FLOW INJECTION ANALYSIS (FIA) TECHNIQUES FOR THE DETERMINATION OF INORGANICS IN MOLECULAR AND ATOMIC SPECTROMETRY

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1. INTRODUCTION

Flow injection belongs to a family of methods, based on simple injection into a flowing stream, which carries the analyte through a chemical modulator into a detector /1/. This broad spectrum of methods includes flow injection (FI) or flow injection analysis (FIA), chromatography, electrophoresis and field flow fractionation. These techniques differ in the function of the chemical modulator, which alters original square wave input, provided by sample injection into a fiagram, chromatogram, electrophoretogram or

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fractogram respectively. Whereas chromatographic techniques aim at a high resolution obtained through mega repetitive interactions which modulate the migration velocities of analytes through the system, flow injection exploits chemical reactions to transform analytes into species that can be selectively modified by a detector. Although FI is the youngest of the flow based techniques /2/, its applications have encompassed a full range of reagent assays from inorganic to enzymatic, from ions to proteins and from traces to highly concentrated analytes in aqueous or non-aqueous media.

Since its introduction, interest has been sustained in the use of FIA techniques due to the development of automated, online sample pretreatment procedures /3,4/. The advantages of preconcentration FIA techniques include high efficiency, simple online operation, low sample reagent consumption, relatively simple and compact hardware and freedom from contamination. FIA techniques offer improvement in efficiency and in automation of different separation and preconcentration processes /5/. Pretreatment steps performed using FIA are rapid and require less than 1 min for pretreatment and analysis including chemical conversions /6/. More interesting is the use of FIA to implement online derivatization reactions /7/, separation processes /8,9/, as well as a number of sample handling modes to fit the initial sample conditions and the most suitable single- and multidetection /10-12/ or implementation of flow through (bio)chemical sensors /13-15/ among others.

The growing interest in the use of FIA techniques was demonstrated in several reviews /16-26/ and in a recent book /27/. This article intends to provide an overview on the determination of inorganics by FIA described in literature since 1990. Various FIA procedures with a number of molecular and atomic spectrometric detection techniques for the determination of inorganics are classified into four types viz. (a) cations, (b) anions, (c) multi-element cations, (d) multielement anions. The salient features of these procedures are summarized in Tables 1-4 respectively.

2. APPLICATION TO FLOW INJECTION ANALYSIS OF INORGANICS

A. Determination of Cations

(a) *UV-Vis spectrophotometry*

FI-spectrophotometric procedures were described for the analysis of silver in mineral standards /29/, ammonium ion in sea water /77/, pH in lake water /66/, aluminum in tap water, tea leaves and flour /30/, cobalt in tobacco leaves and pyrite ore reference materials /45/. Further, cobalt /43/, molybdenum /75/, tin /110/ and titanium /116/ in steels, titanium in bauxite /115/ and uranium in standard ores /118/ were determined by FI spectrophotometry. A few FI-spectrometric procedures were developed for the sensitive determination of copper in water and plants /4/, rock samples /52/, Al alloys /55/, natural waters /56/, Cu based alloys and pig foods /57/, and palladium in anode slime and sludges /98,99/, metallurgical samples /101/ and ores /104/.

(b) *Flame AAS*

FI-flame AAS procedures were described for the sensitive determination of copper in potable water /53/ and bovine serum /54/ and lead in various waters /97/. FI-hydride generation AAS procedures were developed for the trace determination of tin in low alloy steels /111/ and lead in various water samples /95/. Mercury in zinc battery anodes and water samples /70/ was determined by cold vapour FI-AAS.

(c) *GF-AAS*

Sensitive FI-GF-AAS procedures were described (i) directly for the determination of lead in standard reference materials of sea and river water /85/, biological tissues and natural waters /91/, (ii) via hydride generation for the determination of tin in steel, sediment, orchard leaves and bovine liver /112/ and germanium in soil and Chinese herbal drugs /64/ and (iii) by carbonyl vaporization for the determination of nickel in water and grass /81/.

(d) *ICP-MS*

A FI-ICPMS procedure for the determination of lead in undiluted urines and standard reference urine samples /92/ was described during this period.

TABLE 1. Features of FIA determination of cations

Element	Detection method	Sample volume (μ l)	Sampling frequency (min^{-1})	Detection limit	Linear range	Other features	Ref.
Ag	AAS	-	-	4.6 nM	-	Precipitation	28
Ag	UV-Vis	35	-	3 μ M	10-400 μ M	Reaction with nickel cyanide	29
Al	UV-Vis	-	90	-	0-0.4 ppm	Stopped flow	30
Al	ICP-AES	-	-	2 $\mu\text{g/l}$	up to 200 $\mu\text{g/l}$	Amberlite x AD column	31
Au	FIA-AAS	-	45 48	5.2 ppm 2.3 ppm	-	Single column Dual column	32
Be	UV-Vis	-	-	20 ppb	0.04-2 ppm	-	33
Be	UV-Vis	-	-	0.1 ppm	1-300 ppm	-	34
Bi	FIA-AAS	200	300	0.17 ng	up to 50 ppb	Hydride generation (NaBH ₄)	35
C	IR	-	-	1.5 $\mu\text{g/L}$	4.5-770 $\mu\text{g/L}$	Converted C to CO ₂	36
Ca	AAS	-	12	0.25 ppm	-	Precipitation as oxalate	37
Ca	Fluorescence	250	50	-	3-7 ppm	Calcium as reagent	38
Cd	UV-Vis	-	-	-	up to 3.5 ppm	-	39
Cd	AAS	-	-	0.074 ppm	0.5-20 ppm	Coprecipitation on iron(III) hydroxide	40
Ce	UV-Vis	-	-	-	0.3-1.8 ppm	-	41

Co	UV-Vis	-	-	0.14 ppm	-	-	42
Co	UV-Vis	260	-	-	-	-	43
Co	UV-Vis	98	-	1 ppb	-	-	44
Co	UV-Vis	-	-	3.5 ppb	-	Alumina column	45
Cu	AAS	-	-	0.01 ppb	-	Precipitation	46
Cu	UV-Vis	-	-	0.04 ppm	up to 2 ppm	Extraction	47
Cu	UV-Vis	-	50	0.1 ppm	-	-	48
Cu	AAS	-	-	5 ppb	-	Acetate phosphate buffer	49
Cu	UV-Vis	200	300	50 ppm	50-1600 ppm	-	50
Cu	AAS	-	-	-	up to 2 ppb	-	51
Cu	UV-Vis	-	-	0.08 ppb	-	Ion-exchange, phase adsorption	52
Cu	AAS	-	180	7 ppb	up to 0.4 ppm	Extraction	53
Cu	AAS	800	100	-	0.5-2 ppm	-	54
Cu	UV-Vis	-	14	1.85 ppb	up to 120 ppb	-	55
Cu	UV-Vis	215	30	0.05 ppb	-	-	56
Cu	UV-Vis	250	20	0.42 ppm	up to 100 ppm	Extraction	57
Fe	UV-Vis	-	12	-	7.3-60.8 μ M	-	58
Fe	UV-Vis	-	-	0.2 μ M	up to 80 μ M	-	59
Fe	UV-Vis, Amperometry	-	-	-	-	-	60
Fe	UV-Vis	-	-	-	-	-	61

Table 1, continued

Element	Detection method	Sample volume (μ l)	Sampling frequency (min ⁻¹)	Detection limit	Linear range	Other features	Ref.
Fe	UV-Vis	-	-	-	up to 25 ppb	-	62
Fe	UV-Vis	24	20	-	up to 30 ppm	-	63
Ge	GF AAS	500	30	1.3 pg	-	Hydride generation	64
Ge	GF AAS	-	-	-	-	Hydride generation	65
H ⁺	UV-Vis	-	100	-	-	-	66
Hg	AFS	-	-	0.18 ppb	0.5-20 ppb	SnCl ₂ in 0.5 M H ₂ SO ₄	67
Hg	UV-Vis	125	-	-	2-40 ppb	-	68
Hg	AAS	-	-	-	-	Sn(II) & tetrafluoride	69
Hg	AFS	-	-	<0.01 ppb	up to 0.1 ppm	-	70
Ir	UV-Vis	-	61	0.02 ppb	0.05-0.4 ppm	-	71
K	Flame photo	-	-	2 ppb	-	-	72
Li	UV-Vis	-	-	0.1 μ M	-	-	73
Mg	AAS	-	-	-	50-250 μ g	-	74
Mo	UV-Vis	250	-	-	0.11-10 ppm	-	75
NH ₄ ⁺	pH-ISFET	-	-	0.05 mM	0.1-10 mM	-	76
NH ₄ ⁺	UV-Vis	200	-	-	up to 3 ppm	-	77

NH ₃	Piezoelectric	-	-	-	1 ppb - 1000 ppm	-	78
NH ₃	UV-Vis	-	0.15 µg	-	0.15-4 µg	-	79
NH ₃	UV-Vis	-	-	-	0.5-10 ppm	Nessler's reagent	80
Ni	GF AAS	-	0.18 pp.m	-	-	Carbonyl vaporization	81
O ₂	UV-Vis	-	-	-	0.009-8 ppm	-	82
O ₃	UV-Vis	200	3 pg/ml	-	0.1-100 ppb	-	83
O ₃	UV-Vis	100	3 ng/ml	-	4-100 ppb	-	84
Pb	GF AAS	-	3 ng/l	-	-	-	85
Pb	ICP-AES	10	-	-	-	-	86
Pb	UV-Vis	170	-	-	up to 4 µg	-	87
Pb	AAS	65	3 ng	-	-	-	88
Pb	AAS	-	-	-	-	Hydride generation	89
Pb	AAS	-	10 ppb	-	-	Ion exchange	90
Pb	GF AAS	-	2 pg/ml	-	-	ethylation	91
Pb	ICPMS	70	-	-	-	Urine samples	92
Pb	GFAAS	500	0.25 ng	-	-	-	93
Pb	UV-Vis	30	-	60	0.1-10 pp.m	-	94
Pb	AAS	500	0.2 ng	-	-	Hydride generation	95
Pb	GF AAS	20	75 ng/l	-	-	-	96
Pb	AAS	-	2.9 ppb	-	up to 300 ppb	-	97

Table 1, continued

Element	Detection method	Sample volume (μ l)	Sampling frequency (hr ⁻¹)	Detection limit	Linear range	Other features	Ref.
Pd	UV-Vis	-	-	-	0.08-0.72 ppm	-	98
Pd	UV-Vis	-	-	0.15 ppm	up to 8 ppm	-	99
Pd	UV-Vis	100	60	0.15 ppm	0.25-1.25 ppm	-	100
Pd	UV-Vis	100	90	0.05 ppm	0-8 ppm	-	101
Pd	UV-Vis	-	-	-	1-5 ppm	-	102
Pd	UV-Vis	50	240	-	2-12 ppm	Catalysts, alloys	103
Pd	UV-Vis	392	20	1 ppm	2-10 ppm	-	104
Pt	ICFMS	200	-	25 ng/L	-	-	105
Pt	UV-Vis	200	-	3 ppm	-	-	105
Fu	UV-Vis	20	50	5 ng/L	up to 0.12 ppm	-	107
Sb	AAS	-	-	-	-	Hydride generation	108
Sc	ICPAES	500	-	8.4 ppb	-	-	109
Sn	UV-Vis	-	-	-	up to 8 ppm	-	110
Sn	AAS	-	-	-	0.008-0.1%	Hydride generation	111
Sn	GFAAS	-	-	7 ng/L	-	Hydride generation	112

Sn	Amperometry	20	-	0.1 μ M	0.25-20 μ M	-	113
Te	Thermal lens detection	-	-	-	0.1-10 μ M	-	114
Ti	UV-Vis	-	-	25 ng	50 μ M-0.47 mM	-	115
Ti	UV-Vis	80	100	-	up to 0.1 μ g/g	-	116
Tl	AAS	-	-	-	-	-	117
U	UV-Vis	100	60	0.5 ppm	1-15 ppm	-	118
Zn	UV-Vis or Fluorimetry	-	-	-	-	-	119

TABLE 2. Features of FIA determination of anions

Species	Detection method	Sample volume (μl)	Sampling frequency (hr ⁻¹)	Detection limit	Linear range	Other features	Ref.
As(III)	AAS	-	-	8 ng/ml	40 ng to 0.5 μg/ml	Hydride generation	120
As(III)	ICPAES	-	-	5.2 μg/ml	-	Hydride generation	121
As(III)	GFAAS	-	-	-	-	Hydride generation	122
As(III)	UV-Vis	-	30	-	-	Hydride generation	123
As(III)	AAS	-	-	3.9 ng/ml	-	Hydride generation	125
As(III)	AAS	-	-	-	-	Hydride generation	125
As(III) & As(V)	AAS	-	10	0.25 μg/ml	up to 30 μg/ml	Hydride generation	126
As(III)	AAS	-	-	3 ng/l	-	Hydride generation	127
As(III), As(V)	AAS	-	-	0.4 μg/l	5-50 μg/l	Hydride generation	128
As(III)	ICPAES	-	-	50 ng/ml	up to 100 ppm	Hydride generation	129
As(III)	UV-Vis	-	15	-	-	Hydride generation	130
As(III)	PSA	100	-	-	-	-	131
B	UV-Vis	-	20	20 μg/l	up to 1.2 mg/ml	-	132

B	Conductometry	-	60	-	10 ppm - 16 mg/ml	-	133
Cl ⁻	UV-Vis	-	-	-	4.5 ppb - 2 ppm	-	134
Cl ⁻	Reflectance	-	-	-	up to 10 mM	-	135
CN ⁻	UV-Vis	100	-	-	<10 ppb	-	136
CN ⁻	Piezoelectric crystals	10	-	-	up to 2 ppm	-	137
CN ⁻	UV-Vis	50	160	-	10 ⁻⁷ 0 mM	-	138
CN ⁻	Fluorimetry	-	10,30,12 & 6' h	0.4, 5.0, 25 & 0.03 ppb	2.3-160, 17-200, 1-200 and 0.15-50ppb	-	139
CN ⁻	UV-Vis	50	-	0.1 ppm	0.6-4.3 ppm	-	140
CO ₃ ²⁻	UV-Vis	100	20	2.5 µM	0.1-0.27 mM	-	141
Cr(VI)	AAS	-	100	62 ppb	-	-	142
Cr(VI)	UV-Vis	-	45	0.01 & 0.5 ppm	0.02-1.0 ppm & 1-30 ppm	-	143
Cr(VI)	Reflectance	500	-	9 ppb	10-220 ppb	-	144
Cr(VI)	UV-Vis	300	-	0.005 ppm	up to 0.8 ppm	-	145
Cr(VI)	UV-Vis	-	-	-	0.09-1.74 µg Extraction chromatographic preconcentration	-	146

Table 2, continued

Species	Detection method	Sample volume (μ l)	Sampling frequency (min^{-1})	Detection limit	Linear range	Other features	Ref.
Cr(III) & Cr(VI)	AAS	-	-	-	-	Ion exchange	147
Cr(III) & Cr(VI)	AAS	-	30	0.02 ppb	0.2-200 ppb	Solid phase extraction	148
F ⁻	Fluorescence	-	40	0.05 ppm	0.15-10 ppm	-	149
F ⁻	UV-Vis	300	-	-	4-100ppb	-	150
I ⁻	UV-Vis	-	80	-	up to 1 ppm	-	151
I ⁻	UV-Vis	200	-	-	-	-	152
I ⁻	UV-Vis	-	90	0.2 ppb	-	-	153
I ⁻	ICP-AES	300	-	0.04 ppm	-	-	154
IO ₃ ⁻	UV-Vis	100	84	0.6 μ M	2-20 μ M	-	155
Mn(VII)	UV-Vis	250	-	0.91 ppm	0-25 ppm	-	156
Mn(VII)	UV-Vis	-	20	1.1 ppm	up to 40 ppm	-	157
Mn(VII)	UV-Vis	183	25	10 pg/ml	0.05-1 ppb	-	158
Mn(II)	AAS	-	-	0.076 ppm	-	-	159
MoO ₄ ²⁻	AAS	-	30	5 ppb	5-200 ppb	Solid phase extraction	160

NO_2^-	UV-Vis	-	72	46 ppb	0.07-0.46 ppm	-	161
NO_2^-	UV-Vis	-	60	9 ppb	-	-	162
NO_2^-	UV-Vis	75	-	2 ppb	1-5 ppb	-	163
NO_2^-	UV-Vis	120	83	0.018 ppm	0.05-1 ppm	-	164
PO_4^{3-}	UV-Vis	-	120	0.5 ppm	0-10 ppm	-	165
PO_4^{3-}	Fluorescence	500	-	0.343 ppb	0-80 ppb of P	-	166
PO_4^{3-}	FTIR	-	60	-	0.1-1 g/l	-	167
PO_4^{3-}	UV-Vis	-	-	0.6 ppb	1-50 ppb	-	168
ReO_4^-	UV-Vis	-	-	-	up to 1.5 ppm	-	169
S^{2-}	UV-Vis	100	90	0.01 mM	-	-	170
S^{2-}	UV-Vis	120	-	2 ng	40-200 ppb	-	171
S^{2-}	UV-Vis	190	20	0.25 ppm	0.25-25 ppm	-	172
Se(IV)	UV-Vis	-	-	-	-	-	173
Se(IV)	UV-Vis	250	-	8 ng/g	0.1-0.5 $\mu\text{g/g}$	-	174
Se(IV)	AAS	-	17	2.1 ppb	-	Hydride generation	175
$\text{Se(IV) \& Se(VI)}$	AAS	-	-	0.7 ppb of Se(IV) or Se(VI)	≤ 125 ppb	Hydride generation	176
Se(IV)	AAS	-	-	0.0001 $\mu\text{g/l}$	-	Hydride generation	177
Se(IV)	AAS	-	33	0.005 $\mu\text{g/l}$	0.01-0.3 ppb	Hydride generation	178
Se(IV)	ICP MS	200	-	1 pg	5-80 ng/l	Hydride generation	179
Se(IV)	UV-Vis	250	-	1 ppb	2.5-500 ppb	-	180

Table 2, continued

Species	Detection method	Sample volume (μ l)	Sampling frequency (min ⁻¹)	Detection limit	Linear range	Other features	Ref.
Si(IV)	UV-Vis	-	40	-	0.2-2 ppm	-	181
S(IV)	UV-Vis	100	60	2.3 ppb	-	-	182
SO ₄ ²⁻	UV-Vis	-	40	-	1-20 ppm	-	183
SO ₃ ²⁻	UV-Vis	-	-	-	0.1-5 μ M	-	184
SO ₄ ²⁻	UV-Vis	200	40	0.8 μ g	up to 120 μ g	-	185
SO ₃ ²⁻	UV-Vis	15	-	-	10 μ M - 0.7 mM	-	186
SO ₄ ²⁻	UV-Vis	500	-	1.7 ppm	up to 50 ppm	-	187
VO ₄ ³⁻	UV-Vis	100	60	40 ppb	0-10 ppm	-	188
V(V) & V(IV)	UV-Vis	-	-	-	2-20 μ M	-	189
V(V) & V(IV)	UV-Vis	-	-	-	-	-	190
VO ₄ ³⁻	UV-Vis	-	-	-	20-200 ppb	-	191

TABLE 3. Features of multielement FIA determination of cations

Elements/ species	Detection method	Sample volume (μ l)	Sampling frequency (min ⁻¹)	Detection limit	Linear range	Other features	Ref.
Ag, Co, Ni & Cu	UV-Vis	-	-	0.5-8 μ M	5-240 μ M, 1-50 μ M, 25-200 μ M 4-200 μ M	-	192
Al & Mn or Al & Fe(III)	UV-Vis	-	32	-	-	-	193
B, Cu, Mo, W & Zn	DCP-OES	600	100	21,14,28,120 & 20p.pb	up to 500 ppb	-	194
Ca & Mg	UV-Vis	-	15	-	up to 30 ppm	-	195
Cd, Co, Cu & Pb	ICP-AES	-	10-12	-	-	-	196
Cd, Cr, Cu, Mg & Zn	ICPAES	500	-	-	-	-	197
Cd, Cu & Zn	AAS	-	-	7, 40 & 6 ppb	-	-	198
Cd, Cu & Pb	AAS	-	-	1.9, 8.5 & 27 ng	-	-	199
Cd, Cr, Fe, Mn, Ni, V, Ca, Co, Cu, Mg & Zn	ICPAES	-	-	-	-	-	200
Cd, Cu, Pb & Au	AAS	-	-	-	-	-	201
Cd, Cu, Pb & Ni	GFAAS	-	-	0.6, 8.5, 21 & 4 ng/l	-	Sorbent extraction	202

Table 3, continued

Elements/ species	Detection method	Sample volume (μl)	Sampling frequency (min ⁻¹)	Detection limit	Linear range	Other features	Ref.
Cd, Cu, Mn & Zn	AES	-	-	1.8-3.6 ppb	0.01-20 ppb	Online column preconcentration	203
Cd, Cu & Pb	AAS	-	-	0.8, 1.4 and 10 ppb	-	-	204
Cd, Co, Cu, Mn, Ni, Pb & Zn	AAS	-	40	-	-	-	205
Cd, Co & Ni	UV-Vis	-	-	-	0.4-30 ppm for Co & Ni and 0.5-50 ppm for Cd	-	205
Cd, Cu, Mg, Zn, Pb & Hg	AAS	-	-	0.5-25 ppb	0-100, 100-1000, 20-220, 10-10, 10-300 & 20-2000 ppb	-	207
Co & Fe	UV-Vis	-	-	0.33 & 0.045 μg/ml	1.2-2.5 & 0.15-6 ppm	-	208
Cu, Cd & Pb	AAS	-	30	1.2, 0.6 & 3.0 ppb	0-40, 0.6-15 and 3-40 ppb	Sorbent extraction	209
Cu & Au	AAS	-	-	1 and 0.08 ppb	-	-	210
Cu & Fe	UV-Vis	-	-	-	0.4 to 100ppb & 0.1-4 ppm	-	211

Cu & Fe	AAS	-	-	1 & 1.8ppb	-	-	212
Cu, Mn, Fe & Pb	ICPAES	-	-	0.54-11.34 ng	-	-	213
Fe Co, Ni, Mn & Zn	AAS	-	30	5, 1, 1, 0.7 & 0.2 ppb	0.5-50 ppb	Solid phase extraction	214
Fe & Ti	UV-Vis	-	-	-	-	-	215
Fe & Ti	UV-Vis	-	25	-	-	-	216
Fe(II), Fe(III) & Ti(IV)	UV-Vis	-	-	-	up to 70, 70 & 7 ppm	-	217
Fe, Ti & V	UV-Vis	-	-	12, 20 & 18 ppb	up to 2.2, 3.1 and 1.8 ppm	-	218
Fe(II) & V(IV)	UV-Vis	-	-	0.012 & 0.018 ppm	up to 1.2 & 1.8 ppm	-	219
Fe(III) & Al(III)	UV-Vis	-	-	-	15-30 µg/25 ml	-	220
Hg(II) & Ag(I)	UV-Vis	-	-	0.5 & 1 ppb	0.75 & 0-64 ppb	-	221
Lanthanides	UV-Vis	-	-	-	-	-	222
Sm & Eu	Fluorescence	-	60	-	-	-	223
La, Pr, Nd, Er, Tm & Y	UV-Vis	-	-	-	-	-	224
Lu, Sm, Tb, Pr & Ho	ICPAES	-	-	-	-	-	225
Lanthanides	UV-Vis	-	80-100	0.43 ppm	-	-	226
Mg & Zn	UV-Vis	-	-	-	-	-	227
Mg & Zn	AAS	-	-	20 ppb Mg & 100 ppb Zn	20-200 ppb Mg & 100-500 ppb Zn	-	228

Table 3, continued

Elements/ species	Detection method	Sample volume (μ l)	Sampling frequency (min ⁻¹)	Detection limit	Linear range	Other features	Ref.
Mo & W	ICP-AES	-	-	15 & 65 ppb	-	-	229
Mo & V	UV-Vis	-	33	-	0.76-28.8 & 0.3-9.1 ppm	-	230
Mo & W	UV-Vis	-	-	40 & 60 nM	0.2-3.2 μ M	-	231
Mo, W & Ti	UV-Vis	40	1:8	-	0.05-0.35, 0.25-1 & 0.025-0.3 ppm	-	232
Na & K	UV-Vis	-	12	-	up to 0.5 mM & 80 μ M	-	233
Na, K, Mg & Ca	AAS	40-50	70	-	-	-	234
Ni, Co & Mn	GFAAS	20	-	0.07	up to 4 ppb	Sorbent extraction	235
Ni & Fe	UV-Vis	-	-	-	-	-	236
Pb, V & Cu	UV-Vis	-	-	-	-	-	237
Pb, Cd & Mn	UV-Vis	-	-	1.9, 1.5 & 4.8 ppb	up to 150, 150 & 300 ppb	-	238
Pd, Au & Ag	UV-Vis	-	-	-	0.1-2, 0.3-4.5 & 2-19 ppm	-	239
Pd, Pt & Ge	ICPMS	-	-	0.2-1.0 ppb	-	-	240
Pf & Rh	UV-Vis	392.4	-	-	2-10 ppm	-	241

Pt & Pd	UV-Vis	-	-	-	10-800 & 10-200 ppm	-	242
Ti, Mo & W	UV-Vis	40	-	-	0.05-0.35, 0.025-0.3 & 0.25-1 ppm	-	243
Tl, Pb & Bi	ICPMS	-	-	1.4 & 7 ppb	-	-	244
U & Th	ICPMS	-	-	0.2 ng/g	-	-	245
U(IV) & Fe(II)	UV-Vis	20	-	0.024 & 0.008 ppm	-	-	246
V(V) & Ti(IV)	UV-Vis	120	75	-	up to 2 mM V and 3.5 mM Ti	-	247
Zn & Cd	AAS	-	-	1 ppb	-	-	248
Zn, Cd	Fluorescence	-	-	0.05 & 0.05 μM	-	-	249
Zn, Cu & Ca	AAS	130	-	-	-	-	250
Zn & Cd	UV-Vis	-	-	-	0.6 μg/g of Zn & 1.0 μg/g of Cd	-	251
Zn & Cd	AFS	-	-	-	0.22-1.22 ppb	Hydride generation	252
Multielement mixture (51 elements)	ICPMS	-	-	-	15% H ₃ PO ₄ , 16% NaNO ₃ & 6% Na ₂ PCl ₃ solutions	-	253
Multielement mixture (70 elements)	DC-AOES	-	-	-	-	-	254

TABLE 4. Features of multielement FIA determination of anions

Elements/ Species	Detection method	Sample volume (μ l)	Sampling frequency (hr^{-1})	Detection limit	Linear range	Other features	Ref.
As, Sb, Bi, Se	AAS	-	-	-	-	Hydride generation	255
As, Se, Mo, S & Cr	ICPAES	-	-	13, 252, 2.04, 6.19 & 3.64 ppb	-	Anion exchange preconcentration	256
As, Hg, Se, Sb, Sn & Bi	GF AAS	-	-	-	-	Hydride generation	257
As, Sb, Bi, Hg, Se & Te	AFS	-	-	0.02-0.2 ppb	up to 300 ppb	Hydride generation	258
As, Sb & Se	ICPAES	-	-	1, 2.2 & 1.3 ppb	-	Hydride generation	259
As & Se	AAS	-	-	10-20 pg/ml	-	Hydride generation & Cold trap collection	260
As & Se	AAS	-	-	10-20 pg/ml	-	Hydride generation & Cold trap collection	261
Cl^- & Br^-	UV-Vis	60	100	5.5 & 10 μ M	28 μ M - 0.85 mM Cl^-	-	262
Cl^- & CO_3^{2-}	AAS	-	-	0.3-0.5 μ M	0.5-16 & 1-14 μ M	Preconcentration by precipitation as AgCl & CaCO_3	263
Cl^- , Br^- & I^-	MPAES	-	60	0.12, 0.04 & 0.23 ppm	0.5-500, 0.2-50 & 1-500	-	264

Chlorine & Chloramine	UV-Vis	-	-	0.05 ppm for chlorine	0.1-10 ppm for chlorine	-	255
CN ⁻ & SCN ⁻	Fluorimetry	-	-	-	0-50 μ M CN ⁻ & 0-40 μ M SCN ⁻	-	256
CN ⁻ & SCN ⁻	AAS	-	-	3 & 1 μ M	up to 0.17 mM & 0.14 mM	-	217
CN ⁻ & S ²⁻	UV-Vis	-	-	0.2 & 0.4 ppm	-	-	268
CO ₃ ²⁻ & Cr ₂ O ₇ ²⁻ & C ₂ O ₄ ²⁻	AAS	-	-	1-8 μ M	0.01-0.22 mM	-	269
C ₂ O ₄ ²⁻ , MoO ₄ ²⁻ & Fe ³⁺	Potentiometry	-	-	-	-	-	270
I ⁻ & IO ₃ ⁻	UV-Vis	-	30	0.5 μ M & 5 μ M	10-10 μ M & 0.5-1.3 μ M	-	271
I ⁻ & NO ₂ ⁻	UV-Vis	-	-	-	20-160 & 0.4-10 μ M	-	272
NO ₂ ⁻ & NO ₃ ⁻	UV-Vis	-	-	-	0.01-2.2 & 0.1-3.5 ppm	-	273
NO ₂ ⁻ & NO ₃ ⁻	UV-Vis	80	-	1.6 & 3.1 μ M	up to 400 mM	-	274
Selenate	ICFMS	-	-	200 pg/ml	-	-	275
SiO ₃ ²⁻ & PO ₄ ³⁻	UV-Vis	-	-	-	0.01-2 ppm & up to 2.5 ppm	-	276
SiO ₃ ²⁻ & PO ₄ ³⁻	UV-Vis	-	-	0.05 & 0.8 ppm	0.05-2.5 & 0.8-15 ppm	-	277

(e) Miscellaneous

Spectrofluorimetric /38/ and pH ISFET /76/ detectors were used in combination with FI for the online determination of calcium and ammonia respectively.

B. Determination of Anions

(a) UV-Visible spectrophotometry

FI-UV-Vis spectrophotometric procedures were developed for the determination of cyanide /136,140/, chromium /145,143/, fluoride /149/, manganese /157/, nitrite /161,162/, silicate /181,182/, sulphide /171/, total phosphorus /168/ in various water samples. Trace amounts of boron in eye lotion and sea water /132/, sulphite in lemon juice /185/, nitrite in wine /159/, arsenic in soil /130/, selenium in lobster /173/ and hair, Cu^{2+} and Fe^{3+} /174/, iodide in tablets, table salt and animal feed /150/ and vanadium in peanut, rice and wheat flour /191/ were determined by using FI-spectrophotometry. Manganese in Cu, Ni alloy /155/ and steel and alloys /156/, selenium in ores and personal care products /180/ and cyanide in mineral leach liquors were determined by sensitive FI-spectrophotometric procedures.

(b) AAS

Sensitive FI-AAS procedures were developed for the determination of manganese in hair, surface water and traditional Chinese medicines /158/ and molybdenum in sea water and sediments /160/. Two speciative procedures were developed for the simultaneous determination of chromium(VI) and chromium(III) in various water samples and sediments /148/ and selenium(IV) and selenium(VI) via hydride generation in sea water /176/ using a FI-AAS technique.

(c) ICP-AES

A FI-ICPAES procedure was described for the determination of iodide in cooking salt /153/.

(d) *ICP-MS*

A FI-ICPMS procedure was developed for the ultratrace determination of selenium via hydride generation in estuarine water samples /179/.

(e) *Miscellaneous*

Flow injection coupled to fluorescent /148/ and FTIR /166/ detectors were described during this period for trace determination of fluoride and phosphate, which find application in their determination in river water and soft drinks respectively.

C. Determination of Multielement Cations

(a) *UV-Visible spectrophotometry*

Simultaneous FI-spectrophotometric procedures were developed for the determination of zinc and cadmium /251/, calcium and magnesium /197/, cobalt and iron /208/, copper and iron /211/, sodium and potassium /233/, mercury and silver /221/, and iron(II) and vanadium(IV) /219/ in various water samples. The determination of aluminum and manganese /193/ aluminum and iron /193/ and calcium and magnesium /193/ in soil extracts and sedimentary rocks, Co, Ni and Cd in catalysts /206/, molybdenum and vanadium in steels, pharmaceuticals and petroleum products /230/, lead, cadmium and manganese in rice flour samples /238/, U(IV) and Fe(II) in Sc_2O_3 , phosphate ore and thorium nitrate /246/ and Mo and W in minerals /231/ was described by various authors, using FI-spectrophotometric techniques based on a variety of chromogenic reagents.

(b) *Flame AAS*

FI-flame AAS procedures were described for the simultaneous determination of Cu, Cd and Pb /209/ and Fe, Co, Ni, Mn and Zn /214/ in sea water and marine sediments, Cu, Cd and Pb in urine /201/ and digests of environmental, biological and industrial materials /204/ and copper and gold in standard ores /210/.

(c) *GF-AAS*

A FI online sorbent extraction GF-AAS procedure was described for the determination of Cu, Cd, Pb and Ni in sea, estuarine and river waters /202/.

(d) ICP-AES

Multielement determination of rare earths in mixed rare earth samples was described by Shen *et al.* /225/ by using flow injection ICPAES.

(e) ICP-MS

Flow injection coupled to ICP-MS procedures was developed for the determination of thallium, lead and bismuth in nickel based alloys /244/ and uranium and thorium in aluminum samples /245/.

D. Determination of Multielement Anions

(a) UV-Vis spectrophotometry

FI-spectrophotometric procedures were described for the simultaneous determination of free chlorine and chloramine in natural and drinking water /265/, silicate and phosphate in natural waters /277/ and power plant water /276/ and nitrite and nitrate in atmospheric aerosol filter extracts and waste water /274/.

(b) AAS

Hydride generation AAS (FI or CF) methods were described for the simultaneous determination of arsenic and selenium in environment materials /260/ and CRM's of water, liver, citrus and tomato leaf /261/.

(c) ICP-AES

An online flow injection anion exchange preconcentration and ICP-AES procedures is described for the simultaneous determination of arsenic, selenium, molybdenum, sulphur and chromium and is utilized for the analysis of standards for geological samples, hair and bovine liver /256/.

3. CONCLUSIONS

Flow injection UV-visible spectrophotometry was widely used for the determination of inorganics during the last decade. However, as pointed out by us recently /278/, only a few FI-spectrophotometric procedures are based on ternary complex formation. The coming years should see the development

of such procedures in addition to development of more and more FI-spectrophotometric procedures for the determination of multielement cationic and anionic species.

Another technique that has attracted a great deal of attention is FI-AAS. Unfortunately, most of these procedures are applied only to various water samples. In the next few years, it is expected that FI-AAS procedures will be developed for the multielement determination of cationic and anionic species present in complex matrices.

In spite of the great potentiality of ICP-AES and ICP-MS techniques, relatively few procedures were developed for the determination of inorganics in conjunction with flow injection. The future lies in the multielement analysis of inorganic species by using flow injection – ICP-AES and ICP-MS techniques and their application to determine these species when they are present in complex matrices.

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