

Table 5. Applications of spectrophotometric infrared detection in FIA.

Analyte	Detection limit	Reference
Aliphatic esters	14 mM	330
Allyldiisopropylamine oxide		332
Benzene	0.02% v/v	327
<i>tert</i> -Butyl ether	0.035% v/v	328
Carbaryl	1.6 ppm	325
Choline compounds	0.02 pg/l	331
Ethanol	0.02% v/v	333
Ibuprofen	80 ppm	324
Phenyl isocyanate	4 ppm	322
Silicate	0.5 $\mu$ M (Si)	321
Toluene	0.01% v/v	329
<i>o</i> -Xylene	0.02% v/v	323

Various procedures using FTIR detection have been employed in the determination of toluene in gasoline [329]. In the simplest one, the determination is based on measurements of the absorbance at  $728\text{ cm}^{-1}$ , the position of the most intense band due to toluene, using a base-line established between  $835$  and  $575\text{ cm}^{-1}$ . The determination can also be based on first-derivative spectra to avoid matrix interferences. FIA-FTIR procedures have also been developed for the determination of several other components in gasoline, such as *o*-xylene [323], benzene [327] and *tert*-butyl ether [328]. In the determination of benzene, a rapid quality control procedure has been developed, based on the on-line injection of gasoline samples into a carrier stream of a solution of benzene in hexane. Samples with a benzene content higher than the upper limit provide positive peaks, so any gasoline product with an unfavourably high content can be easily rejected.

A technique for the introduction of volatilised compounds into an FTIR gas cell has also been developed [333]. A liquid sample is injected into an electrically heated glass reactor where vapour phases are generated and then transported by carrier gas into a temperature-stabilised detector of 100 ml volume. This method has been applied in the determination of ethanol in chloroform. Examples of other applications are shown in Table 5.

#### 4. Turbidimetric Detection

Turbidimetric and nephelometric detection methods are based on the scattering of radiation by a solution containing solid particles. The intensity of

radiation observed at a particular angle in such a medium depends on the number of particles, their size and shape, and the wavelength of the radiation. Turbidimetric detection is based on the measurement of the attenuation of the power of a light beam as a result of scattering by solid particles. A relationship analogous to Lambert–Beer’s law applies:

$$\log(P_0/P) = kbc, \quad (4)$$

where  $k = 2.303 \tau/c$ ,  $\tau$  is the turbidity coefficient,  $P_0$  and  $P$  are respectively the power of the light beam before and after passing through a layer of turbid solution of thickness  $b$ , and  $c$  is the concentration of solid particles. Nephelometric methods are based on the measurement of scattered radiation, usually at right angles to the incident light beam. In FIA systems, however, turbidimetric detection has only been used with simple photometers or spectrophotometers equipped with flow-through cuvettes. The value of the turbidity coefficient depends on the wavelength according to  $\tau = s\lambda^{-t}$ , where  $s$  is constant for a given system, and  $t$  is a constant dependent on particle size. Very frequently an ordinary white light is utilised in turbidimetric measurements.

Most of the turbidimetric FIA procedures reported in the literature have been developed for the determination of sulphate, which is difficult to determine with other detection methods. These determinations are based on the precipitation of barium sulphate [256, 334–339] or lead sulphate [340, 341]. Examples of these and several other applications are listed in Table 6.

These determinations are usually carried out in conventional spectrophotometric flow cuvettes or flow cells, with light-emitting diodes as radiation sources [335]. The sheath flow optical cell used for the turbidimetric measurement of  $\text{BaSO}_4$  is shown in Fig. 6A. The light source is one arm of a bifurcated

Table 6. Applications of turbidimetric detection in FIA.

Analyte	Detected precipitate	Concentration range	Reference
Amitriptyline	Amitriptyline-bromocresol purple	30–200 ppm	344
Ammonia	$\text{NH}_{n-1}\text{Hg}_2\text{L}_n$	0.5–6.0 ppm (N)	342
Sulphate	$\text{BaSO}_4$	20–140 ppm	334
		50–200 ppm	336, 337, 339
		1–200 ppm	338
		0.25–20 mM	256
		0.3–20 ppm	340
Total sulphur	$\text{PbSO}_4$	5–25 ppm (S)	341

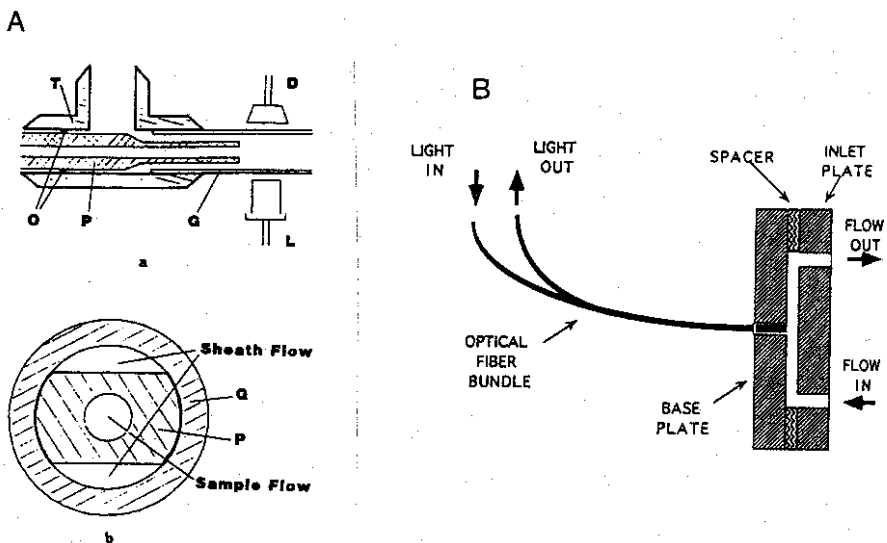


Fig. 6. Flow-through cells used in FIA systems with (A) turbidimetric detection [256] and (B) using light reflectance of the precipitate formed [343]. In A: a — longitudinal cross section; b — radial cross section; D — detector; L — light source; G — glass tube; O — o-ring; T — T-connector; P — Teflon tube. (Reprinted by permission of copyright owner.)

fibre optic and the source arm is connected to a miniature tungsten lamp. Such a cell can be operated over day-long periods with no indication of a rise in the baseline indicative of precipitate deposition on the optical window. In other developed procedures, polyvinyl alcohol [334, 335, 338] or gelatine [336, 337, 339] has been added to the carrier solution in order to reduce the accumulation of the precipitate on the walls of the cuvette and tubings. This can also be achieved by periodic rinsing of the FIA system with alkaline EDTA solution, or by injection of EDTA solution between sample injections [336, 337]. System performance can be improved by alternate pumping of the reagent stream and an alkaline EDTA solution at a high flow rate [338]. Another reported approach is based on the use of a reversed FIA system with continuous sample aspiration and alternating injections of barium reagent or alkaline solutions (Fig. 7A).

A filtration unit with activated carbon paper is incorporated into the conduits of the sampling line before the peristaltic pump. In another reported procedure, strongly acidic sulphate sample solutions are injected into the alkaline carrier solution containing barium and EDTA [335]. The decrease

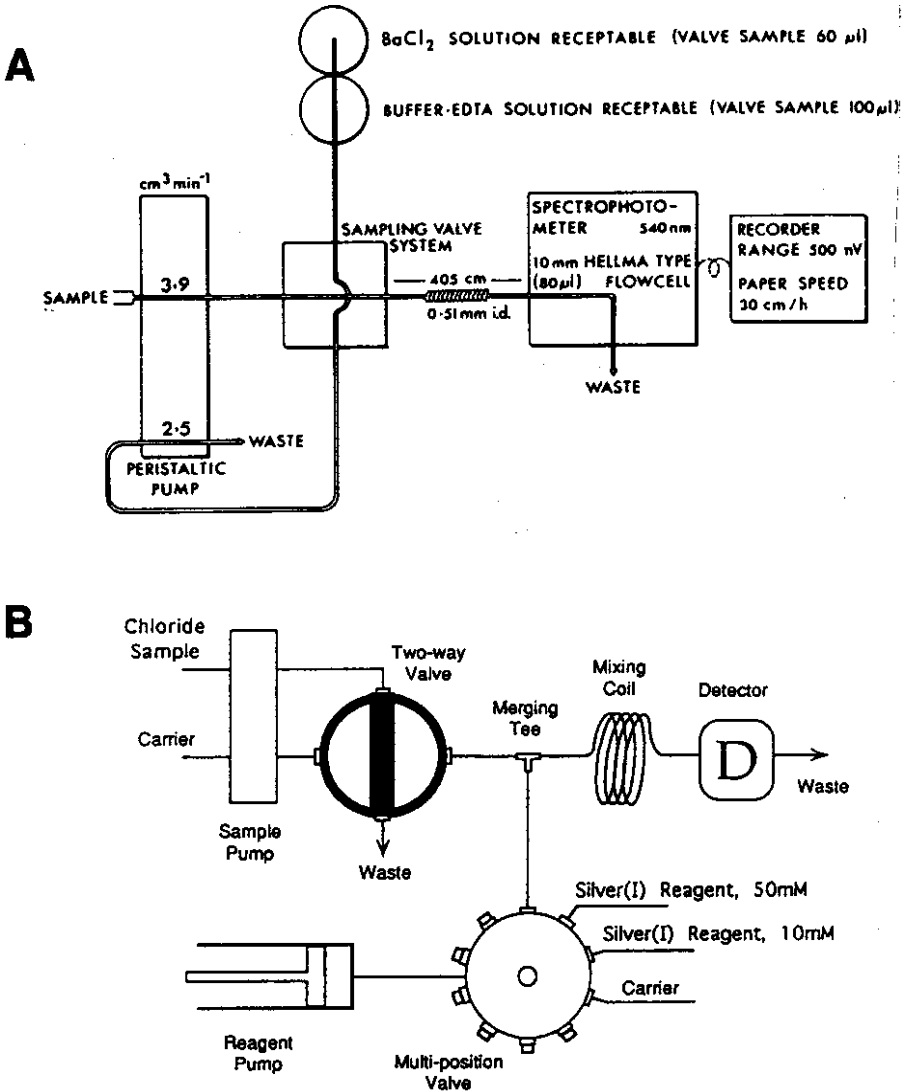


Fig. 7. Schematic diagrams of (A) a reversed FIA system with turbidimetric detection of sulphate [339] and (B) an FIA system for chloride determination using the light reflectance of the precipitate formed [343]. (Reprinted by permission of copyright owner.)

in pH within the sample segment is sufficient for precipitation of  $\text{BaSO}_4$  at simultaneous continuous rinsing of the flow system with EDTA.

In FIA turbidimetry, satisfactory results have also been obtained for the precipitation of colloidal  $\text{PbSO}_4$  in the determination of sulphate [340] and  $\text{NH}_{n-1}\text{Hg}_2\text{I}_n$  in the determination of ammonia [342].

The addition of an on-line-produced suspension of lead phosphate has been used to improve the rate of crystal growth in a turbidimetric FIA system for the determination of total sulphur by lead sulphate precipitation [341]. This accelerates the turbidimetric process, permits the use of more dilute reagents, and enables more efficient system washing.

In the determination of chloride by precipitation as silver chloride in the system shown in Fig. 7B, light reflectance by the precipitate is used as the method of detection instead of turbidimetry [343]. The flow cell used for this purpose is shown in Fig. 6B. Such an approach generally increases the dynamic range of detection when compared with turbidimetry.

## 5. Molecular Luminescence Detection Methods

The use of luminescence detection techniques in chemical analysis is based on the formation from the analyte, or with participation of the analyte, of an excited species whose emission spectrum provides analytical information. If the excited state species are formed by the absorption of photons, the subsequent emission of radiation is called *fluorescence*, or more generally *photoluminescence*, for a wide range of electronic transitions. Analytical detection based on fluorescence is called *fluorimetry*. If excited species that emit radiation are formed chemically, the process of emission is described as *chemiluminescence*. In both cases, the emitted radiation allows analytical detection at levels that are one to three orders of magnitude smaller than those usually obtained in molecular absorption spectroscopy. The number of developed conventional methods using fluorescence is much larger than for those using chemiluminescent procedures. Both of these luminescent detection methods usually exhibit a much wider range of response and better selectivity than by absorption detection. Instrumentation for luminescent detection, including flow measurements, is widely available, so these techniques are finding an increasing number of applications in FIA [345].

### 5.1. *Fluorimetric Detection*

A molecule excited by the absorption of photons can return to its ground state by various deactivation steps, one of which is fluorescence, where the