

preconcentrated on microcolumn with Chelex-100, whereas in the second one preconcentration and ethylation of organotin species was carried out on a microcolumn with C18 sorbent.

Incorporation of a separation column in the flow system between the injection valve and the detector, and then acquisition of signals corresponding to several analytes, is a typical arrangement of the column chromatographic setup. Regardless of the size of a column, used pressure or flow rate, such a system should not be considered as a flow injection system, which sometimes can be found in the literature. Such systems are low pressure liquid chromatography systems with post-column reaction detection. They were developed, for instance, for determination of inorganic polyphosphates [291], for speciation of dissolved organic and inorganic phosphorus in environmental samples [292], for simultaneous determination of silicon and phosphorus in biological standards [293], and for determination of silicate, phosphate and arsenate [294]. Sodium and potassium were separated on a column packed with silica gel as complexes with crown ether [295]. Cobalt(II) preconcentrated on a chelating column is then separated from the excess of Mn(II) and Fe(III) on a strongly acidification resin, but chromatographic signals for both Co(II) and Mn(II) are recorded [296].

## 2. Detection in the Ultraviolet Region

Absorption in the UV region (185–400 nm) generally results from the excitation of  $\pi$ ,  $\alpha$  and non-bonding electrons to higher energy levels. Absorbing compounds containing these electrons mostly include organic molecules, but also some inorganic ions, e.g. nitrite, nitrate, azide or carbonate. Spectrophotometric measurements in the so-called vacuum ultraviolet ( $\lambda < 185$  nm) are much more difficult, because components of the atmosphere absorb strongly in this region, and so it is not used for analytical purposes. The instrumentation for measurements in the visible and UV ranges differs in the sources of radiation used and materials for cuvettes. Deuterium or hydrogen lamps are the most common UV radiation sources, while the cuvettes used are made of quartz, fused silica or certain polymeric materials that pass UV radiation.

The similarity between the detection processes in the visible and UV regions means that their applications in FIA involve the same instrumental designs, measuring procedures and interpretation of experimental data. The majority of the applications reported involve procedures which use conventional UV/VIS

spectrophotometers with flow-through cuvettes or commercial HPLC detectors. Developed flow injection procedures are based either on the direct absorption of UV radiation by the analyte or on the indirect measurement of the absorption by a product of a reaction involving the analyte. Several applications using diode array detection in the UV region for multicomponent determinations have been reported.

A direct determination of nitrate at 210–220 nm has been reported in a simple, single component system [298], as well as in a computer-controlled multichannel system, together with the spectrophotometric determination of chloride and ammonium ions [158]. In order to remove interfering organic impurities, on-line filtration is used [298]. A direct measurement of the absorbance of the chloro-complex of iron(III) at 335 nm has been employed for the determination of total iron in silicate rocks [299], and some benzodiazepines in pharmaceuticals [300]. Additional on-line solvent extraction is needed in the direct determination of bittering compounds in beer [301], while phenols and some neutral compounds can be determined using extraction with a silicon rubber membrane [302]. Matrix correction has been employed in the direct determination of ascorbic acid in soft drinks and pharmaceuticals [303]. Following a direct measurement at 245 nm, a second measurement is carried out after the decomposition of a fraction of the analyte with sodium hydroxide. The reduction in signal provides the analytical information. A similar procedure has been used in the determination of thiamine (vitamin B1) with the decomposition of the analyte carried out by on-line UV photodegradation [304].

Indirect determinations may involve the measurement of the absorbance of a product formed by a reaction of the analyte or of the decrease in the absorbance of a UV-absorbing substrate, which reacts with the analyte. Examples of the first type are the determinations of Cu(II) as a diethanolodithiocarbamate chelate [305], sulphate as  $\text{FeSO}_4^+$  ion (with the effective removal of organic interferences on a charcoal column) [306], and boron, through the detection of chromotropic acid complexes [307]. The slow reaction occurring in the last example requires the use of a reactor consisting of 10 m of packed tubing connected in series with 3 m of open tubing. This allows a sample residence time of 7 min with a dispersion coefficient of about 2. Iodide can be determined by UV-FIA spectrophotometry by direct oxidation to iodine, but if iodide is first oxidised (with bromine water) to iodate, which in turn is reduced to iodine, the sensitivity of the determination can be increased six-fold [308]. In the determination of nitrite, the product of the reaction with

5,7-dihydroxy-4-imino-2-oxochroman is first extracted on-line with a mixed solvent prior to UV detection [309].

In several FIA systems with UV detection, a decrease in the absorbance of a chromophore as a result of its reaction with the analyte is measured. Sulphur dioxide can be determined by its reaction with pyridine bromide perbromide [310]. Determinations of ascorbic acid have been based on the reduction of tri-iodide ion [311] and vanadotungstophosphoric acid [312]. The reaction of water with  $\text{SnCl}_4$  or  $\text{SbCl}_5$  has been utilised for trace water determination in non-polar organic solvents such as benzene, 1,2-dichloroethane and n-hexane [313]. The maximum absorption of  $\text{Ce(IV)}$  is found at 320 nm. A procedure for determining chemical oxygen demand has been developed in an FIA system with a 20 m reaction tube of 0.5 mm i.d. [314]. This method gives much better detectability than FIA methods with visible spectrophotometric detection using dichromate [78] or permanganate [315].

A decrease in  $\text{Ce(IV)}$  absorbance has been utilised in the indirect catalytic determination of thiocyanate and iodide [316] using the redox reaction between cerium(IV) and arsenic(III), in a system with a double injection valve. Another catalytic FIA system with UV detection has been reported for the trace determination of Mo in manganese process solutions, based on its catalytic effect on the peroxide-iodide reaction [317]. The matrix problem in this system is minimised using a high concentration  $\text{Mn(II)}$  solution for both carrier and sample, but with a small, on-line anion exchange column to remove the molybdate in the carrier.

Diode array detectors can be used in FIA UV spectrophotometry to enhance the selectivity of a single analyte determination or for multicomponent determinations. An example of the first type of application is the previously mentioned multiwavelength detection of teniposide in blood plasma, with advanced multivariate data analysis based on partial least squares modelling [276]. Multicomponent determination has been developed for mixtures of up to four active components of pharmaceutical formulations [318], mixtures of nitrophenylhydrazines [319] and priority pollutant chlorophenols [320]. It has been shown that as the complexity of the mixture increases, third-derivative spectra generally give better results [318]. The determination of hydrazines is carried out in a 1 mm optical path length flow cell packed with C18-bonded silica, which gives a very low detection limit [319]. In a determination of chlorophenols, the analytes are first preconcentrated off-line in an XAD-4 adsorbent resin. The FIA determination is preceded by on-line extraction of

ion-pairs of the chlorophenols with tetrabutylammonium ion into chloroform [320]. More details about these determinations can be found in Table 4.

Table 4. Applications of spectrophotometric UV detection in FIA systems.

Analyte	Species absorbing UV radiation	$\lambda$ , nm	Concentration range	Reference
Ascorbic acid	Ascorbic acid	245	0.2–50 ppm	303
	Tri-iodide ion	350	0.1–40 ppm	311
	Vanadotungstophosphoric acid	360	1–80 ppm	312
B	Chromotropic acid complexes	361.6	0.008–6 ppm	307
Chemical oxygen demand	Ce(IV)	320	0.5–130 ppm	314
Chlorophenols	Analytes	200–430*	60–200 ppb**	320
Clotiazepam	Clotiazepam	260, 390	6–500 $\mu$ M	300
Cu(II)	Diethanolodithiocarbamate	385	1–20 ppm	305
Doxylamine, etafedrine, phenylephrine, theophylline	Analytes	200–300*	4–125 $\mu$ M	318
Fe	Chloro-complex of Fe(III)	335	10–60 ppm	299
Iodide	Tri-iodide ion	351	0.05–15 ppm	308
Iodide, thiocyanate	Ce(IV)	254	0.1–1.0 ppm	316
Mo	Tri-iodide ion	350	7–100 ppb	317
Nitrate	Nitrate	210	0.1–40 ppm	298, 158
Nitrite	Product of reaction with oxochroman	361	5–280 ppb	309
Nitrophenylhydrazines	Analytes	300–500*	0.5–50 $\mu$ M	319
Sulphate	FeSO <sub>4</sub> <sup>+</sup>	355	10–600 ppm	306
Sulphur dioxide	Pyridium bromide perbromide	300	25–140 ppm	310
Teniposide	Teniposide	200–400*	1–25 ppm	276
Thiamine	Thiamine	264	1.2–30 ppm	304
Triazolam	Triazolam	228	3–55 $\mu$ M	300
Water	SnCl <sub>4</sub> or SnCl <sub>5</sub>	300 or 350–420	1–100 ppm	313

\*with diode array detector

\*\*with preconcentration