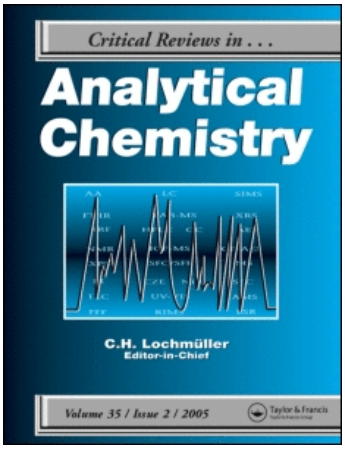

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Flow Injection Methods of Analysis for Waters. II. Organic Pollutants

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ABSTRACT: A comprehensive, critical and updated review for the applications of flow-injection analysis (FIA) techniques for the analysis of organic pollutants in several types of water samples, except marine waters, is presented. The methods of indirect determination of organic pollutants in water by using flow injection coupled with atomic absorption spectroscopy are also discussed.

KEY WORDS: flow-injection analysis, analysis of organic pollutants.

I. INTRODUCTION

In the first part of this review,[1] we briefly described the principles of FIA, the principal advantages of this technique, and the areas of its applications. Water analysis is one of the principal application of FIA. The main monographs related to FIA and the databases available on internet were also cited in the first part of this review. Over 10,000 papers devoted to FIA have been published up to now, and at most international analytical conferences there are special sections devoted to flow (injection) analysis. Moreover, there are many scientific meetings devoted to FIA of which "Flow Analysis" and "Conferences on Flow Injection Analysis" are the most recognized international venue.

In the first part of this review a comparison between FIA and sequential injection analysis (SIA) was made, presenting the advantages and disadvantages of each of these techniques. Multicommutation flow analysis, which is a novel approach of flow analysis together with automatic FIA equipment for water analysis, was also presented in the first part of this review. The application of FIA to water analysis has been reviewed by several authors.[2-12] However, there are few review papers regarding water analysis that are updated or comprehensive.

The present article selectively reviews the FIA application for the determination of organic species in water samples of all kinds except marine waters. We shall also present some methods regarding the indirect deter-

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mination of organic pollutants in waters by using flow injection coupled with atomic absorption spectrometry (AAS). The most important flow injection methods of analysis for organic substances in waters are presented in Table 1.

II. INDIRECT FLOW INJECTION METHODS FOR DETERMINATION OF ORGANIC POLLUTANTS IN WATERS BY AAS

An interesting approach for the determination of organic pollutants in waters is represented by indirect flow injection atomic absorption spectrometry.[13-15] It used nonchromatographic continuous separation methods. These methods are classified into three categories based on: liquid-liquid extraction, precipitation, and utilization of solid-phase reactors (solid-phase extraction, solid-phase chemical reaction, reactors that do not involve a chemical reaction).[16]

Indirect determination using AAS based on the formation of ion pairs between a charged analyte and a cationic or anionic metal chelate have been used by Valcarcel's group for the determination of anionic and cationic surfactants.[17,18] The ion pair formed by charged analyte and charged metal chelate was extracted into an imiscible organic solvent, and thus the atomic absorption signal of the tag element from the organic phase is proportional to the analyte concentration.

Galego et al.[17] developed an indirect AAS method for the determination of anorganic surfactants in waste waters by FI liquid-liquid extraction. The method involves the formation of the detergent-1,10-phenanthroline-copper(II) ion pair and extraction into methyl isobutyl ketone (MIBK). The concentration of anionic surfactants in the range 0.1 to 5.0 μg/mL was determined by measuring the copper in the separated organic layer. The method, reported to be highly selective, being free of interference of nonionic surfactants and a high precision of 0.8% RSD was achieved.

Martinez-Jimenez et al.[18] determined cationic surfactants in natural, tap, and waste waters indirectly by flame AAS. The method is based on the on-line extraction of the detergent-tetrathiocyanatocobaltate(II) ion-pair into IBMK. The surfactants were determined by the measurement of cobalt in the separated organic phase. A sampling frequency of 35 samples/hour was achieved with a precision of 1.2% RSD.

The indirect FI-AAS methods compare favorably with their batch counterparts and even surpass them in several respects such as the use of smaller samples and reagents volumes, higher sampling frequency, and higher sensitivity and precision arising from the less extensive sample manipulation required. The main drawback of indirect FI-AAS methods is the selectivity, in that it is difficult to achieve specificity in the reactions between the analyte (organic compound) and metal ions.

CONCLUSIONS

Flow injection methods of analysis have been used widely in the analysis of environmental parameters, and especially in water analysis. The potential and great capability of different FIA systems in water laboratories for organic substances analysis is demonstrated in this review. However, flow injection analysis was applied to a much lesser extent for the analysis of organic substances in waters than for inorganic species, as demonstrated by the number of published papers.

Nevertheless, it appears that flow injection analysis has taken a prominent place in routine water laboratories, where a widespread application of FIA methodologies is possible.

TABLE 1
Organic Species Determined Using FIA Procedures

Species	Sample Matrix	Detn. range	LOD	RSD (%)	Sampling Rate (h^{-1})	Detn. Method	Interferences	Other Features	Ref.
Oxalic acid	Waste waters	0.020-4.70 µg/mL	0.005 µg/mL	1.7 – 2.2		Spectrophotometric method based on analyte catalytic effect on redox reaction between dichromate and Brilliant cresyl blue	No serious interference		19
Chloroform	Water	ppm level		0.80	15	Fluorescence method based on Be-Schiff base complex formation between salicylaldehyde, etylenediamine and Be.		Reimer-Tiemann reaction used for obtaining salicylaldehyde	20
Formaldehyde	Drinking water	0.5-10 µM		3.0		Fluorimetric detection using immobilized formaldehyde dehydrogenase on tresylate poly(vinyl alc) packed into a stainless-steel column.		Analyte off-line preconc. on poly(allylamine) beads	21
Hydrazine	Water	30 ng/mL – 1.5 µg/mL	30 ng/mL			Immobilized formaldehyde dehydrogenase and Os(bpy) 2-poly(vinylpyridine) modified sceen-printed electrode as biosensor for hydrazine detn.			22
Hydrazine	Drinking water, river water	Three orders of magnitude	3.2 µg/mL			Nafion/Ru(III) modified glassy carbon electrod as amperometric sensor	Several interferents studied	Electrooxidn. of compds. in perchloric acid	23
Hydrazine	Boiler feed water	< 100 ppb	0.2 ppb	0.4 – 1.1		Spectrophotometric method using p-dimethylaminobenzaldehyde as reagent	Metal ions and ammonia not interfere	Carrier (H_2O) containing injected sample and reagent merged and reaction coil kept in an air bath at 80 °C.	24
Chloramine T	Waste water	< 65 µg/mL	0.5 µg/mL	2.8	220	Biamperometric detection of iodide/iodine ratio obtained by analyte oxidation of iodide to tri-iodine	Few foreign substances interfere		25
Phenolic compounds	Waters	0.01-0.5 mg/mL	20 ng/mL	<3.5	60	Cyclic voltammetric unit for potential scans connected to three-electrode cell		Resolution and selectivity improved by derivatizing current/potential recorgings	26
Phenolic compounds	Waters	0.05-15 mg/L 0.02-5 mg/L *	30 µg/L 12 µg/L*	2 3*	40-60	Spectrophotometric detn. using two different color reagents: 4-aminoantipyrine and 3-methyl-2-benzothiazoline hydrazone*		Comparison of two reagent	27

TABLE 1 (continued)

Species	Sample Matrix	Detn. range	LOD	RSD (%)	Sampling Rate (h^{-1})	Detn. Method	Interferences	Other Features	Ref.
Total phenolics	Waters	0.02-0.5 mg/L 0.02-500 mg/L* 0.005-200 mg/L**	8 µg/L 11 µg/L* 0.4 µg/L**	5 3**		Spectrophotometric detn. using 4-aminoantipyrine and involving in-line preconcn. by solvent extn., sorbent extn. with detection in eluent* and sorbent extn. optosensing**		Reaction product extracted into chloroform (solvent extn.), retained on C18-modified silica material (sorbent extn.)	28
Phenols	Waters	0.5-60 ng/mL	0.2 ng/mL		8	On-line preconcn. and separation on a commercially adsorbent column of Amberlite XAD-4 and spectrophotometric detection with 4-aminoantipyrine		Reaction product extracted in chloroform.	29
Phenol	Waters	0.1-2 µM	0.02 µM	0.8-3.5	20	Enzymatic procedure based on fluorescent detection of generated reaction product in presence of flow background signal and automated system	Cd(II); Pb(II); Ni(II0; Cu(II); Hg(II); nitrite and chloride	Detn. of phenol, catechol and ascorbic acid .	30
Phenol	Water	Trace lavel	5 µg/L	2.7-8	12	In-line liq.-liq. extn. and spectrophotometric deten.			31
Phenol	Waters	0.05-8 µg/mL	5 µg/mL	2.8	70	Biamperometric detn. based on bromination reaction		Sample injected into a carrier gas and merged with a acidic bromine stream	32
Phenols	Surface, drinking waters	0.05-1.0 mg/L	0.01 mg/L	<1.5	25	On-line preparation and detn. according to German std. Method DIN 38409-H16-2 applied to a flow injection system		Integration of an air segmented part in FIA system for steam distillation in order to interferences elimination	33
Phenol	Natural waters	1-50 mg/L	0.9 mg/L	1 - 4	5	Amperometric method using a glassy carbon electrode based on complete transfer of analyte from headspace of donor chamber of pervaporation unit through a membrane into a static solution in acceptor chamber			34
Phenols	Natural waters	<0.05 mg/L <0.08 mg/L*	5 ng/mL	0.5-1.4	12* 60	Analyte chemiluminometric detection with* and without preconcn. step on a column filled with Amberlite XAD-4 resin	Low interferences	FI-system with computer controlled solenoid valves for sample introduction	35
Phenols	Natural waters	0.5-30 µg/mL				Luminescent detn. based on extraction-chromatographic separation of analyte, back extraction into aqueous solution and chromatomembrane separation of aqueous and organic phases			36

Species	Sample Matrix	Detn. range	LOD	RSD (%)	Sampling Rate (h^{-1})	Detn. Method	Interferences	Other Features	Ref.
Phenols									
Chlorophenols	Waste waters	0.01-1 µg/mL	0.004 µg/mL	2.4	12	On-line preconcn. on Amberlite XAD-4 resin column and spectrophotometric detn. with 4-aminoantipyrine and potassium ferricyanide			37
Penta-chlorophenol	Tap water	0-200 ng/mL		2-4		Preconcn. on XAD-4 and multicomponent detn. using photodiode array detection, derivate spectrometry based on tetrabuthylammonium nitrate reaction		Data treatment using three different multivariate calibration methods	38
Penta-chlorophenol	Spiked drinking water	0.01-0.1 ppm	3.7 ppb			Amperometric detection with a glassy carbon electrode		Sample injected into carrier stream of Britton-Robinson buffer and methanol	39
Nitro-phenols (2-; 3-*; 4-** nitrophenols)	Waters		250 nM 25 nM*			Biosensor system using substrate recycling scheme comprising immobilized bilirubin oxidase in presence of excess of NADH and spectrophotometric detn. Detection limit improved using a fluorescent detector.		Results compared well with capillary zone electrophoresis.	40
Cetyltrimethyl-ammonium bromide (cationic surfactant)	Tap, ground watrs	0.4-4.6 mg/L 0.6-11.2 mg/L* 55.6-938 mg/L**	36.1µg/L 45.9 µg/L* 4.9 µg/L**	2-5.8	4	SIA sytem based on extn.-bak-extn. of analyte and a photodiode-array as detector. Extn. in butyl chloride in 1-octanoland retroextn. in NaOH	Minimization of other phenols interference by narrowing range of spectra wavelengths	Simultaneous detn. of several phenolic compd. using multicomponent techniques	41
Cationic surfactants	Natural waters	1-5 mg		2.8-3.2	11	On-line extraction of analyte-eosin red complex into benzene and fluorimetric detn.	Little interferences		42
Dodecyl-sulfate (anionic surfactant)	Waters			0.4-0.9	60	Liq.-liq. Extn. with chloroform after ino-pair formation with Orange II.			43
Anionic surfactants	Water	0.02-5.0 mg/L		3		Photometric detn. using a chromatomembrane cell for preconcn. and extraction of analyte-Methylene Blue complex.			44
Anionic surfactants	River water	0.04-3.5 µg/mL				Ion-pair extn. reaction with methylene blue in chloroform and spectrophotometric detn.		Time-base continuous sampling improved sensitivity	45
	River water		5 µg/L	0.9	20	Liq.-liq. extn and using of Methylene blue and 1,2-dichlorbenzene for spectrophotometric detn.			46

TABLE 1 (continued)

Species	Sample Matrix	Detn. range	LOD	RSD (%)	Sampling Rate (h^{-1})	Detn. Method	Interferences	Other Features	Ref.
Anionic surfactants	River, lake waters	$1x10^{-8}$ – $7.5x10^{-7}$ M		0.28		Solvent-extn. spectrophotometric method based on ion asociates formation with 4-(4-N,N-dimethylaminophenylazo)-2-methylquinoline and extn. into chloroform	Effect of several foreign ions studied.		47
Cetyl-pyridinium (anionic surfactant)	Waters	1.4-25 mg/L	0.22 mg/L	0.4	90	Spectrophotometric method based on ion associates formation with Methyl orange			48
Anionic surfactants	River, waste water	1-1000 µM	0.03 ppm	2		Preconcn. on Perplex column packed with Sep-Pak C18, LiChrolut EN or LiChrolut RP-18e and potentiometric detn. with plasticized PVC working electrode.	Chloride, nitrate and non-ionic surfactants not interfere	Working electrode contained quaternary ammonium salt of dodecylbenzene and Ag/AgCl reference electrode with K_2SO_4 salt bridge	49
Atrazine	Drinking water	0-10 ppb	0.1 ppb			Transparent aminosilanized indium tin oxide coated glass electrodes derivatized with aminodextran covalently modified with atrazine caproic acid used in an electroCL flow injection analyzer.		Antibodies to atrazine labeled with glucose oxidase and used in colorimetric enzyme linked immunosorbent assay	50
Atrazine	Tap, ground water	10-30 µg/L	0.7 µg/L	2-4	12	Oriented antibody covalently bound to Protein-A immobilized on controlled pore glass as fluoroimmunosensor	Little interferences	Analyte detected in-situ by placing immobilized antibody in optical path of flow cell	51
Atrazine	Natural waters	30 ng/L-1 µg/L				Automted quasi-continuous immuno sytem			52
Atarzine and Diuron	Waters	> 0.01µg/L				Immunochemical detection system based on FIIAA and on specific binding of esp. developed antibodies to analyte	Simazine interferes		53
Atrazine and Diuron	Water	0.02-0.5 µg/L				Computer contolled immunochemical system based on enzyme reaction carried out in an immunoafiinity column with Protein-A on polymetacrylate surface.	Monuron, atrazine and izoproturon decrease signal of Diuron		54
Triazine herbicides, atrazine, propazine	Waters	<0.1 µg/L				Automated quasi-continuous immunoanalysis system including a membrane reactor for exchange of used antibodies.		Analytes cross-react with polyclonal antiserum	55
Triazine herbicides	Drinking waters		0.1 µg/L			Time-resolved fluoroimmunoassay using Eu chelates as fluorescent labels		Pulsed laser as fluorescent detection in FIIA	56

Species	Sample Matrix	Detn. range	LOD	RSD (%)	Sampling Rate (h^{-1})	Detn. Method	Interferences	Other Features	Ref.
s-Triazine, (Desethyl-atrazine, Aziprotryne)	Environ-mental, tap water		0.3 μg/L 0.5 μg/L	2.7-6.3		Cyclic-voltammetry and amperometric methods using a metallic copper electrode and a glassy carbon electrode.			57
Triazine herbicides and their degradation products	Surface waters	0.05-1 μg/L 0.20-0.45 μg/L	0.05-0.15 μg/L	<10		Solid-phase extraction on C18 cartridge and eluate injection by means of FIA into source of tandem MS		Identification of compounds in suspected samples confirmed with a multiple reaction monitoring procedure	
Triazines	Surface waters		4-5 μg/L	<6		Extraction-preconc. cell consisting of a membrane separation module inserted in sample loop of injection valve and detection of analyte with a diode array spectrophotometer		Partial least squares regression method used for simultaneous detns. of both chloro- and methylthiotriazines	58
Simazine, Atrazine, Propazine	Waters	sub-μM levels				Electrochemical monitoring using stabilized system of filter-supported bilayer lipid membranes composed of egg phosphatidylcholine and dipalmitoylphosphatidic acid		Different times appearance of transient signal for each triazines allowed selective detection and analysis of analytes	59
2,4- dichloro-phenoxyacetic acid (2,4-D)	Waters	0.2-70 μg/L			5	Amperometric FIIA system based on immunoreactor with immobilized biocomponents on a silica surface			60
2,4- dichloro-phenoxyacetic acid (2,4-D)	Drinking water	<0.1 μg/L				Bienzyme substrate-recycling biosensor for sensitive detn. of alk. phosphatase and applied to fast readout of a competitive immunoassay for 2,4-D		Phenol-indicating biosensor consisting of a Clark-electrode covered by a membrane with coentrapped tyrosinase and quinoprotein glucose dehydrogenase	61
2,4- dichloro-phenoxyacetic acid (2,4-D)	Waters	4 μg/L – 160 mg/L	4 μg/L	12.5	3	Semi-automated CL competitive immunosensor based on anti-2,4-D polyclonal antibodies directly labeled with horseradish peroxidase allowing *p*-iodophenol CL detection		2,4-D co-injected with labeled antibodies in system, incubating solution with antigen immobilized membrane	62
2,4- dichloro-phenoxyacetic acid (2,4-D)	Environ-mental water	0.03-3 μg/L* 0.2-100 μg/L**	0.03 μg/L* 0.2 μg/L**			Two sensitive methods based on: monoclonal anti-2,4-D andibody (FIIA)* and a fiber optic immunosensor**		No preconc. or cleanup steps required in FIIA	63

TABLE 1 (continued)

Species	Sample Matrix	Detn. range	LOD	RSD (%)	Sampling Rate (h^{-1})	Detn. Method	Interferences	Other Features	Ref.
Chloro-phenoxy-acid herbicides	River water	Linear graphs over about two orders of magnitude	From 23 to 98 ng/mL	0.7-2.7		Photochemically induced fluorescence detn. based on two procedures: continuous or stopped-flow mode		PTFE tubing helically coiled around a low-pressure mercury lamp.	64
Isoproturon	Natural waters	µg/L levels				Fluoroimmunosensor consisting of a solid support containing immobilized antibody		Best performance obtained when used antibody permanently immobilized on CPG-Prot A	65
Diclorvos	Natural water	0.05-0.5 mM		3.2	3	Selective fluorimetric biosensing system based on inhibitory effect of analyte on acetylcholinesterase catalysis after pervaporation step of pesticide		Two-step derivatization reaction involving choline oxidase and horseradish peroxidase	66
Warfarin	Surface waters	< 2 µM	2 ppb* 10 ppb**	2.3		Fluorimetric sensor fabricated by packing commercial bound β-cyclodextrin material material into flow-cell.		Two procedures performed: continuous* and flow injection** mode	67
Fenvelerate	Tap water	2-10 µM	0.5 µM		30	Analyte photodegradation in micellar mediumby UV irradiation and fluorescent detn. of resulting products			68
Dimethyldithio-phosphate (DDTP)	Natural, potable waters		5 ppb	3		Indirect detn. by copling FIA with liq-liq extraction and AAS with hydride generation in organic phase		Reducing agent: $NaBH_4$ in DMFand glacial acetic acid; organic medium: IBMK	69
8 aromatic pesticides	Water	Linear graphs over about two orders of magnitude	From 0.02 ng to 22 ng	1.4-5.8	180	Fluorescence and photoinduced fluorescence detection			70
Paraoxon	Water	0.05-0.5 µg/L* 2-20 µg/L**	4.1* 1.2**	2* 20**		Spectrophotometric detn. based on inhibition of acetylcholinesterase immobilized on polymer carrier VA Epoxy Biosynth. Inhibition time: 30 min* and 3 min**		Enzymatic hydrolysis of acetylthiocholine iodide and reaction of resulted thiocholine with 5,5'-dithiobis(2-nitrobenzoic acid)	71
Organo-phosphate and carbamate pesticides	Tap water		From 1 ng/L to 4 µg/L		4	Biosensor consisting of a cartridge containing immobilized enzyme acetylcholinesterase and a photothermal detector based on thermal lens spectrometry			72
Thiabendazole (TBZ) and fuberidazole FBZ)	River, tap water	Linear graphs over about two orders of magnitude	0,07 ng/mL (TBZ) 0.1 ng/mL (FBZ)	0.5 (TBZ) 0.8 (FBZ)		Rapid, precise and sensitive fluorescent analysis method			73

Species	Sample Matrix	Detn. range	LOD	RSD (%)	Sampling Rate (h^{-1})	Detn. Method	Interferences	Other Features	Ref.
Oil (I-octane, cetane, benzene)	Water		0.1 µg/mL	2	15	On-line extn.-solvent and infrared detector with a quartz cell		1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane as solvent	74

FIA – flow injection analysis
SFA – Segmented flow analysis
FIIA – flow injection immunoanalysis
FIIAA – flow injection immunoaffinity analysis
Electrooxidn – electrooxidation
CL - chemiluminescence
ElectroCL – electrochemiluminescence
MS – mass spectrometry
AAS – atomic absorption spectrometry
Extn. – extraction
Concn. – concentration
Preconc. – preconcentration
Alc. – alcohol
Alk – alkaline
Compd. – compound
Detn. – determination
Std. – standard
Esp. – especial
Liq-liq – liquid-liquid

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