use in natural waters (47). This analyzer used a novel on-line purge- and -trap system combining flow injection and dual gold amalgamation preconcentration together with cold vapor fluorescence detection. Both laboratory-based and shipboard determinations in the Long Island Sound were performed.

TABLE 2
Selected FI techniques (2000–2004) and performance data in relation to environmentally important analytes

Analyte	Matrix	Detection limit (unit as reported)	Technique/Detection method	Notes	Reference no.
Cd, Co, Cu, Fe, Ni, Pb, Zn	Seawater	Cd: 5.5 ng/L^{-1} Co: 0.1 ng/L^{-1} Cu: 3.0 ng/L^{-1} Fe: 11 ng/L^{-1} Ni: 11 ng/L^{-1} Pb: 1.0 ng/L^{-1} Zn: 12 ng/L^{-1}	FI-ICP-MS	On-line removal of Ca, Na, and Mg using iminodiacetate resin.	(45)
Ni(II)	River water and sediment	9 ng/L^{-1}	FIA/SIA with electrothermal atomic absorption spectrometry (ETAAS).	Renewable ion exchange microcolumn integrated into a micro FI-system.	(46)
Dissolved Hg	Freshwater, estuarine	0.23 pM	Shipboard FI chemical analyzer based on cold vapor atomic fluorescence detection.	On-line Au amalgamation preconcentration.	(47)
S^{2-}	River and industrial waters	0.15 mg/L^{-1}	Multisyinge FI system employing a minaturized optical fiber spectrophotometer	FI method based on the coupling of Fisher's reaction of sulfide with *N,N*-dimethyl-*p*-phynylenediamine in the presence of Fe(III).	(48)
Cl^{-}, NO^{3-}, SO^{4-}, HPO_4^{2-} K(I), Ca(II), Na(I), Mg(II)	Drainage water from a farm pasture	Range: 20 to 200 μg/L^{-1} for all ions.	FI-capillary electrophoresis (FI-CE) with contactless conductivity detection.	On-site determination with an automated FI-CE method.	(53)
PO_4^{3-}	Freshwater	0.67 μM	In situ FI system with diode array detection.	Automated FI system incorporating on-line tangential flow filtration.	(54)
$NO_3^{-} + NO_2^{-}$ Total S^{2-}	Seawater	0.5 μM 0.8 μM	Submersible FI chemical analyzer based on spectroscopic detection.	Measurements performed at depths of up to 1650 m at 22 analysis h^{-1}.	(55)
p-aminophenol	River and industrial waters	1.9×10^{-10} g mL^{-1}	FI luminol-dimethylsulfoxide-NaOH-EDTA chemiluminescence	No sample pretreatment required.	(57)

Cetylpyridinium chloride	Pond water, industrial water, and sewage	110 μg/L^{-1}	FI system employing spectrophotometric determination.	FI method based on the absorptivity of a Bi(III)-I^{-} complex in the presence of cationic surfactants.	(58)
Paraoxon, methyl parathion	Well water	Paraoxon (20 nM) Methyl parathion (20 nM)	FI amperometric enzyme biosensor.	Biosensor incorporating an immobilized enzyme reactor.	(59)
Dissolved organic carbon (DOC)	Fresh and seawater	0.8 mg C/L^{-1}	FI system with conductimetric detection.	UV photooxidation/peroxydisulfate digestion of DOC.	(60)
Chemical oxidation demand (COD)	Freshwater	0.5 mg COD/L^{-1}	Spectrophotometric detection of the resulting decrease in concentration of permanganate.	Low-power UV irradiation and permanganate oxidation of aquatic organic compounds.	(64)
Dissolved oxygen (DO)	Freshwater, seawater	4.9×10^{-7} mol/L^{-1}	Extraction FI with spectrofluorimetric detection.	Reaction of 2-thionaphthol with iodine liberated in Winkler's method utilized as the DO detection system.	(65)
Cd, Cu, Mn, Ni, Zn	Estuarine	Cd: 0.013 nM Cu: 0.27 nM Mn: 1.6 nM Ni: 0.48 nM Zn: 0.70 nM	FI coupled with inductively coupled mass spectrometry (ICP-MS).	On-line preconcentration using metal chelating resins.	(66)
Cd(II), Co(II), Pb(II), Ni(II), Zn(II)	Wastewater	Cd(II): 8.0×10^{-6} L^{-1} Co(II): 8.0×10^{-6} L^{-1} Ni(II): 4.0×10^{-6} L^{-1} Pb(II): 2.0×10^{-6} L^{-1} Zn(II): 4.0×10^{-6} L^{-1}	FI-CE with UV-Vis detection.	Separation of heavy metal ions by FI-CE using xylenol orange.	(67)
Fe(II) + Fe(III)	Sediment, freshwater	42 nM	FI with UV-Vis detection.	On-line preconcentration with oxine-derivatized Fractogel.	(68)
Fe(II)	Seawater	8–12 pM	Shipboard FI-based instrument with chemiluminescence detection.	Automated, real-time monitoring capabilities in a graphical programming environment.	(69)

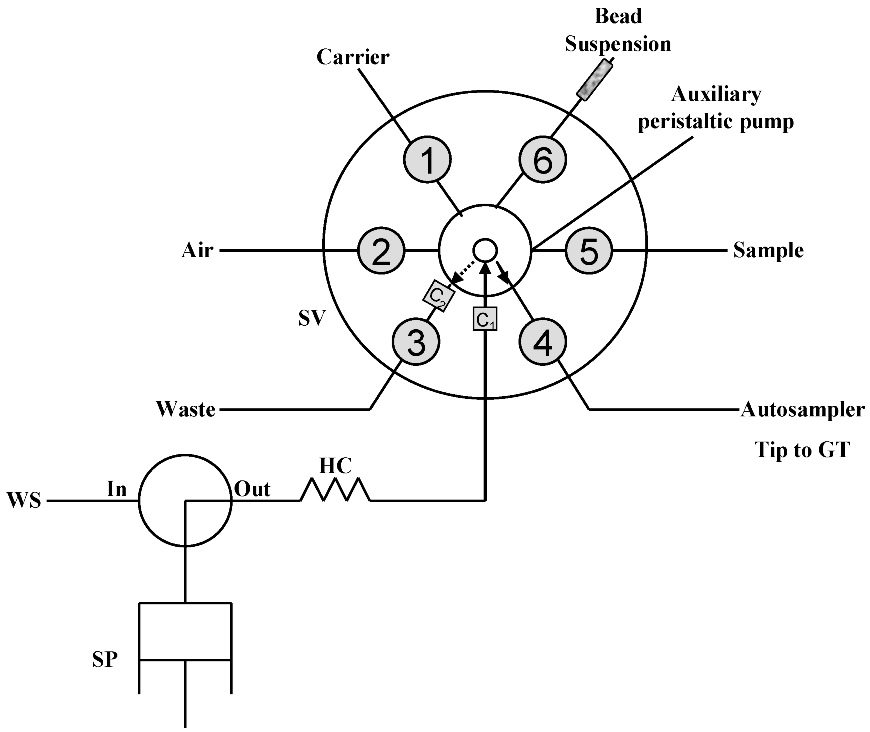

FIG. 2. The FI/SI manifold for sequential bead injection on-line ion exchange. SV, six-port selection valve; SP, syringe pump; HC, holding coil; C_1, C_2, microcolumns; GT, graphite tube in the ETAAS instrument. Modified with permission from Ref. (48).

Anions

A multisyringe FI method for the determination of sulfide in environmental and wastewaters was developed by Ferrer et al. (48). This novel, automated technique incorporated ancillary solenoid valves into the flow network allowing numerous injection modalities. This novel use of technology enabled high injection frequency with high sensitivity and excellent repeatability. Overall, this system achieved a detection limit of 0.15 mg/L^{-1} with a dynamic working range of 0.5 to 5.0 mg/L^{-1}.

The coupling of capillary electrophoresis (CE) with FI has resulted in enhanced separation techniques with advanced sample introduction and pretreatment capabilities (49–52). Kubáň et al., for example, performed on-site determinations of anions and cations ($Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}$ $K^+, Ca^{2+}, Na^+, Mg^{2+}$) in farm drainage water using flow injection-capillary electrophoresis (FI-CE) with contactless conductivity detection (53). This automated technique, using dual injection at both ends of the separation capillary, achieved detection limits between 20 and 200 $\mu g\ L^{-1}$ for all ions.

Nutrients

Flow injection has also been successfully used for the design and development of submersible and field-based systems. For example, a high temporal resolution FI field monitor for the determination of phosphate in riverine water was developed in 2001 (54). This monitor, shown schematically in Figure 3, incorporated solenoid, self-priming micropumps and solenoid operating switching valves for fluidic control and a miniature CCD spectrometer of full spectrum (200–1000 nm) acquisition. This unit operated in a graphical programming environment for full data acquisition and automotive control and incorporated an on-line tangential flow filtration unit to remove suspended particulate material and prevent blockage of the micropumps and valve. The system allowed high temporal resolution monitoring (every 30 min) with a detection limit of 0.67 $\mu M\ PO_4^{3-}$.

Le Bris et al. (2000) developed an in situ analyzer for the measurement of nitrate + nitrite (N + N) and total sulfide over hydrothermal vents (55). This system, based on FI with spectrophotometric detection, was installed on a remotely operated vehicle (ROV) and employed at depths of 1650 m. This analyzer achieved a rate of 22 analyses per h with 0.8 μM and 0.5 μM detection limits for total dissolved sulfide and (N + N), respectively.

A miniature continuous flow system for nitrate incorporating the novel use of osmotic pumps driven by a NaCl gradient was reported by Jannasch et al. (56).The method had a limit of detection of 0.1 μM, a linear range of 0.1 to 20 μM, a response time of 30 min, and low sample (12 $\mu L/\ h^{-1}$) and reagent (1 $\mu L\ h^{-1}$) consumption making it suitable for longer-term field deployments.

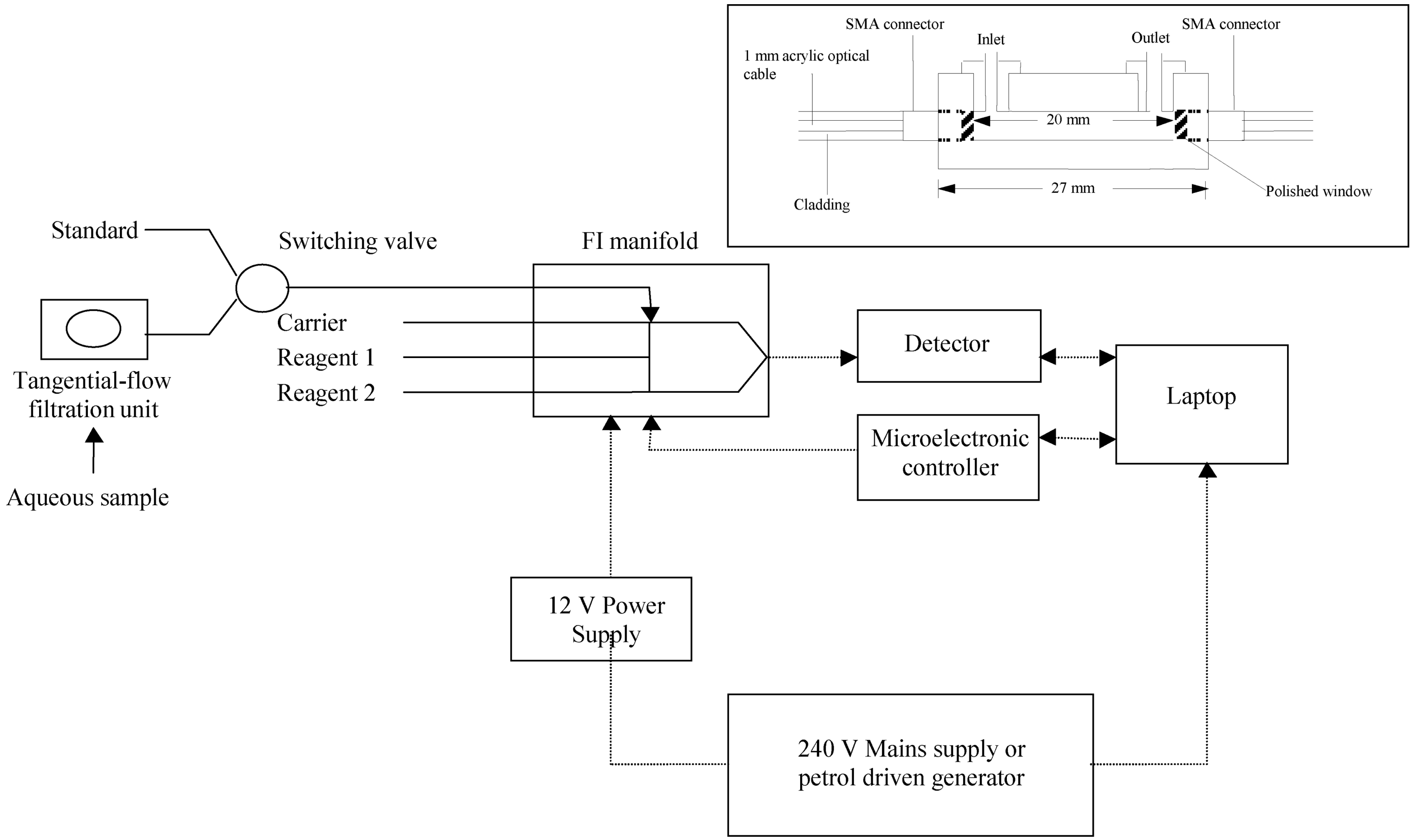

FIG. 3. Schematic diagram of the FI system for PO_4 determination with an insert showing the PVC flow cell incorporating 1-mm acrylic optical fiber cables. Modified with permission from Ref. (57).

Organic Species

Xu et al. developed an FI procedure for the determination of *p*-aminophenol (PAP) in industrial waters and river water (57). This procedure, based on the inhibition by PAP of the chemiluminescence from a luminol-dimethylsulfoxide (DMSO)-NaOH-EDTA system, achieved an overall detection limit of 1.9×10^{-10} g/mL^{-1} and was applied for PAP determination in the range of 2.5×10^{-10} to 5.0×10^{-8}.

Agrawal et al. developed an FI method for the determination of cationic surfactants (CSs) in pond water, industrial wastewater, and sewage runoff (58). This method was based on the absorptivity of a Bi(III)-I$^-$ complex in the presence of CSs with subsequent spectrophotometric detection. This system achieved a detection limit of 110 μg/L^{-1} for cetylpyridinium chloride (CPC) with a sample throughput of 140 h^{-1}.

An FI amperometric enzyme biosensor for the direct determination of organophosphate nerve agents in well water was developed in 2001 by Mulchandani et al. (59). This biosensor incorporated a novel immobilized enzyme reactor and an electrochemical flowthrough detector containing a carbon paste working electrode, a silver/silver chloride reference electrode, and stainless steel counter electrodes. The amperometric response of the biosensor was linear up to 140 μM with detection limits of 20 nM for both paraoxon and methyl parathion.

Increasing awareness about the importance of the dissolved organic carbon (DOC) pool and the associated organic fraction of many environmentally important elements has led to the development of several FI methods for the determination of DOC in aquatic systems. UV photooxidation coupled to peroxydisulfate digestion and FI conductimetric detection was used to determine DOC (60). The method had a reported linear range of 0 to 35 mg/C L^{-1}, an LOD of 0.8 mg/C L^{-1}, a sample throughput of 60 h^{-1} and was not affected by the presence of high concentrations of chloride ions. Flow injection coupled to a gas-liquid transfer microreactor, a turbidimetric spectrophotometer, and incorporating microwave digestion has also been used to determine DOC (61). A dynamic range of 20 to 800/mg C L^{-1} and a calculated LOD of 17/mg C L^{-1} was reported.

Generic Environmental Indices

Flow injection methods (62–64) have also been developed for the determination of chemical oxygen demand (COD) in aquatic systems. Dan et al. (64) reported the use of low-power UV irradiation and permanganate oxidation of aquatic organic compounds with spectrophotometric detection of the resulting decrease in permanganate concentration. The method had an LOD of 0.5 mg COD L^{-1} and a linear range of 0.5 to 50 mg COD L^{-1} and is suitable for in-situ deployment.

A further generic environmental indice, dissolved oxygen (DO), was determined by FI with fluorimetric detection. The system utilized the reaction of fluorescent 2-thionaphthol with iodine liberated in Winkler's method. The method was linear over the range 2×10^{-6} to 1.2×10^{-5} mol/L^{-1} iodine, had an LOD of 4.9×10^{-7} mol/L^{-1} with an RSD of less than 1% for a 6×10^{-6} mol/L^{-1} iodine standard ($n = 8$). The sample frequency was 18 h^{-1} (65).

FUTURE TRENDS

The drive toward "green chemistry" promotes techniques such as FI that are inherently low in reagent consumption, operate in a contained environment, and produce minimal waste. An increase in awareness of the synergistic impact of chemicals on the environment and of environmental legislation provides an impetus for the increased use of FI-based techniques to monitor the efficiency of industrial processes and minimize discharges. Flow injection techniques have some speciation capability (e.g., determination of Fe(II) and total Fe), but the influence of elemental speciation on, for example, bioavailability will drive the development of further FI methodologies with increased speciation capability.

A further important advance in environmental monitoring will be the development of FI-based multiparameter analyzers, enabling a suite of environmentally important species to be determined. In addition the recent trend toward miniaturization, the use of low-power detectors and increasingly sophisticated and adaptable software for instrument control coupled to data telemetry promotes the use of FI for in situ high-resolution monitoring. Not only would this provide considerable savings in costs and logistics, it would also lead to extended deployment in remote locations, especially when coupled to other technological advances (e.g., photovoltaics for power supply). These developments will play an important role in the elucidation of the biogeochemical cycles of environmentally relevant elements.

Flow injection is also suitable for determining generic environmental indices such as chemical oxygen demand. A significant challenge for the future will be to integrate FI with appropriate preconcentration and detection methodologies to allow for the direct determination of individual organic compounds and/or classes of organic compounds.

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