

3. Infrared Detection

Absorption in the infrared (IR) region can be used for the detection of molecules that exhibit small energy differences between various vibrational and rotational states. A molecule with an oscillating dipole moment as a consequence of its vibrational or rotational motion may absorb IR radiation with a wavelength ranging from 0.78 to 15 μm . When the frequency of the radiation matches a natural frequency of vibration of the molecule, a net transfer of energy takes place, resulting in a change of the amplitude of the molecular vibration, and absorption of the radiation. With few exceptions, practically all molecular species exhibit infrared absorption. IR spectroscopy is used mostly for the identification of organic compounds from absorption bands in the middle region of wavelengths from 2.5 to 25 μm . IR measurements are also finding increasing use in quantitative analysis, although they differ from UV/VIS measurements because of the greater complexity of the spectra, the narrowness of the absorption bands and the limitations of infrared instruments. The most common analytical applications are being developed for the analysis of mixtures of organic compounds of a similar structure, as well as mixtures of gases, such as in the analysis of air contaminants. When especially high resolution measurements are required, as in the determination of components in mixtures, or when fast scanning is needed in flow or chromatographic determinations, Fourier transform (FTIR) instruments are very useful.

Infrared detection is finding an increasing number of applications in FIA systems. In the simplest case, near-infrared detection is employed in the determination of reactive silicate by the formation of molybdenum blue [321]. A high output infrared LED with a maximum output at 886 nm is used as the radiation source. Dilution of the reductant solution with the sample in the developed procedure has proved to be an effective way to match the refractive indices of the carrier stream and the injected solution. Most IR applications in FIA have been developed for the middle IR spectral region, using FTIR instruments. A variable-filter IR spectrometer has been used for the determination of phenyl thiocyanate, based on absorption by the $\text{N}=\text{C}=\text{O}$ functionality [322]. Flow cells with KBr windows have been used in FIA FTIR determinations with organic solvents [323–329], while a cell with a zinc selenide window has been used with aqueous solutions [330, 331]. In the monitoring of the decomposition of allyldiisopropylamine oxide in an FIA system, a high pressure flow cell was used when a supercritical carbon dioxide was used as the carrier [332]. Sample volumes in such determinations usually range from 100 to 300 μl .

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 μ 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 cm^{-1} , the position of the most intense band due to toluene, using a base-line established between 835 and 575 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