Analytical Science

A course (in 15 Chapters) developed as an Open Educational Resource, designed for use at 2nd year UK & Wales undergraduate level and as a CPD training resource

Author	Brian W Woodget
Owner	Royal Society of Chemistry
Title	Chapter 14 – Introduction to Automation and Process Analysis
Classification	F180, Analytical Chemistry
Keywords	ukoer, sfsoer, oer, open educational resources, metadata, analytical science, cpd training resource, analytical chemistry, measurement science, off-line, at-line, on-line, in-line, sampling systems, performance characteristics of analytical techniques, flow injection analysis, fia, process gc, process ir, process ms, process uv/visible.
Description	This chapter looks at how important analytical technologies have been developed for use in chemical process situations. It also considers laboratory automation particularly the technique of 'Flow Injection Analysis'.
Creative Commons licence	http://creativecommons.org/licenses/by-nc-nd/2.0/uk/
Language	English
File size	1.83 Mbytes
File format	Microsoft PowerPoint (1997 – 2003)

RSC | Advancing the Chemical Sciences

Chapter 13 – Introduction to automation and process analysis

Contents

Introduction

Industry (chemical, pharmaceutical, manufacturing, food, water) has always required the use of measurement techniques to assess whether the processes are working efficiently and effectively. Traditionally, samples were removed from the process and taken to a remote laboratory for subsequent analysis. As can be imagined this would require some time for some chemical information to be determined and the result acted upon, all of which could lead to a loss of production and be economically unfavourable.

Figure 14.1 - examples of products and processes from industry

Therefore over the past 30 years more and more analytical chemistry is being done outside the laboratory and in the production environment where the data obtained can be used to make decisions and control processes.

The term often used for this is **process analytical chemistry or PAC**. PAC is the tailoring of laboratory-based analytical techniques to allow their direct use in the manufacturing environment.

A range of different analysis approaches are available. It is possible to describe analytical measurements that are either **invasive** or **non-invasive**.

An **invasive** approach has the potential to modify the sample by insertion of a probe, side stream etc. A **non-invasive** approach on the other hand does not introduce a measurement device in to the process stream.

The analytical approaches to process analysis are generally considered under four group headings:

- Off line;
- At line;
- On line;
- In line.

These different approaches to process analysis are described in the following four slides.

Off-line

This is the traditional approach of taking a representative sample and sending it to the laboratory for analysis. Elsewhere in this Analytical Science unit you will find descriptions of all of the various analytical techniques that can be used in this manner. This is not process analytical chemistry but provides the baseline information by which any automated or remote analysis is judged.

Figure 14.2 – automated laboratory analysis for components in milk – example of off-line analysis

At-line

This is the interim area between PAC and the laboratory. In this approach samples are taken manually from the process, for the analytical measurement to be made close-by [Figure (14.3)]. In this case, the analytical techniques used, require straight-forward operating procedures, minimal interpretation and provide rapid data with minimal instrumental maintenance. This is because, the measurements are often taken by non-analytical scientists, whose primary function is to supervise the process. At-line analysis can be useful if the process being monitored does not change significantly with time.

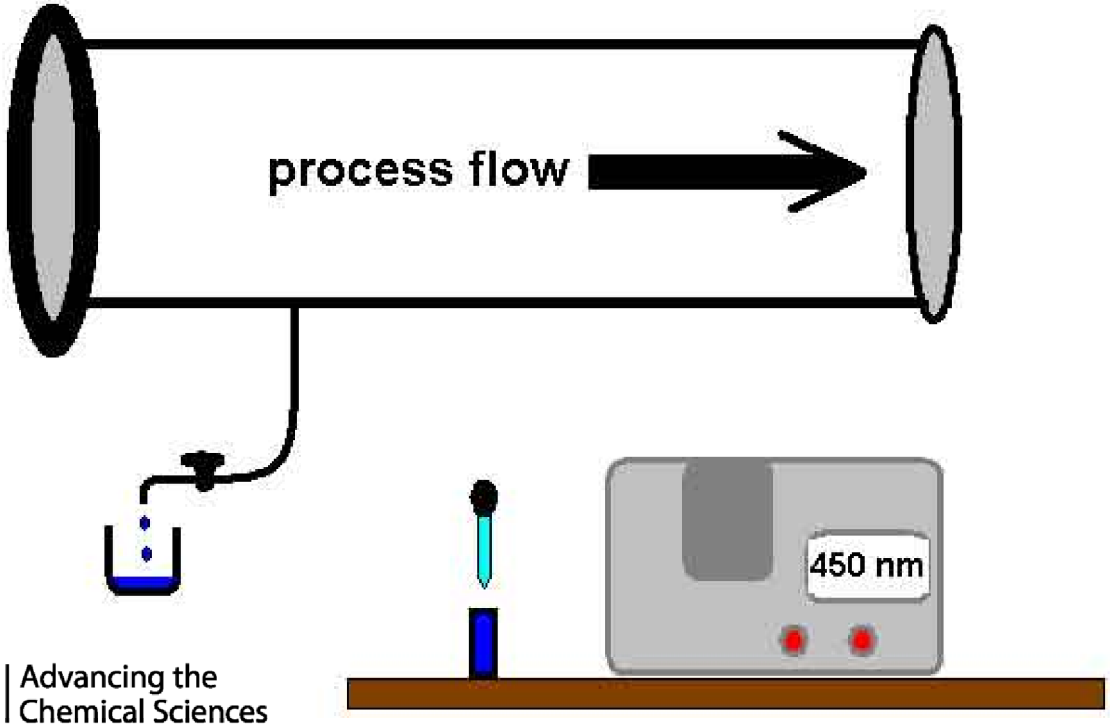


Figure 14.3 - at-line measurement using UV/Visible spectroscopy

On-line

This includes any analytical technique that is directly coupled to the process stream. In order for the on-line description to be used, the sample needs to be withdrawn from the process stream by the analytical instrument. In Figure (14.4) a portion of the sample is withdrawn from the process flow from a side stream and goes directly to the analyzer via connective tubing in which the flow is controlled by a pump. The use of the pump allows a controlled flow of sample to be delivered to the Analyzer. This approach also allows the side stream to be closed off should the Analyzer require maintenance. The disadvantage of the use of a side stream is that they are (a) prone to blockages, and (b) its content needs to be representative of the main process flow.

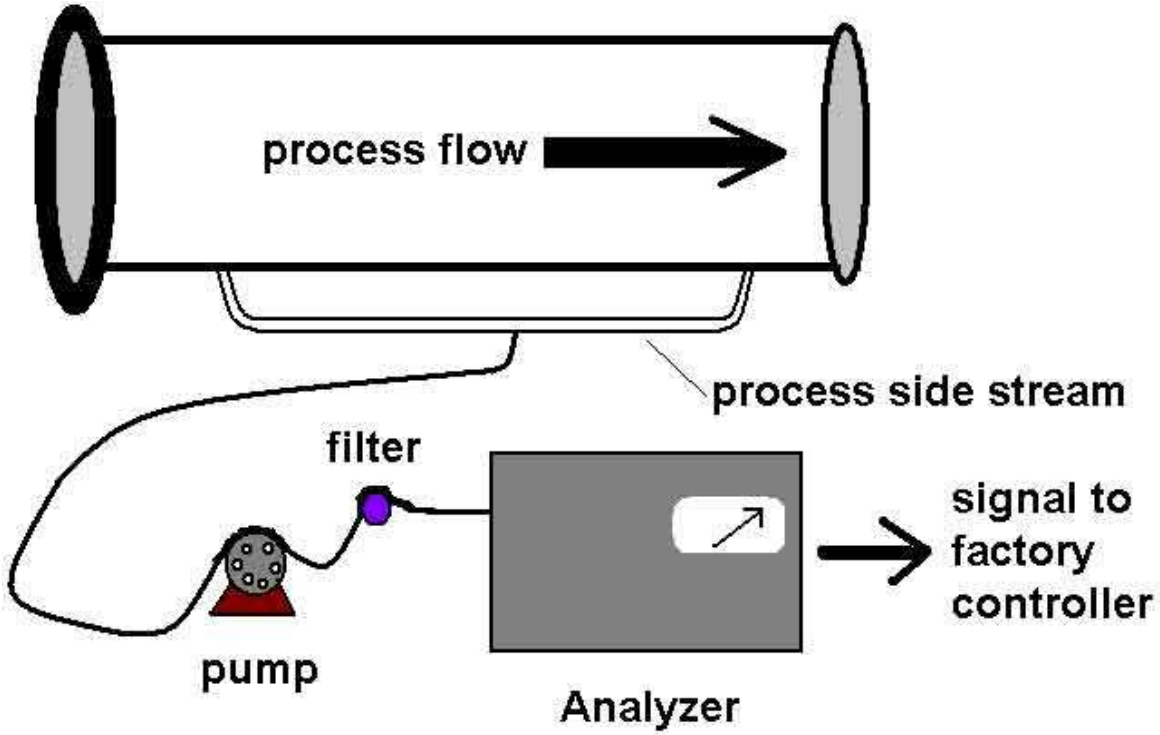


Figure 14.4 - on-line measurement using an Analyzer

In-line

In this approach the measurement is taken directly from within the process flow stream i.e. no sample is withdrawn from the process stream [Figure (14.5)]. The main advantage of this approach is the nil requirement for additional pipe work, valves etc. However, the main disadvantage is the requirement to shut down the process stream in order to allow maintenance and/or replacement of the in-line analyzer. This disadvantage is sometimes negated via the use of special insertion valves.

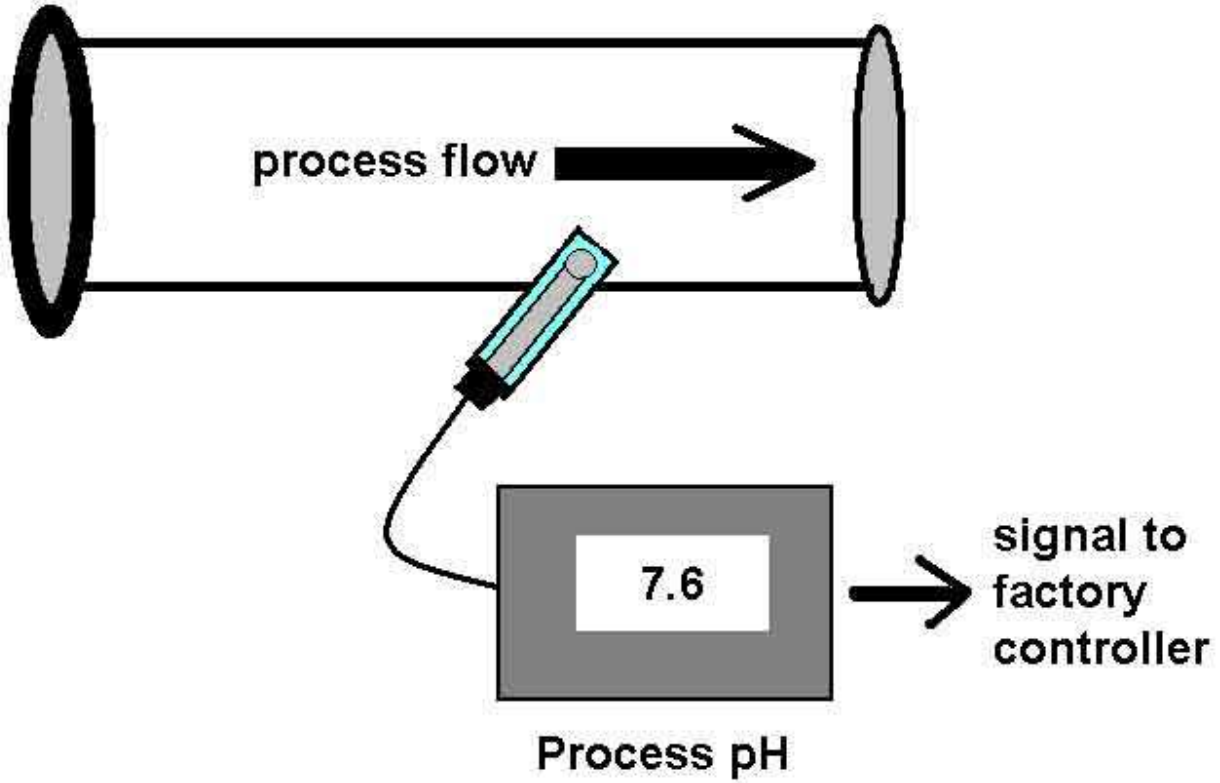


Figure 14.5 - in-line measurement using pH analyzer

Sampling and sampling preparation

While different types of Analyzers are available for process analysis it is the **interface between the process stream and Analyzer** that requires most attention.

The goal of any sampling system is to provide a representative sample to the analyzer without introducing any variation due to the sampling procedure which will inevitably increase the measurement uncertainty associated with the measurement.

Often however, it is the process variability that is being tested for in PAC. In this situation it is often the variation and heterogeneity that is being measured. Typical parameters that can effect the sampling include particle size (e.g. heavy and light particles will behave in a different manner), solvent (e.g. difference in viscosity), pressure, temperature or flow variations.

Continued on the next slide

The main functions for PAC that influence sampling and hence need to be considered are:

- Obtaining a representative and homogenous sample from the process stream;
- Transporting the samples to the Analyzer;
- To appropriately adjust samples as required e.g. in-line filtering, temperature or pressure adjustment;
- To be able to effectively switch flow between sample and process stream;
- To return the samples to the process stream or to waste;

The most important factor in PAC, is deciding upon the most effective location from which to take the sample from the process stream, such that:

(a) It provides minimal disturbance to the process;

(b) Will allow a meaningful determination of a specific parameter that has a significant direct or indirect role in the process.

Important considerations that arise when designing a PAC system:

Sample size determination: what is the minimum sample that can be sampled that will provide a representative sample? What is the minimum sample size required by the Analyzer? Are the two compatible?

Sampling frequency: How often should a sample be withdrawn from the process stream? The ideal scenario is to sample at the appropriate frequency to determine any process stream variation. The main issue often, is to determine the sample frequency.

Sources of error: errors can be derived from several sources including the transfer of sample from the process stream to the sampling line and, from the sample line to the Analyzer. The task of the system developer and operators, is to reduce the errors so that their consequences do not overtly influence the decision making process or compromise safety issues.

Continued on the next slide

Sampling system criteria

There are numerous criteria that need to be considered when designing a sampling system for use in PAC. These include:

- **Robustness of system** – the PAC system needs to withstand the often harsh conditions in which it is required to operate for an extended time period with an acceptable maintenance regime and without too much intervention.
- **Reproducible** – the system should be designed, such that if it is given identical samples, it will produce identical data.
- **Timely** – any sample taken from the process stream must be recognised as a snap-shot at that moment in time, and not what is currently occurring (**see previous slide on sampling frequency**).
- **Economical** – all systems need to operate cost effectively.
- **Safety** – a safe system is an effective system. Caution is required when altering such parameters as pressure and temperature.
- **Maintainable** – a system needs to be designed such that when some basic maintenance is required e.g. change a filter, the whole PAC does not have to come off-line. A good PAC system will therefore probably have an alternate flow path to the Analyzer.

Continued on the next slide

- **Transport time requirements** – important to remember that the time taken by the Analyzer is cumulative. A number of approaches exist to speed up the entire process and include direct in-line process stream measurement, and the use of pumps or gravity feed to speed up the transfer process.

- **Materials of construction** - material compatibility is an essential criteria in designing a sampling system. Materials will behave differently under conditions of pressure, temperature and solvent. Therefore the choice of material (i.e. inertness and corrosion resistance) for the sampling line and its compatibility with the process stream are essential requirements.

Figures (14.6&7) shown on the next slide give an illustration of where process analysis is frequently performed on major chemical plants. Separate buildings are often constructed to house all of the analytical and other measurement equipment. The samples for analysis are then either transported to the instrument and then returned to the process after Measurement, or in the case of some spectroscopic techniques, radiation generated by the analyser is beamed via fibre optics to the process, Returning by the same route after attenuation by the target analyte(s).

Figure 14.6 - outside of analyser house

Figure 14.7 - inside of analyser house

Each of these boxes represents a separate piece of analysis or measurement equipment

Choice of analytical techniques

Having considered the important sampling requirements appropriate to PAC, the next step is to select an analytical measurement technique that will be compatible with the sampling system. Important considerations that need to be taken into account include:

- Is there the optimum analytical technique suitable for the purpose required?
- Are there any regulatory or customer requirements?
- Is the accepted approach already in use within the plant?
- Is the analytical instrument stable or does it drift?
- How often does the analytical instrument need (re-)calibration, and can this be done in-situ?
- How frequently does the analytical instrument require maintenance?

Performance characteristics of analytical techniques

It is also important to consider performance characteristics of the analytical technique when selecting what is most appropriate for PAC. These are:

- Selectivity
- Sensitivity
- Response time
- Resistance to attack by chemicals in the process stream
- Temperature sensitivity
- Pressure sensitivity
- Resistance to physical damage
- Compatibility with operating environment
- Reliability and reproducibility
- Self-diagnostic capability
- Costs: initial capital cost; installation cost; replacement cost; maintenance costs; and, consumable costs

The choice of analytical techniques commonly applicable to process analytical chemistry can be classified as follows:

- Flow injection techniques;
- Chromatographic techniques;
- Spectroscopic techniques.

Each of these three techniques will now be evaluated and described in respect of their use for PAC.

The fundamentals of chromatographic and spectroscopic measurements have been covered in detail in Chapters 6, 7, 11, 12 & 13 of this teaching & learning package. Thus only the specific applications of these techniques appropriate to PAC will be considered in this Chapter

Flow Injection Analysis

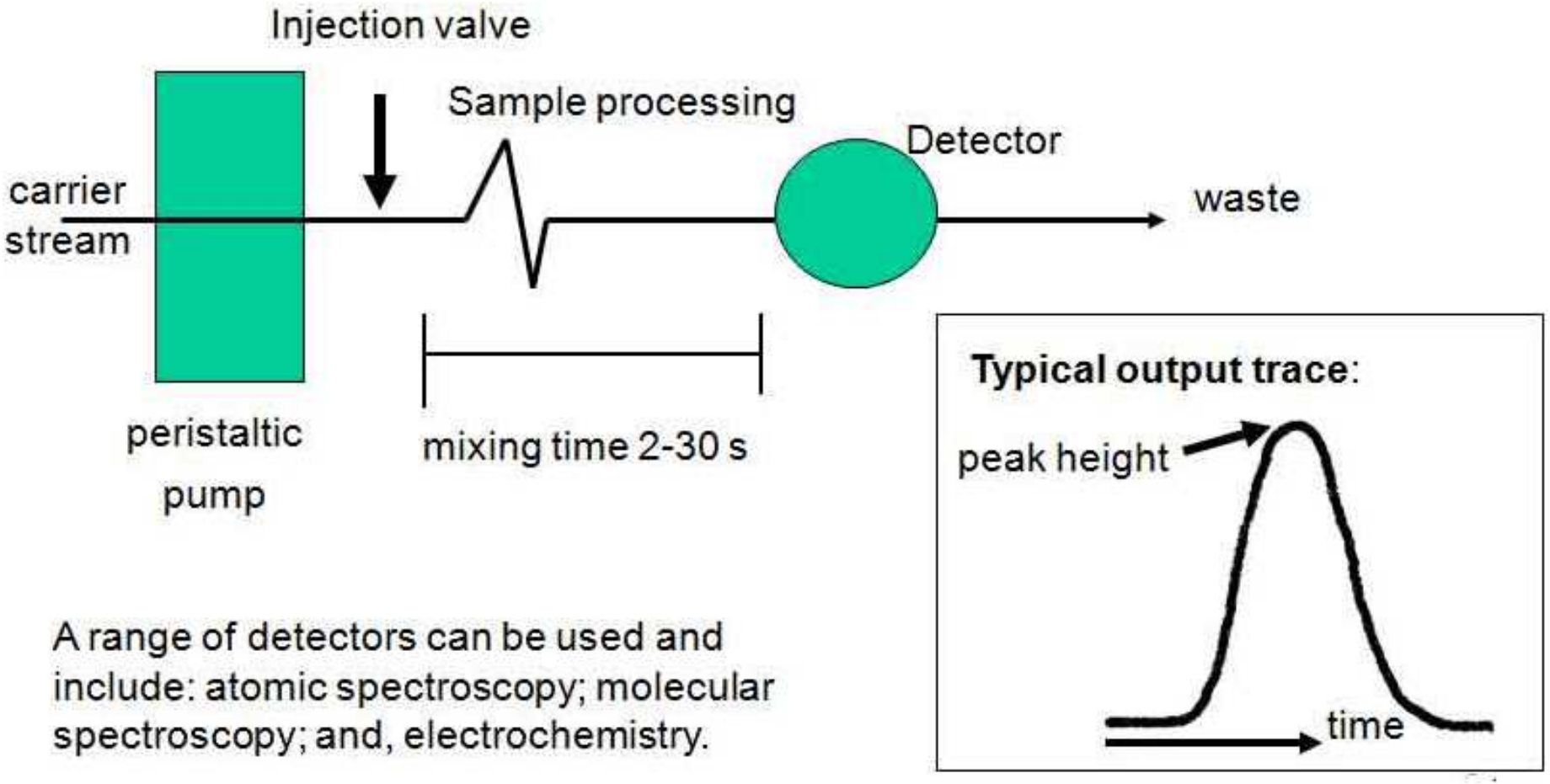
The term Flow Injection Analysis (FIA) was first described in 1975 as the injection of a liquid sample into a moving, non segmented continuous carrier stream. FIA can be used at-line, on-line and in-line for PAC.

The apparatus required for FIA is relatively simple and consists of:

- A peristaltic pump to move liquid (carrier stream);
- An injection valve to introduce a small discrete sample or standard into the carrier stream;
- A sample processing stage (commonly called the reaction coil). This allows for:
  - mixing of reagents/samples/standards;
  - dilution of the sample;
  - enrichment of the sample for trace analysis.
- A flow through detector to measure a response.

All of the components are connected to one another to produce a continuous moving and dynamic system that is capable of being automated. A typical diagrammatic representation of these components is shown as figure (14.8) on the next slide.

Figure 14.8 - a typical diagrammatical representation of a FIA system



Descriptions of the main components used in FIA are shown on the following 3 slides

The **peristaltic pump** works by rotating a series of rollers attached to the outside circumference which compress flexible pump tubing against a hard surface i.e. platen. The continual compression and relaxing (returning to normal dimensions) of the tubing, by the moving rotor, allows liquid to be moved forward. The multi-rollered nature of the pump means that more than one set of pump tubing can be in operation at the same time. In addition, by using different internal diameters of the flexible pump tubing, allows different flow rates to be achieved using a constant rotor speed.

Figure 14.9 - diagram of the operation of a peristaltic pump

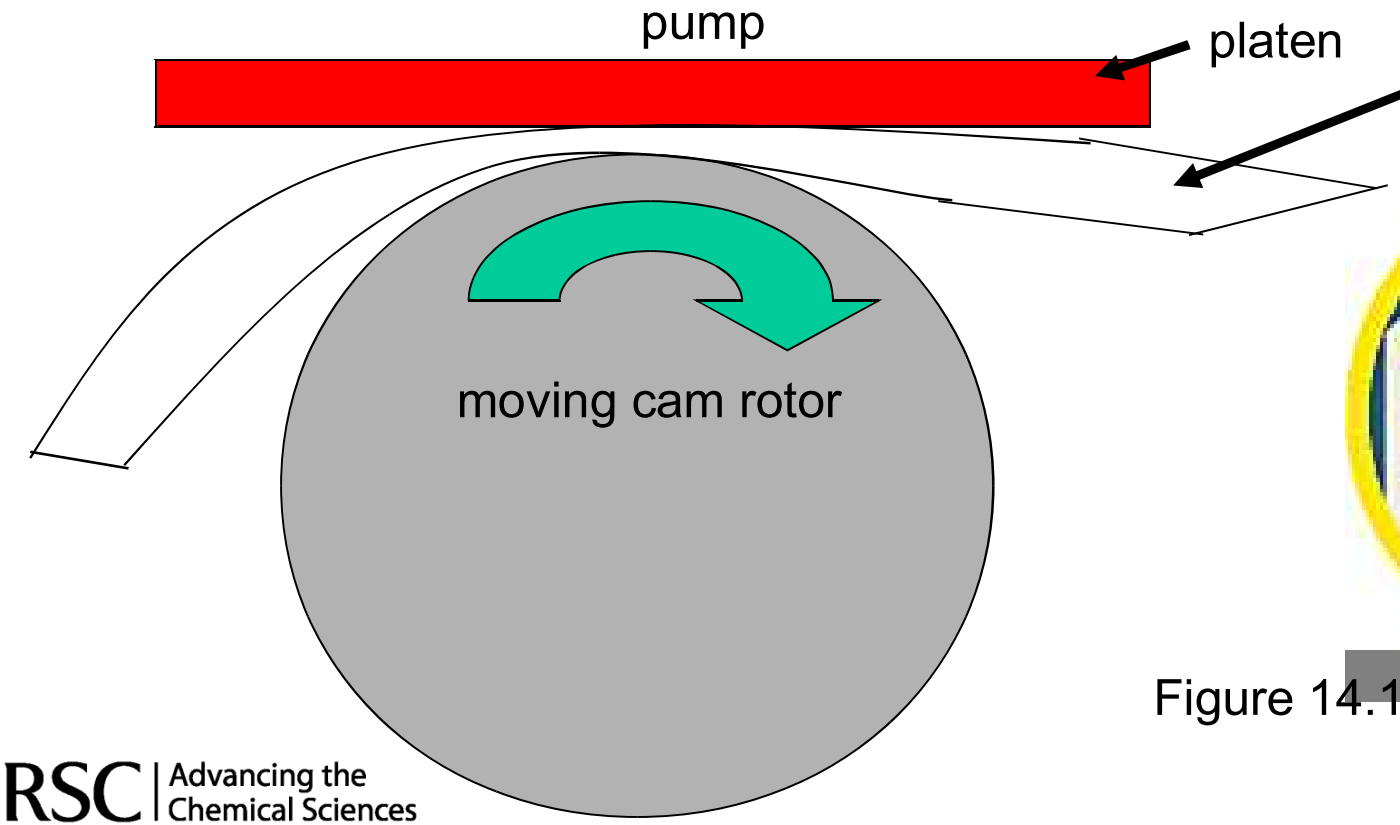


Figure 14.10 - a peristaltic pump in action

The most common **injection valve** for FIA is the 6-port injection port. This device [Figure (14.11)] allows a discrete amount of sample or standard to be reproducibly introduced in to a moving carrier stream with minimal disruption whilst at the same time not interrupting the flow of the carrier stream. The injection valve operates in two positions [Figure (14.12)], shown on the next slide.

Figure 14.11 - photograph of an injection valve

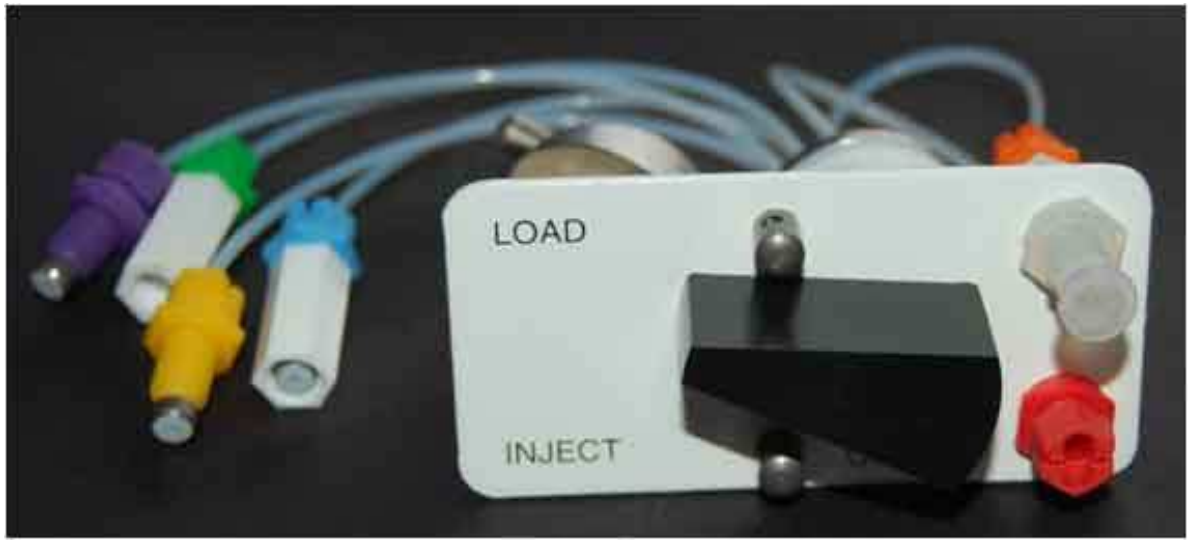


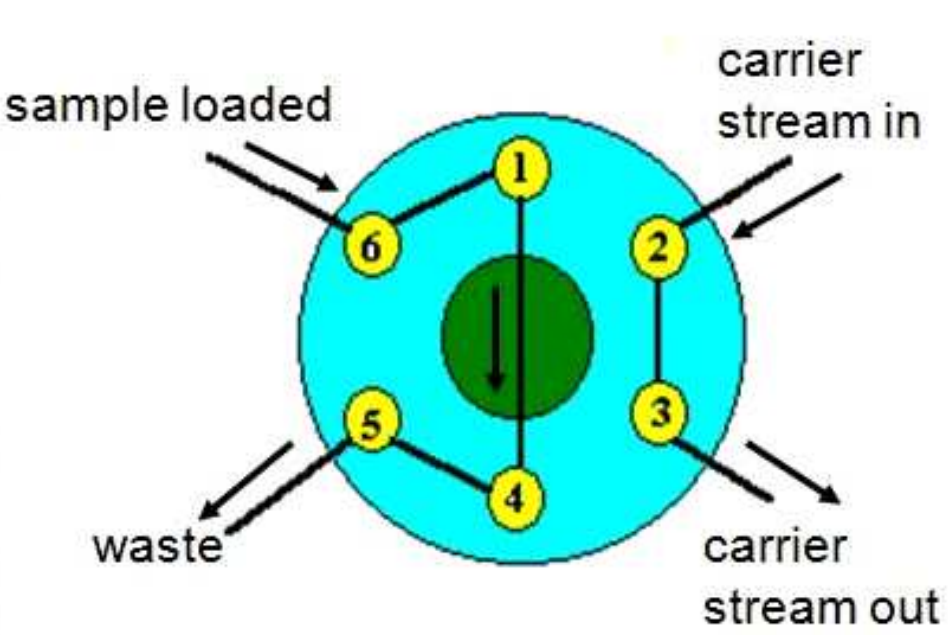
Figure 14.12 - a 6-port injection valve (A) load position, and (B) inject position

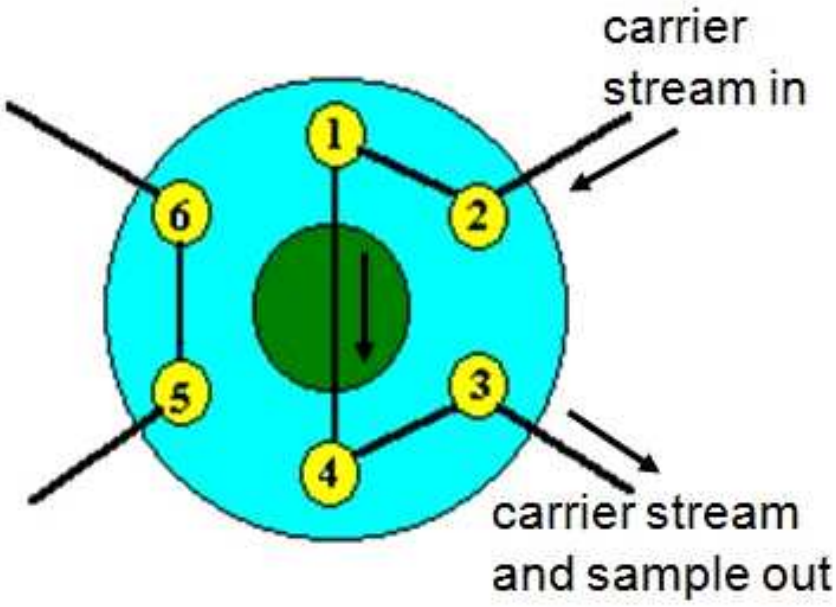
(A)

In this position the sample is loaded into the loop whilst maintaining a constant flow of carrier stream; sample loop is between port 1 and 4.

(B)

In this position the sample is removed from the sample loop by the carrier stream allowing efficient introduction of the sample into the carrier stream.





Dispersion

This can be defined as the ratio of concentrations before and after the dispersion process has taken place in the detector.

Dispersion, D, can be quantified as follows:

$$D = C_o / C_{max}$$

C_o is the un-dispersed sample i.e. no dilution taking place between the sample injection valve and the detector, while C_{max} is a result of sample dispersion e.g. a flow injection detector response.

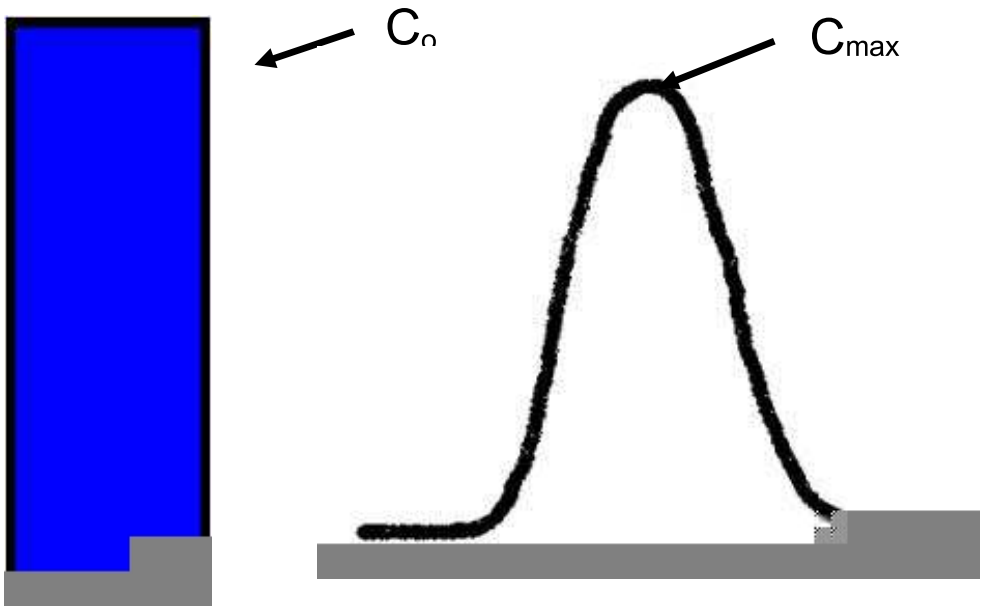


Figure 14.13 - definition of dispersion

Some detectors require an undiluted sample to be reproducibly transported to a detector e.g. pH i.e. no mixing required (D = 1 to 3). However, if analyte conversion to a compound is required, based on the mixing of reagents with the sample e.g. in spectrophotometry, then D is increased (D = 3 to 10). In extreme circumstances more mixing may be required such that the dispersion is very large (D = > 10).

Various parameters can be altered in FIA that affect dispersion including **sample volume** and **tube length**.

Influence of sample loop volume on dispersion

Injecting increasing volumes of the same sample concentration, influences dispersion and affects method sensitivity. This effect is illustrated in figures (14.14) & (14.15) [**next slide**]

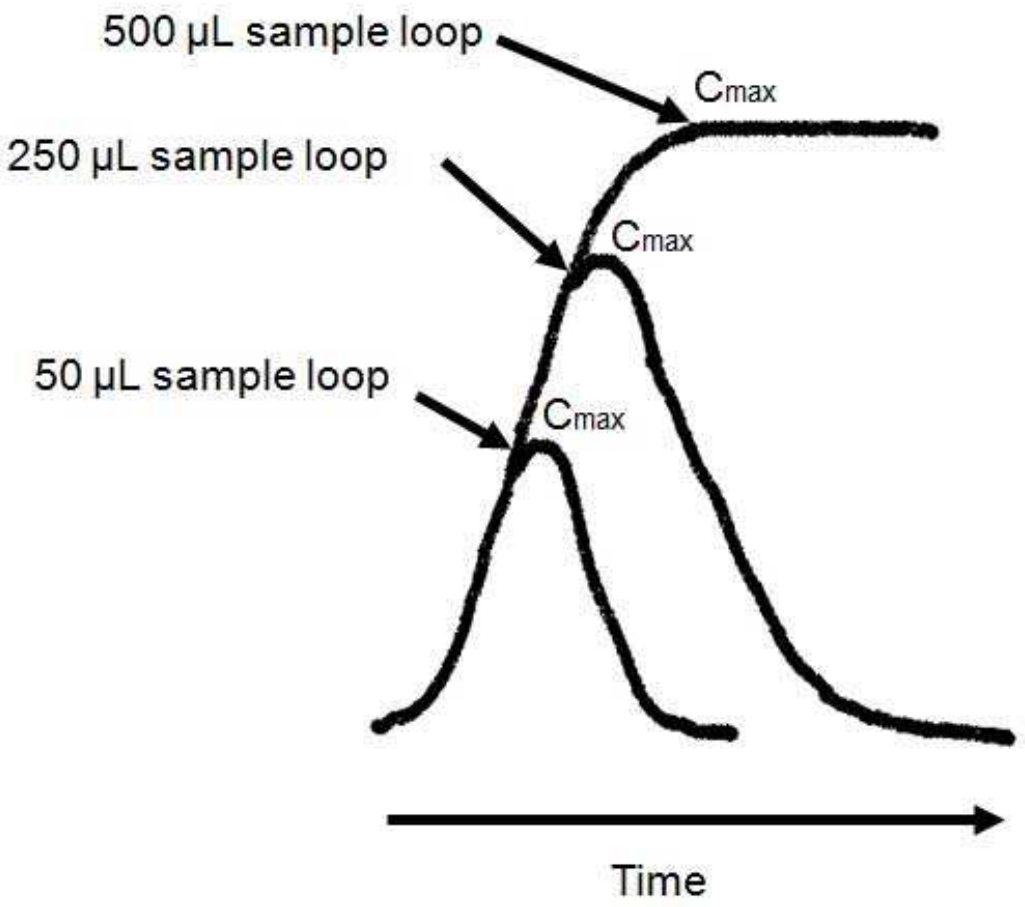
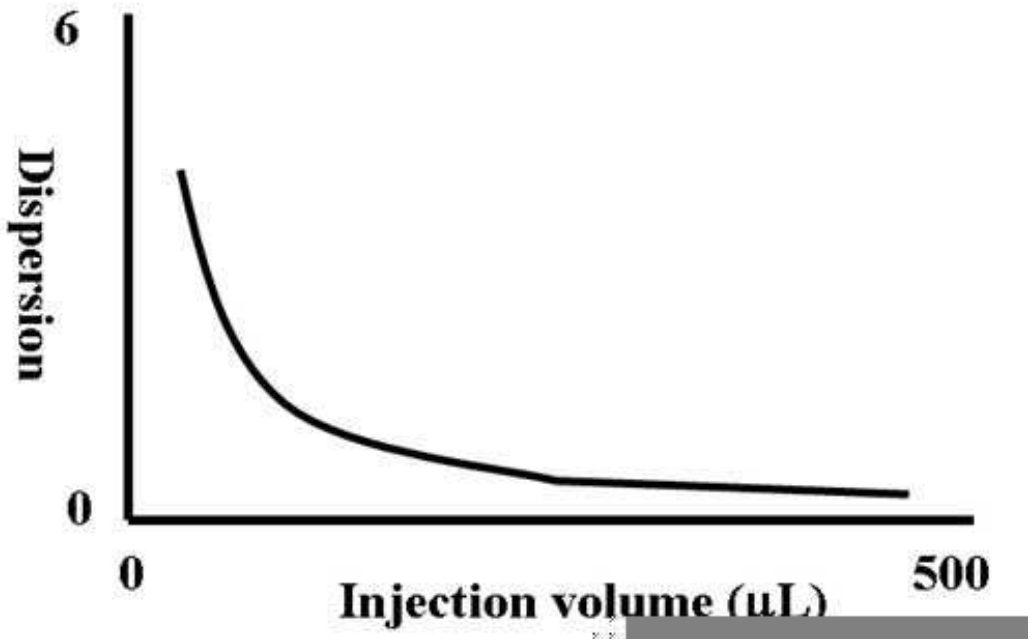


Figure 14.14 - influence of injection volume on peak height.

Continued on the next slide

Figure 14.15 - a plot of injection volume versus dispersion produces a graph with the following general profile.



Changing injection volume has a powerful influence on dispersion. An increase in peak height and sensitivity is achieved by the increasing sample loop volume. Conversely, dilution of concentrated sample material is achieved by reducing injection volume

Influence of tube length on dispersion

The dispersion of the sample zone, increases with the square root of the distance traveled through an open narrow tube. In addition, the dispersion decreases with decreasing flow rate.

The dispersion plots shown in figure (14.16), all relate to a fixed sample loop of volume of 60 µl

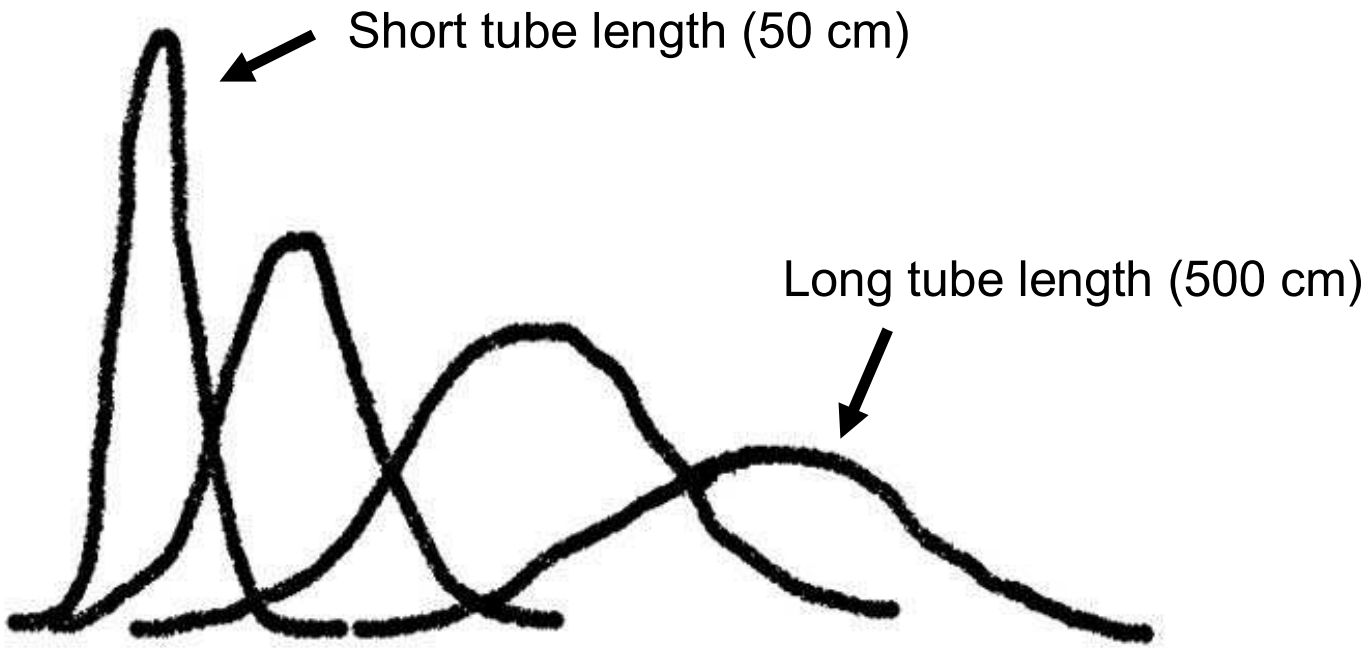
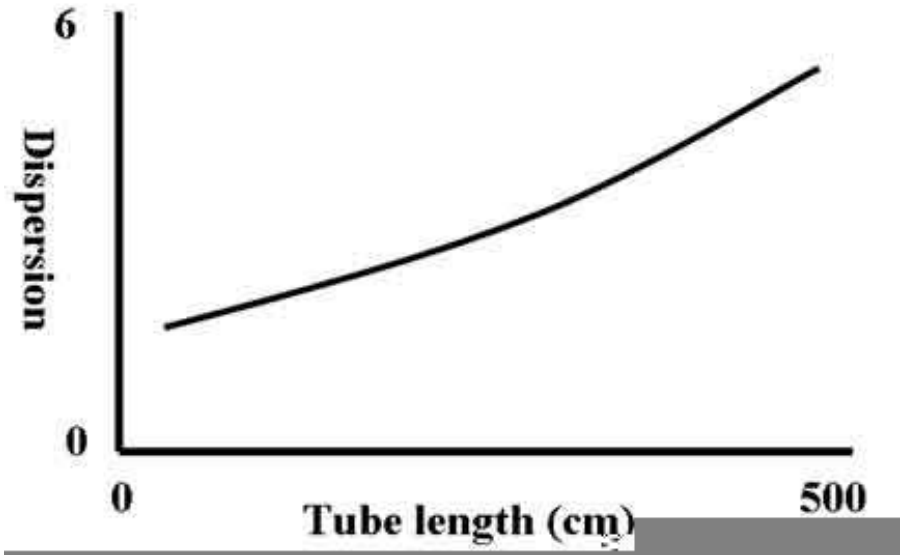


Figure 14.16 - influence of tube length on peak height

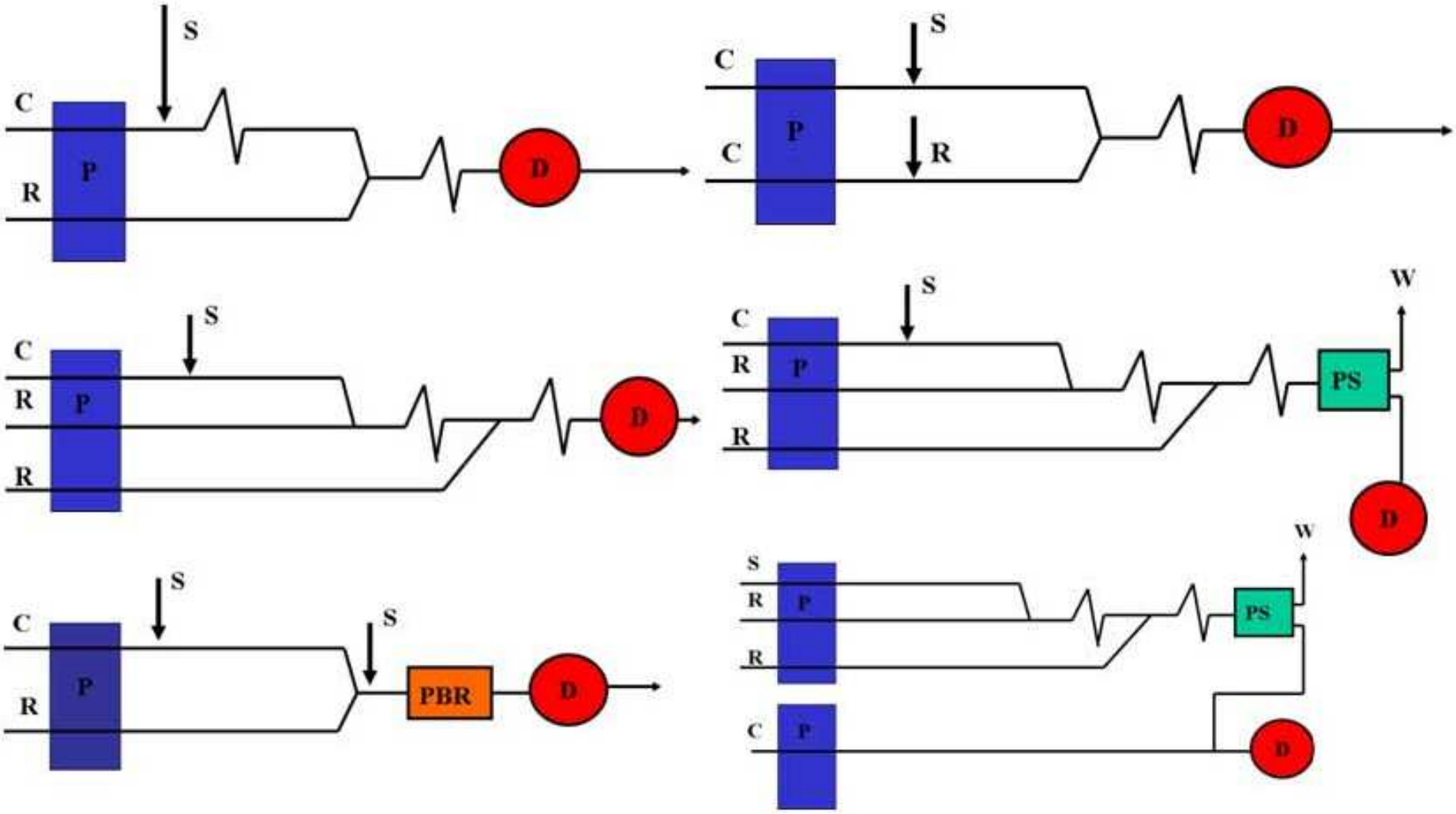
Continued on the next slide

Figure 14.17 - a plot of tube length version dispersion produces a plot with the following profile



Thus if dispersion is to be reduced and residence time increased, the tube length should be kept short and the peristaltic pumping rate decreased.

The most effective way to increase the residence time and to avoid further dispersion is to inject the sample into a flowing stream and then stop its forward movement, and to resume pumping after sufficient reaction time has elapsed. This method is referred to as stopped flow.



S = sample; C = carrier stream; R = reagent; P = peristaltic pump; D = detector;
PS = phase separator; PBR = packed bed reactor

Figure 14.18 - a range of manifolds can be designed and used for a wide variety of applications.

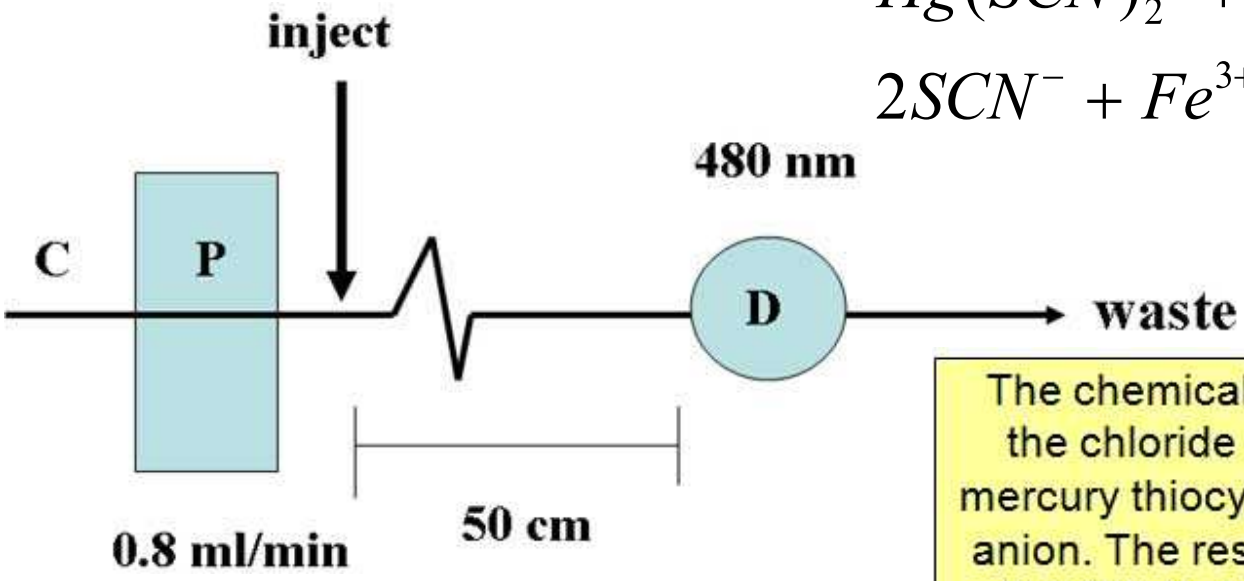
Case study 14.1 - spectrophotometric determination of chloride

The FIA manifold [Figure (14.19)] was assembled as shown with a carrier stream (C) containing mercury thiocyanate and iron (III) nitrate. Standards of chloride were injected in the range 5 to 75 μg/cm^3 Cl^-.

$$Hg(SCN)_2 + 2Cl^- \Rightarrow HgCl_2 + 2SCN^-$$

$$2SCN^- + Fe^{3+} \Rightarrow Fe(SCN)_2^+$$

Red complex at 480 nm



The chemical basis of this FIA system is that the chloride (in the sample) reacts with the mercury thiocyanate producing free thiocyanate anion. The resultant anion then reacts with the iron (III) in the carrier stream to produce a red complex that can be detected at 480 nm.

Figure 14.19 - FI Manifold

Some problems do exist with this approach and include the fact that other higher complex ions might be formed. Also, the calibration graph produced is restricted to a narrow concentration range, typically < 100 μg/cm^3 Cl^-.

Case study 14.2 - determination of sulfite in brine by FIA

During brine purification, potassium sulfite is added to the process stream as a chlorine scavenger. Therefore the ability to continuously monitor sulfite is desirable. The use of FIA offers the possibility of on-line monitoring [Figure (14.20)].

The chemistry underlying this FIA system is based on the fact that sulfite reacts with a reagent (DTNB) to produce the chromophoric species, 2-nitro-5-mercaptobenzoic acid [Figure (14.21)] which is measured at 412 nm.
[DTNB is 5,5'-dithiobis(2-nitrobenzoic acid)]

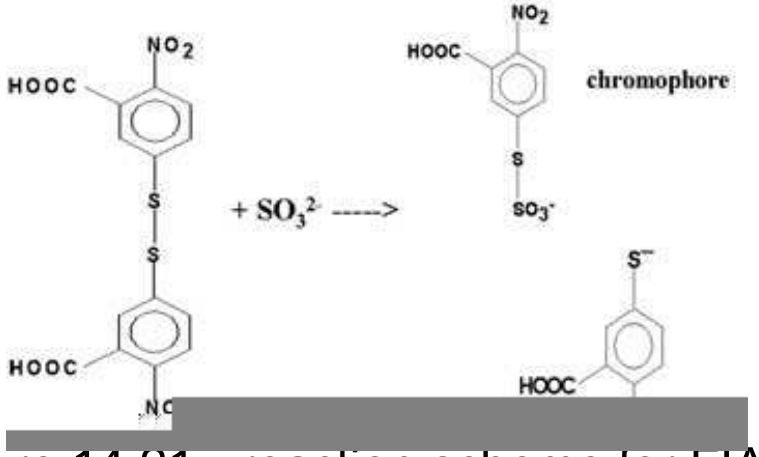


Figure 14.21 - reaction scheme for FIA

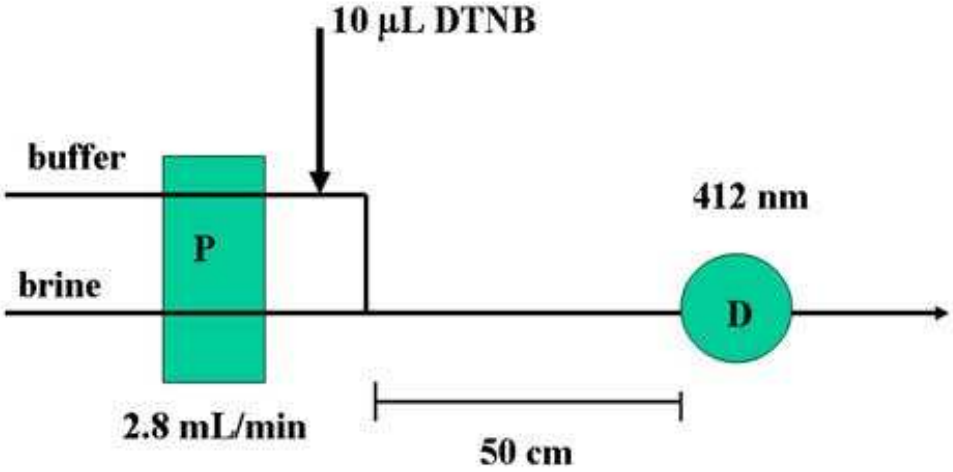


Figure 14.20 - FI Manifold

The developed system was required to monitor sulfite over the range 0-20 mg/dm^3 in 18% (w.v) potassium chloride brine at 70-80 °C and at pH 11-12, and in the presence of potential interferents in the brine.

In this FIA system, the reagent is added via the injection valve to reduce its consumption. In addition, the system requires a stock solution of sodium sulfite and buffer, pH 11.7 (trisodium phosphate). [Adapted from: Anal. Chim. Acta, **238** (1990) 171]

Case study 14.3 - on-line determination of residual aluminium in potable and treated waters by FIA. [*Adapted from: Anal. Chim. Acta,* ***238*** *(1990) 177*]

It is important to monitor water quality parameters continuously on-line. These parameters include: prevention and/or control of transient pollution incidents; gathering of detailed trend data for water management; the need to ensure that industrial discharges and abstracted potable and treated waters conform to the required standards.

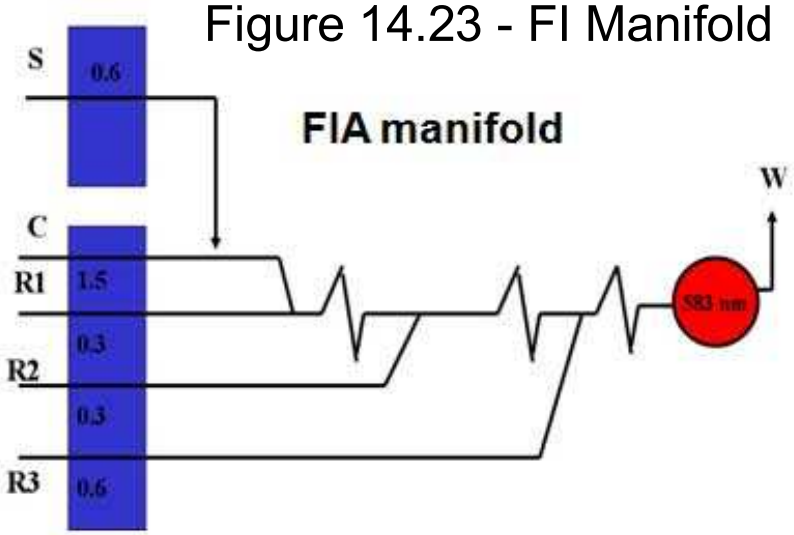
EU standards, are stipulated quantitatively as maximum admissible concentrations (MAC's) and guideline concentrations (200 $\mu g/dm^3$ and 50 $\mu g/dm^3$ for Al resp.). In the UK aluminium salts have traditionally been used as primary coagulants and flocculants in the treatment of raw turbid water. After coagulation, flocculation and filtration it is likely that there will be some residual dissolved aluminium in the treated water.

Coagulation is defined as the process whereby non-settleable colloidal residues are destabilized by the addition of aluminium salts with rapid mixing, resulting in the formation of settleable flocs.

Continued on the next slide

Figure 14.22 - a water waste treatment plant

Figure 14.23 - FI Manifold



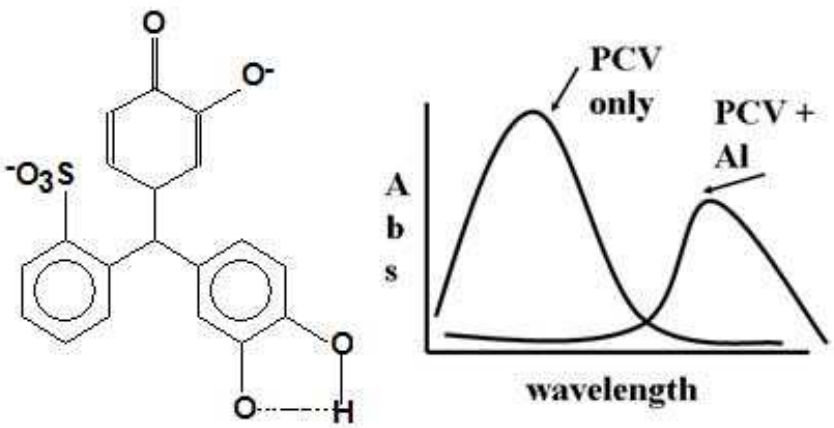


Figure 14.24 - Pyrocatechol violet (forms a 3:1 complex with Al at λ_{max} 583 nm).

R1 hydroxylammonium chloride and 1,10-phenanthroline (Fe masking agent); R2 pyrocatechol violet (colour reagent); R3 hexamine (buffer); C carrier stream; and, S sample or standard.

The only significant interferent in most potable and treated waters is Fe(III), the predominant iron species in surface waters. This can be masked (i.e. hidden) by the addition of hydroxylammonium chloride (which ensures all iron present as +2), followed by complexation with 1,10-phenanthroline.

Potential problems include: adhesion of colloidal Al complex to the flow tubing - this can be overcome by addition of 1% (w/v) Brij 35 (a surfactant to the carrier stream); and, entrainment of air bubbles in flow system – these are prevented by the use of a back-pressure regulator on both sample and manifold waste lines.

Case study 14.4 - an on-line system for metal separation and/or pre-concentration with atomic spectroscopic detection using an inductively coupled plasma.

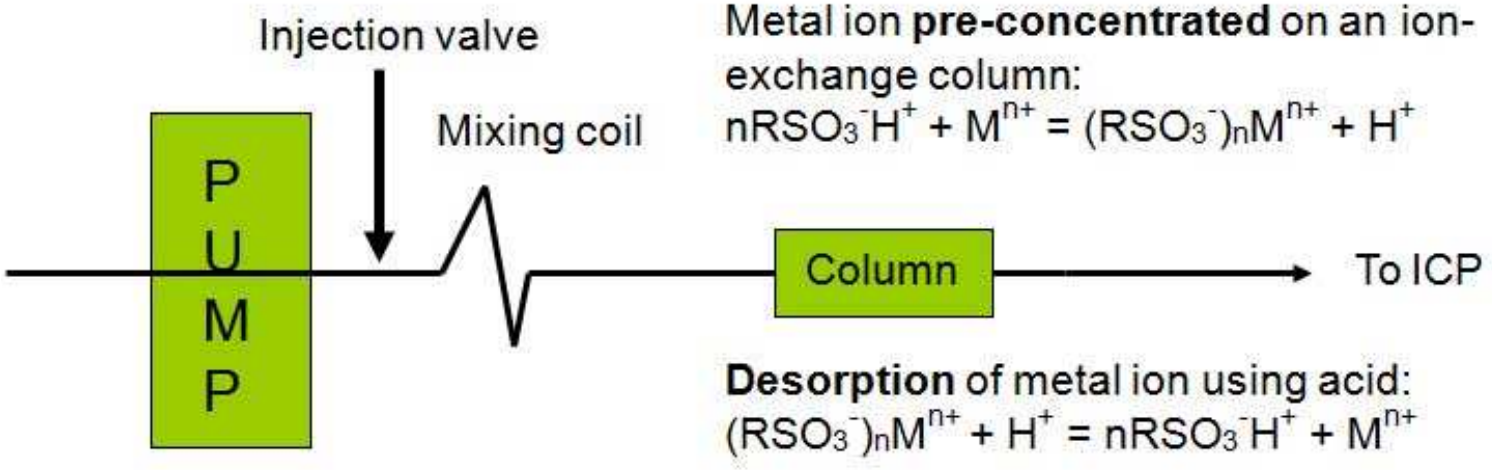


Figure 14.25 – Flow injection manifold

A small volume of sample (e.g. 100 µl) is introduced, via the injection valve, into an aqueous carrier stream (e.g. a buffer solution).

Continued on next slide

Then, after some mixing between the sample and carrier stream the mixture passes to a column e.g. a cation exchange column [Figure (14.26)], where the metal ions in solution are retained (i.e. **pre-concentrated**).
Subsequently, acid is added via the injection valve to **desorb** the metal ions from the ion exchange column allowing the concentrated metal to be carried in to the nebulizer of the ICP.

Figure 14.26 - a column as used in a FIA manifold

Case study 14.5 - an on-line system for pre-concentration using solvent extraction with atomic spectroscopic detection using ICP

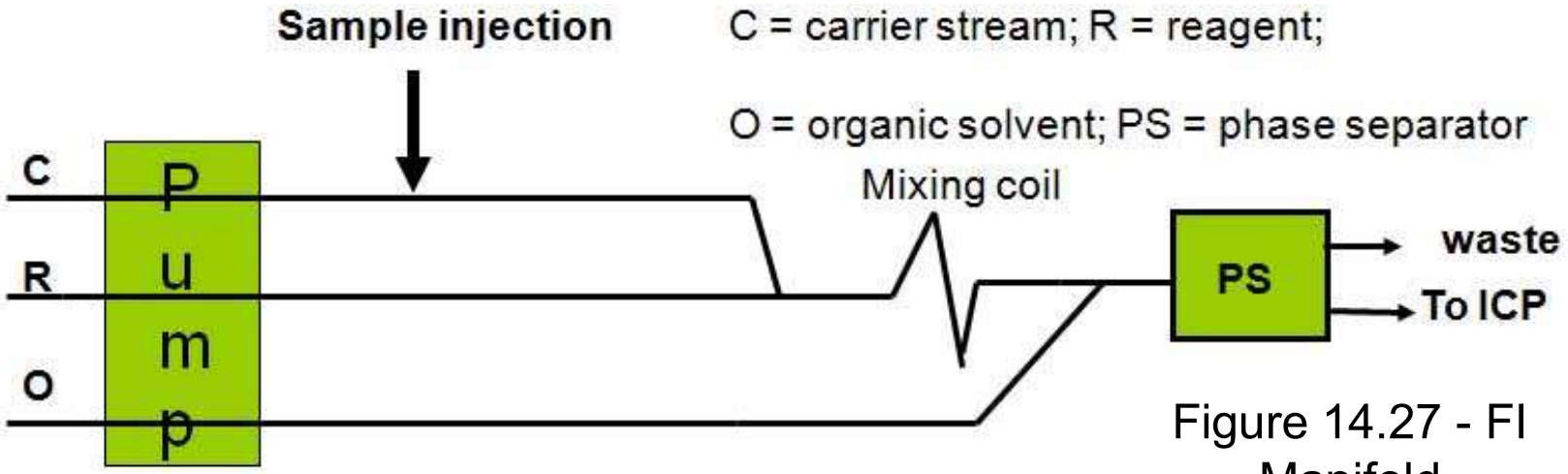


Figure 14.27 - FI Manifold

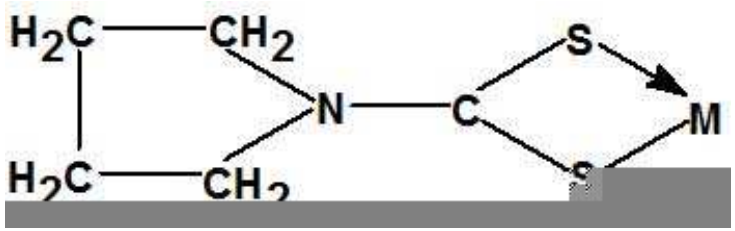


Figure 14.28 - APDC (ammonium ion displaced by metal, M)

A small volume of sample (e.g. 100 µL) is introduced in to an aqueous carrier stream (e.g. dilute acid) and merged with a reagent (e.g. ammonium pyrrolidine dithiocarbamate (APDC). Sample and reagent are then mixed and then combined with an organic solvent e.g. isobutylmethyl ketone (IBMK). The phase separator then allows the analyte – reagent to transfer from the aqueous phase in to the organic phase and directly in to the nebulizer of the ICP.

Chromatographic techniques

The basis of a chromatographic system is that a discrete and small volume of sample is introduced in to a carrier stream (mobile phase), the components of the sample are then separated by a column (stationary phase) and selectively eluted and detected.

Most forms of chromatography are used in PAC including gas chromatography (GC) and high performance liquid chromatography (HPLC).

For more specific details of the different types of chromatography and their mode of operation see Chapter 7 of this teaching and learning programme.

As a chromatographic separation relies on analyzing a discrete sample outside of the process stream, the approach is not compatible with ‘in-line’ PAC but is a useful ‘at-line’ process analytical technique.

GC is used to separate and analyse gaseous and volatile organic liquid samples. For example, GC can be used effectively in the petroleum industry for determining chain length distribution i.e. carbon number.

A typical GC analysis time is between 2-15 mins.

Figure 14.29 – typical laboratory based GC system

The main disadvantage of GC systems relate to maintenance issues linked to the following:

- Column lifetime and influence on compound retention time;
- Carrier gas consumption (i.e. nitrogen or helium);
- Safety issues relating to the use of a flame ionization detector – a small naked flame operating with hydrogen gas, or an electron capture detector – contains a small radioactive source.

Some unique features of a Process GC system

These include:

- A fresh sample is always analysed since the GC is connected directly to the process stream;
- Faster analysis times;
- Multiple columns and valves;
- Less people power for its operation;
- Results available quickly to the process operator;
- Can be operated in closed-loop control;
- Isothermal operation is most common;
- May be designed for operation in hazardous environments.

Continued on the next slide

HPLC is used to separate and analyse non-volatile organic liquid samples. For example, HPLC is used effectively in the pharmaceutical industry for determining component purity. A typical analysis time is between 10 – 30 minutes.

Figure 14.30 - an HPLC system

The main disadvantage of HPLC systems relate to maintenance issues linked to the following:

- Column lifetime and influence on compound retention time
- Mobile phase consumption (i.e. acetonitrile)
- Safety issues relating to the use of organic solvents (mobile phase) and high-pressure pumps.

Typical Process Chromatographic Applications

Petrochemical / Chemical: includes materials derived from hydrocarbon raw materials i.e. crude oil or natural gas. These materials are converted into petrochemicals which are then used as feedstock for other processes e.g. plastics including polyethylene, polypropylene and polystyrene.

A typical process GC use is in the ethylene cracking process.
The low molecular weight feedstock is ethane and propane. It is important to be able to measure the following: furnace inlet – C1-C4 compounds; furnace outlet – C2-C4 compounds; and, ratios between C1:C2 and C1:C3.

Other common applications for the petrochemical / chemical industry include: alcohol production; distillation control; reactor product analysis; ammonia production; vinyl chloride production; aromatics production; chlorine purity; polypropylene production; methyl chloride production; styrene production; methanol; and, napthalene production.

Figure 14.31 - an industrial chemical plant

Refining: The high demand for fuels for motor vehicles makes this one of the largest industries in the world.

In the initial step, the natural gas is removed from the crude oil. Then the refinery takes the crude and performs some reactions to generate more gasoline (petrol). For example, the alkylation unit will convert two butane molecules into one octane molecule. Alternatively, larger molecule are broken down by either catalytic cracking or thermal decomposition in to the more economically viable gasoline (petrol).

All these reactions taking place within the refinery require careful monitoring and control. This is achieved using process GC. An example is the crude distillation process (**see next slide**).

Example - Crude oil distillation using process GC

Crude oil is a combination of a wide range of hydrocarbon fractions. These are:

- Fuel gas (C- - C3)
- Wet gas (C2 – C4)
- Light straight-chain gasoline (petrol) (C5, C6)
- Heavy straight-chain gasoline (C7 – C10)
- Kerosene (C9 – C15)
- Diesel (C13 – C18)
- Gas oils (C13 – C45
- Residuum (C40+)

Process GC is used to analyze the fractions of the crude distillation tower for boiling-point distribution using simulation distillation. Economic advantage exists by operating as close as possible to the boiling-point specifications. For example, gasoline (petrol) is more expensive than kerosene, therefore operating as close as possible to the gasoline range before removing the kerosene is important. Figure (14.32) shows a typical chromatogram of a diesel fraction

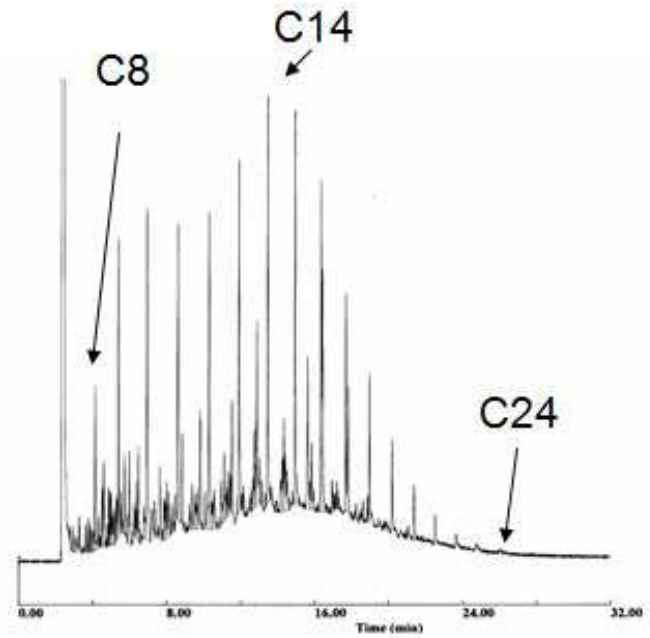


Figure 14.32 – temp. programmed GC of a Diesel fraction, FID detector

Natural gas industry: This provides the energy for households and industry worldwide. Four main areas distinguish this industry: gathering, processing, transmission, and, distribution.

Gathering – the gas wells are drilled, gas collected for processing

Processing – the heavier hydrocarbons are removed and the methane-rich gas is placed in the pipeline for transporting.

Transmission – the transmission companies buy the methane-rich gas and transport it via extensive pipe work to the gas distribution companies.

Distribution – the gas distribution companies buy the gas and deliver to either domestic households or commercial users.

As the gas moves from one area to another so its ownership changes. Each new purchaser needs to check the economic value of the gas by measuring the gases heating value, specific gravity or density, and composition. **This can be done using process GC.**

Example (14.i) - Determination of natural gas heating value by process GC.

The following compounds need to be measured within natural gas: N_2, CO_2, straight and branched chain hydrocarbons plus other heavier hydrocarbons, neopentane and H_2S. The analysis is carried out at custody transfer points in order to assess the economic value of the gas. The gas is normally traded as the heating value per unit volume of gas flow or more recently as heating value. A typical analysis is shown in table (14.1) below:

Component	Concentration (%)	Component	Concentration (%)
Nitrogen	3	Isobutane	0.5
Carbon dioxide	2	Butane	0.5
Methane	85	Isopentane	0.25
Ethane	5	Pentane	0.25
Propane	2.5	Hexane+	1.0

Table 14.1 - typical natural gas stream composition

This analysis is carried out using a thermal conductivity detector as not all of the components are detectable using the FID detector

Other examples of industries that use process GC

Environmental or ambient air monitoring: This application is designed to either provide a safer working environment for employees who operate in hazardous environments or to reduce emissions from industrial processes in to the atmosphere i.e. stack or incinerator monitoring.

Biotechnology industry: for example, fermentation off-gas monitoring

Pharmaceutical industry: for example, organic solvent recovery

Steel industry: for example, blast furnace off-gas monitoring

Beverage industry: for example, alcohol determination

Food industry: for example, moisture determination

Spectroscopic techniques

The use of spectroscopic techniques offers PAC the possibility of non-invasive, in-line and continuous real time measurements of the process stream. The range of spectroscopic techniques that have been and are being used for PAC is extensive and includes:

- Infrared spectroscopy
- Mass spectrometry
- UV/Visible spectroscopy

For more specific details of the different types of spectroscopic techniques and their mode of operation see Chapters 11,12 & 13 of this teaching and learning programme.

Infrared spectroscopy

After chromatography the use of infrared (IR) spectroscopy is the most popular technique used in PAC. Traditional mid-IR spectroscopy was used originally , however more applications now use Near-IR (NIR) and Fourier Transform IR (FTIR) approaches.

Mid-IR refers to the spectral region from 2.5 to 25 μm or 4000 – 400 cm^{-1}, whereas NIR refers to 0.7 – 2.5 μm or 14000 – 4000 cm^{-1}.

IR spectroscopy provides useful information relating to the chemical structure of both organic and inorganic materials and can be applied for both identification and quantitative purposes. IR can be used for at-line, in-line and on-line analyses depending upon the application.

Typical Process IR Spectroscopy Applications

- **Industrial applications**
  e.g. refinery production, fuels, solvents, oils and lubricants, plastics and polymers, detergents, dyes and pigments, ambient air monitoring, combustion gases.

- **Construction and manufactured materials**
  e.g. metal working, coatings, wood, pulp and paper, mining, building materials, inks and printing materials, ceramics, leather goods.

- **Consumer products and finished goods**
  e.g. food products, natural oils, dairy products, flavours and fragrances, beverages, cosmetics, personal care products, polishes, dental materials, pharmaceutical products, medicinal products, veterinarian products, aerosol products, fabrics and fibres, packaging, films.

- **Speciality manufacturing and fabrication**
  e.g. electronics, magnetic and recording media, batteries, semiconductors, aerospace, electroplating, glass and optical materials, high-tech materials.

Mass Spectrometry (MS)

Due to the complexity of the mass spectrometer instrumentation most MS is carried out in the laboratory or ‘at-line’. However, some examples exist where MS is applied ‘on-line’ for PAC. Mass Spectrometry provides useful information relating to the chemical structure of both organic and inorganic materials and may also be used to provide quantitative measurements. **See Chapter 13 of this teaching and learning programme.**

The process Mass Spectrometer consists of four main components, which are illustrated in figure (14.33) below:

- The mass analyzer which separates the mass components of the sample;
- An ion-source which is required to generate gas-phase ions of the sample for mass separation;
- A detector to collect the mass separated sample ions and provide a signal;
- A sample interface through which the sample can be introduced from the process stream.

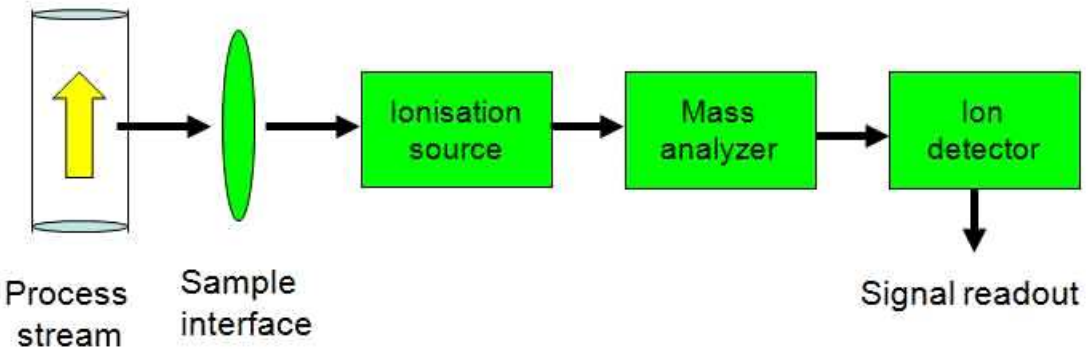


Figure 14.33 components of a process mass spectrometer

Typical Process MS Spectroscopy Applications

- Biotechnology industry - for example, monitoring vial/container integrity for drug containment, transport and delivery; monitoring of penicillin or alcohol production in a fermentor.
- Petrochemical industry - for example, ethylene oxide or polypropylene production.
- Semiconductor industry - for example, vapour deposition; ion implantation; plasma-enhanced chemical vapour deposition; molecular beam epitaxy.
- Environmental industry - for example, monitoring flue gases from incinerators for CO, CO_2, NO_x and total organic carbon.

UV/Visible Spectroscopy

Process UV/Visible spectroscopy analyzers are purpose built to be used as either a continuous or semi-continuous monitor of a specific component for process or environmental control.

Most process UV/Visible analyzers have separate light source, sample and photometer housings. The three housings can be remotely linked to each other via the use of optical fibres which transmits radiation through the sample cell from the monochromator to the detector. This allows the monochromator and detector to be located in a relatively ‘clean area’ while the sample cell can be located in the ‘plant’ room. The analyzer can be adapted to monitor process liquid and gas streams in pipeline cells introduced directly in to the process line. UV/Visible spectroscopy provides useful information relating to both qualitative or quantitative presence of both organic and inorganic materials.

Figure (14.34) on the next slide shows diagrammatically, the optical arrangement of a filter photometer, dedicated to the measurement of a single absorbing gaseous analyte. The sample can be passed continuously or discontinuously through the analyser.

Figure 14.34 on-line filter photometer

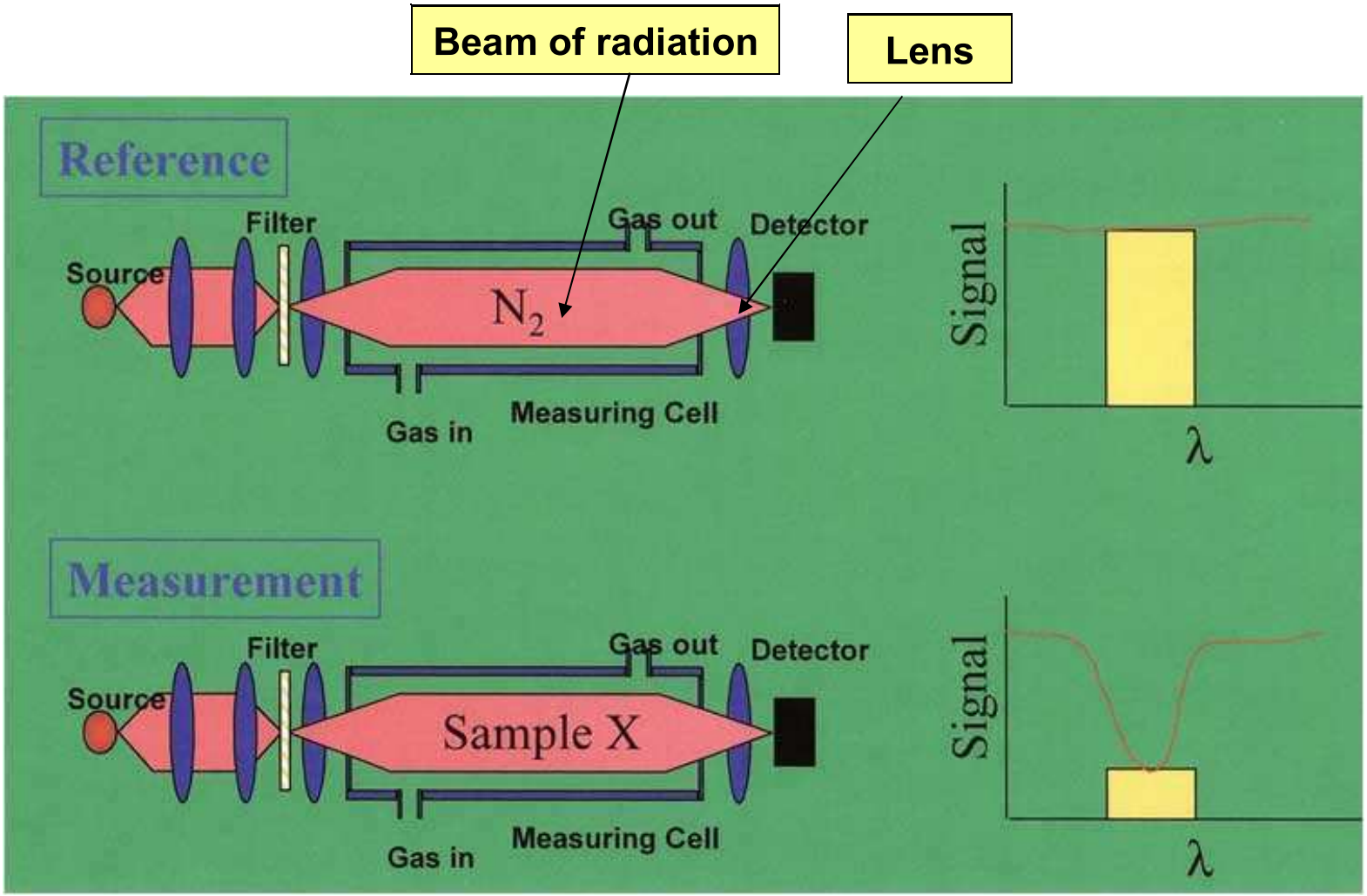


Figure (14.34) shows a simple filter photometer type analyser. The background absorption is determined by using an unabsorbing gas (N_2). When the sample is then passed through the analyser, the target analyte absorbs the radiation, giving a reduction in signal.

RSC | Advancing the Chemical Sciences

Typical Process UV/Visible Spectroscopy Applications

- Environmental - for example, source emissions for SO_2, NO_x, ammonia, mercury, aromatic compounds and elemental halogens.
- Petroleum refining and gas production - for example, monitoring of SO_2 and H_2S in the Claus sulphur recovery process.
- Petrochemical and chemical industries - for example, chlorine monitoring in liquid and gaseous phases in the 0-50 ppm range; monitoring of chlorination process in dichloroethane production; titanium dioxide chloride process; salts of iron, nickel, manganese, vanadium and copper in process control.
- Pharmaceutical processing - for example, antibiotic production
- Wood pulp production for paper industry - for example, monitoring and control of ClO_2 in bleaching process.

Data Treatment

Analysis of data obtained in PAC is fundamental to making an appropriate decision on the process stream. One particular area of analytical science, now known as **chemometrics**, is devoted to the design, understanding and interpretation of complex data.

The consideration of 'Chemometrics' as a topic is beyond the scope of this programme, however a description of the topic may be found at:
http://en.wikipedia.org/wiki/Chemometrics

Use of **chemometrics** in PAC

- **Analysis**: mathematical tools that allow complex data sets to be effectively interpreted and appropriate conclusions drawn. This is of particular importance when using NIR as a process measurement technique
- **Design**: the identification of the major factors that influence the process stream and their use to help reduce the data set.

It is important that all data treatment is rapid, easily understood and dealt with efficiently by the process operator.

Development considerations in PAC

The main driver for the use of PAC is that its implementation will lead to a future cost saving. In deciding to consider the implementation of PAC the following four phases should be considered:

1. **Preliminary phase**
    - Determination of the process need and identification of the financial gain possible, in the future, by implementation.
    - Evaluation and/or development of suitable PAC techniques.
    - Design of PAC system.
2. **Installation phase**
    - Capital purchase of PAC system including Analyzer and controller; sampling system; data collection, communication and storage system; safety and physical protection of system.
    - Modifications to process equipment.
    - Servicing for PAC including gases, water, heating and consumables.

Continued on the next slide

3. **Implementation phase**
    - Specific training of workforce including operators and maintenance technicians.
    - Transition stage: this includes working through the PAC system to remove any ‘bugs’, and that different parts of the system are operating effectively. Gaining acceptance of the technology by the operators.
4. **Operational stage**
    - Development of a scheduled maintenance scheme with associated costs for consumables, cleaning and replacement of worn or wearing parts.
    - Regular monitoring that the PAC system is delivering data as per its specification will require a level of in-built self-diagnostics and calibration
    - Maintaining skills and expertise within the workforce
    - Unscheduled maintenance due to component failure, upgrades by instrument manufacturer.
    - Future replacement of current PAC technology with improved or alternative systems.

Question 14.1 In process analytical chemistry which of the approaches (off-line, at-line, on-line, in-line) offers the (i) least and (ii) most difficulties in linking to an analytical technique?

Question 14.2 Rank in order of importance the sampling system criteria.

Question 14.3 From your knowledge of other Elements in this programme do you think that the following analytical techniques are compatible with incorporation in to a process analytical chemistry system that is operating in-line (see slide 19 for relevant performance factors):

- gas chromatography;

- inductively coupled plasma atomic emission spectroscopy.

Question 14.4 Outline the principal components of a flow injection system.

Question 14.5 The use of a 6-port injection valve leads to the generation of a discrete signal. How might the "signal" be influenced by increasing the sample injection volume?

Question 14.6 What is dispersion and why is it important to assess dispersion in a flow injection system?

Question 14.7 Describe the operation of a peristaltic pump used for flow injection. Also, what other types of pump could be used to move the carrier stream?

Question 14.8 A range of flow injection manifold (see slide 31) are possible. What are the important components of a flow injection system for:

- sample pre-concentration;
- a colorimetric reaction?

Question 14.9 What is the difference between a flow injection manifold containing a column and high performance liquid chromatography?

Question 14.10 What advantages might spectroscopic techniques offer process analytical chemistry? In which industries have process spectroscopic techniques been used?

Outline answer to question 14.1

The answer to this question can be found on slides 4 - 8.

The approach that offers the ***least*** difficulties in linking to an analytical technique is off-line. In this approach the sample is collected from the process analytical stream, then often transported to the laboratory where the sample may be pre-treated prior to analysis using the most appropriate analytical technique. As this is not process analytical chemistry the technique that offers the ***least*** difficulties is at-line. In the at-line approach an analytical technique e.g. UV/Visible spectroscopy, with a simple operating system, capable of providing a rapid output with regular, but minimal maintenance is required.

The approach that offers the ***most*** difficulties in linking to an analytical technique is either on-line or in-line process analytical chemistry. Both have disadvantages that can circumnavigated or negated by use of simple analytical techniques that provide specific and/or selective measurements.

Outline answer to question 14.2

The answer to this question can be found on slides 12 - 13.

A suggested order of importance of the sampling system criteria is as follows:

Most important	Safety
	Materials of construction
	Robustness of system
	Reproducible
	Timely
	Economical
	Maintainable
Least important	Transport time requirements

These suggestions are open to interpretation however, safety needs to be of paramount important in all working environments. In reality all the criteria are important and the true ranking order may be interchangeable depending upon the specific process analytical chemistry being undertaken.

Outline answer to question 14.3

The answer to this question can be found on slide 16 and in Chapters 7 & 12 of this teaching & learning programme.

Gas chromatography (GC): As a discrete sample (1 µL) is normally introduced, by a syringe, in to the column (typically, 30 m x 0.25 mm internal diameter x 0.25 µm film thickness) its use for process analytical chemistry would appear to be limited. While GC is very useful for at-line PAC where samples can be removed from the process stream and analysed it is its use on-line that has become invaluable in certain industries e.g. petrochemical and chemical industries including petroleum refining and gas production, where real-time monitoring by process GC is essential. Process GC was first introduced in the late 1950's and early 1960's. Since then major advances have taken place in the design, operation and control of process GC systems.

Inductively coupled plasma – atomic emission spectroscopy (ICP-AES): As the liquid sample for an ICP-AES is normally introduced at a flow rate of 1 mL min^{-1} this offers possibilities for both at-line and on-line PAC. However, few (if any) examples exist of its use in real-time elemental analysis. In contrast the use of related atomic emission spectroscopy technologies (e.g. DC arc) have been used over many years in the steel production industry for on-line elemental analysis of solid and semi-solid samples.

Outline answer to question 14.4

The answer to this question can be found on slides 18 - 23.

The apparatus required for a flow injection analysis (FIA) system consists of:

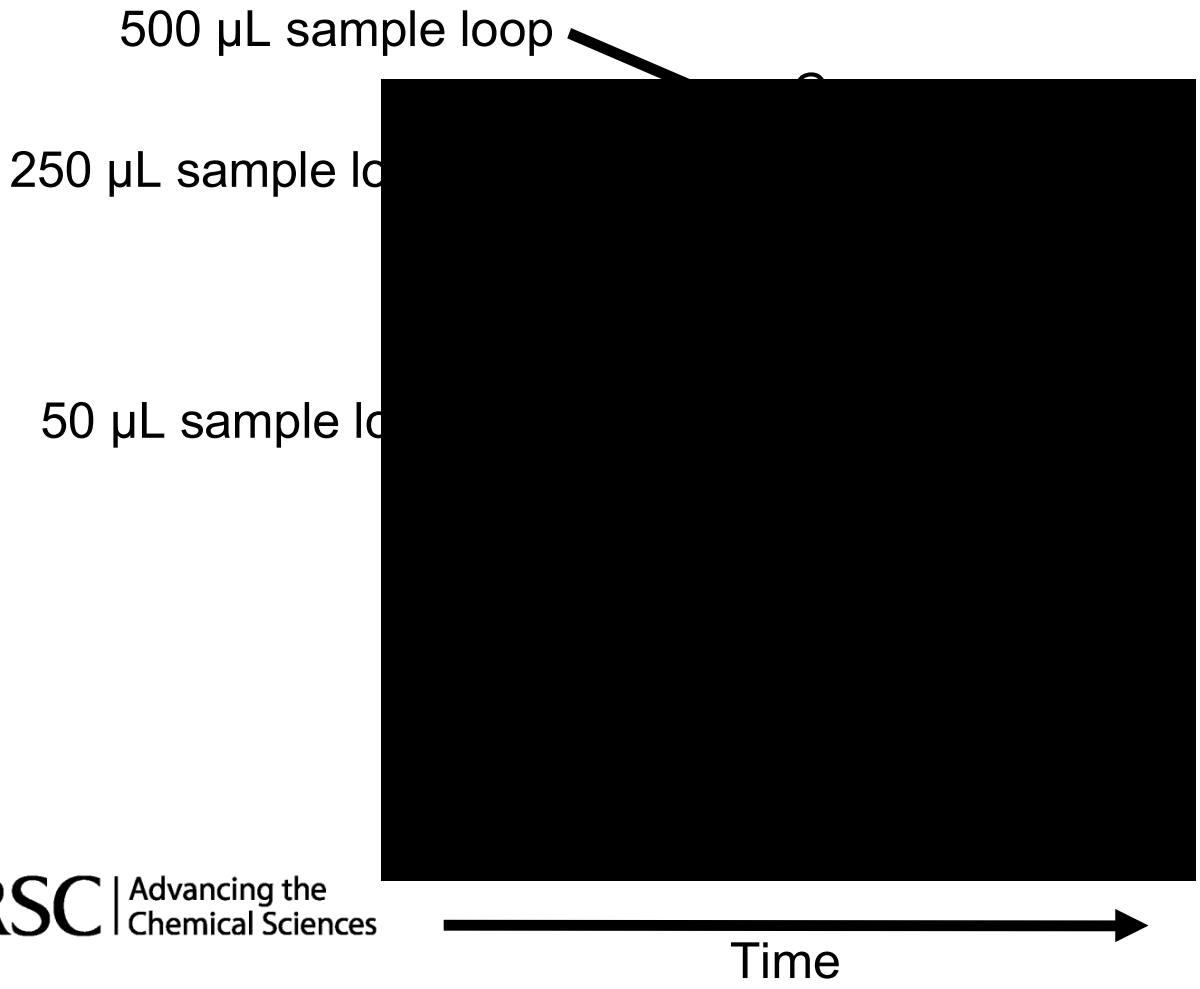
- A peristaltic pump to move liquid (carrier stream);
- An injection valve to introduce a small discrete sample or standard into the carrier stream;
- A sample processing stage (commonly called the reaction coil). This allows for
  - mixing of reagents/samples/standards;
  - dilution of the sample;
  - enrichment of the sample for trace analysis.
- A flow through detector to measure a response.

All of the components are connected to one another to produce a continuous moving and dynamic system that is capable of being automated.

Outline answer to question 14.5

The answer to this question can be found on slides 24 - 25.

The signal is influenced as follows by increasing the sample injection volume. It is shown that a larger injection volume of sample produces a larger system.



Outline answer to question 14.6

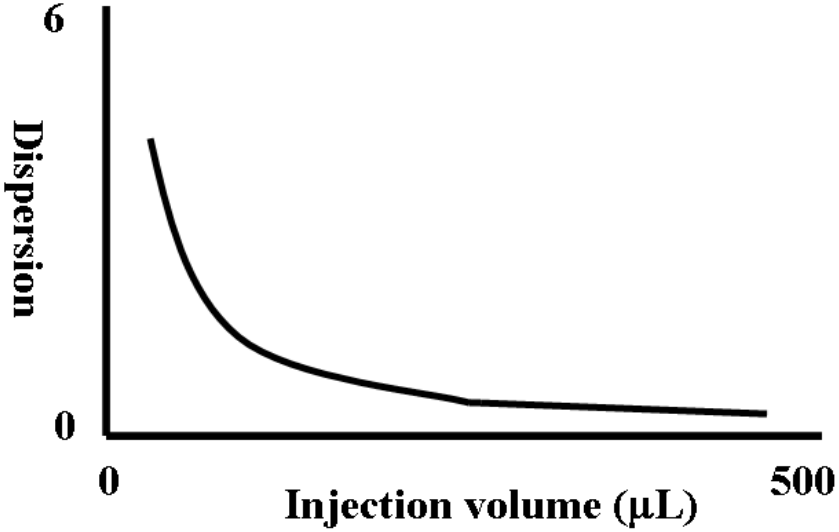
The answer to this question can be found on slide 23.

Dispersion (D) is defined as the ratio of concentrations before and after the dispersion process has taken place in the detector. This can be expressed by the following formula:

$$D = Co / Cmax$$

Where Co is the un-dispersed sample i.e. no dilution taking place between the sample injection valve and the detector while Cmax is a result of sample dispersion e.g. a flow injection detector response.

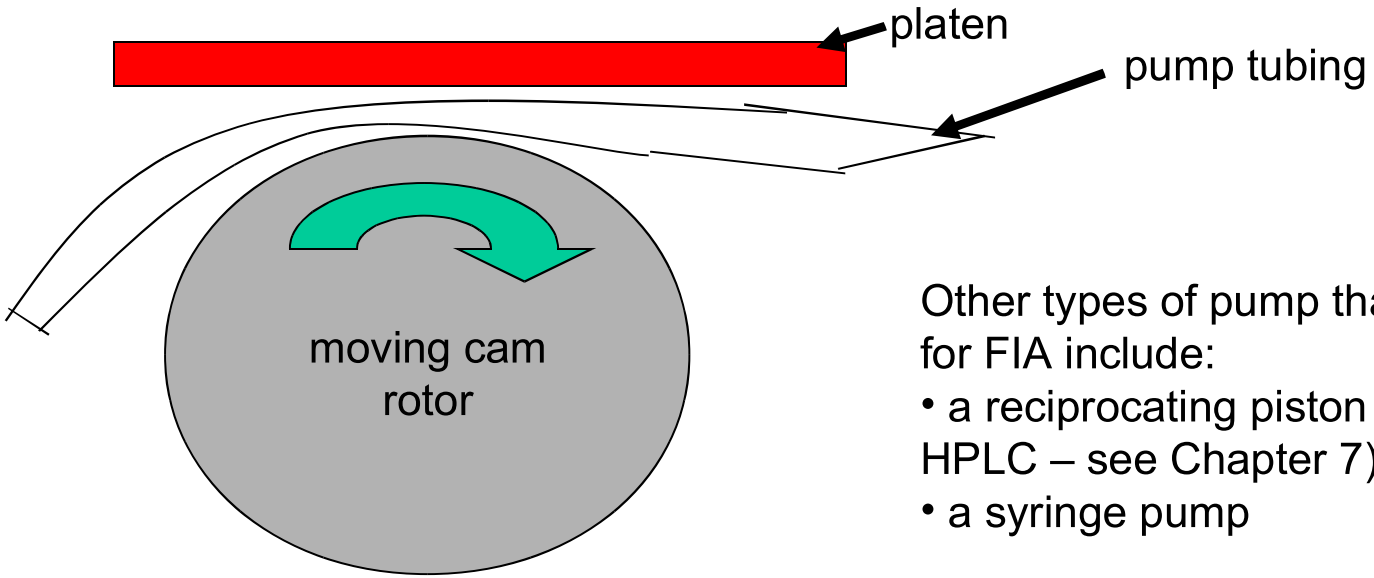
In the case of injection volume (Question 14.5) the influence on dispersion is as follows. An increase in peak height and sensitivity is achieved by the increasing sample loop volume. Conversely, dilution of concentrated sample material is achieved by reducing injection volume



Outline answer to question 14.7

The answer to this question can be found on slide 20.

The peristaltic pump works by rotating a series of rollers attached to the outside circumference which compress flexible pump tubing against a hard surface i.e. platen. The continual compression and relaxing (returning to normal dimensions) of the tubing, by the moving rotor, allows liquid to be moved forward. The multi-rollered nature of the pump means that more than one set of pump tubing can be in operation at the same time. In addition, by using different internal diameters of the flexible pump tubing, allows different flow rates to be achieved using a constant rotor speed.



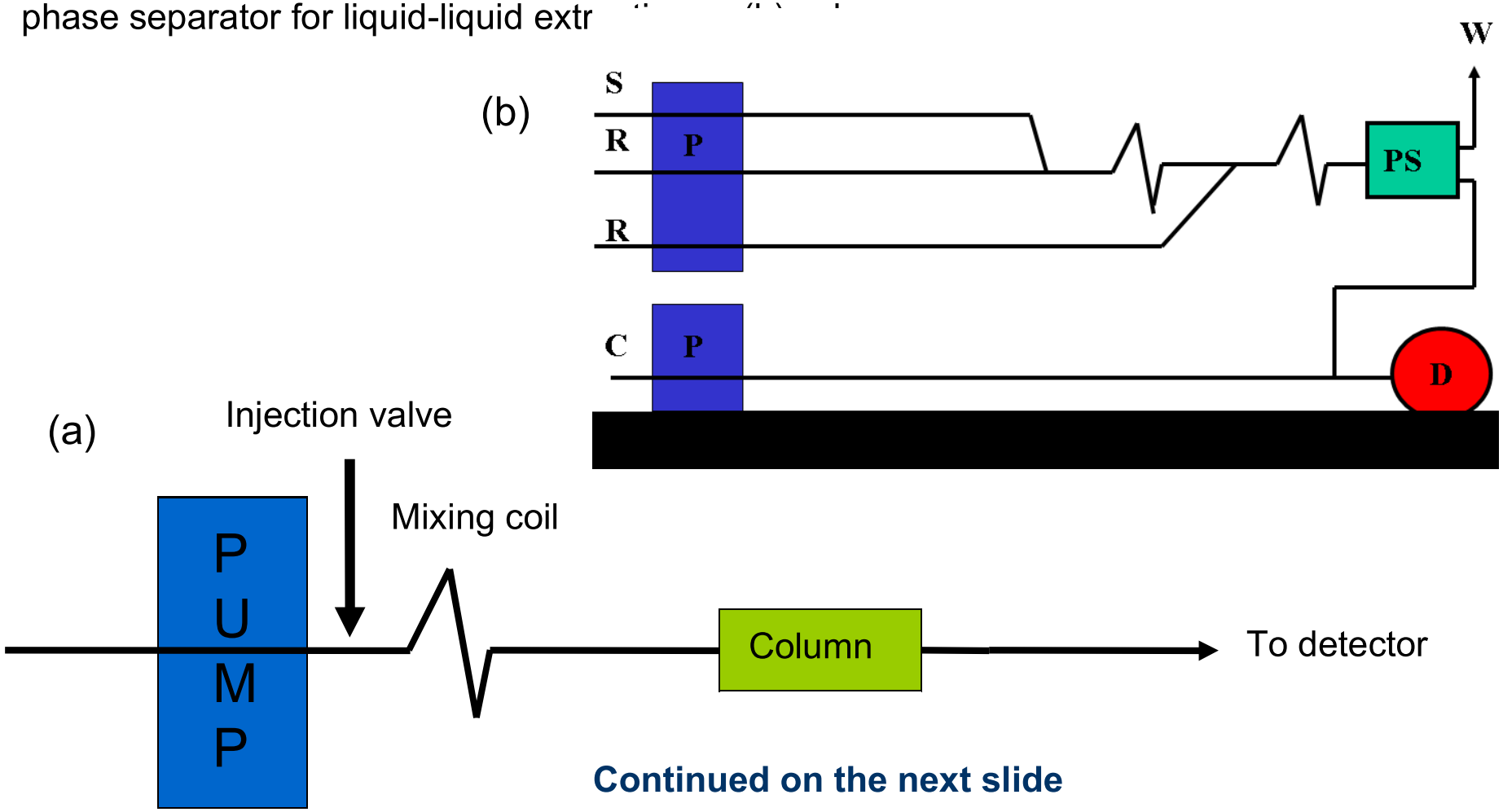
Other types of pump that could be used for FIA include:

- a reciprocating piston pump (As used for HPLC – see Chapter 7)
- a syringe pump

Outline answer to question 14.8

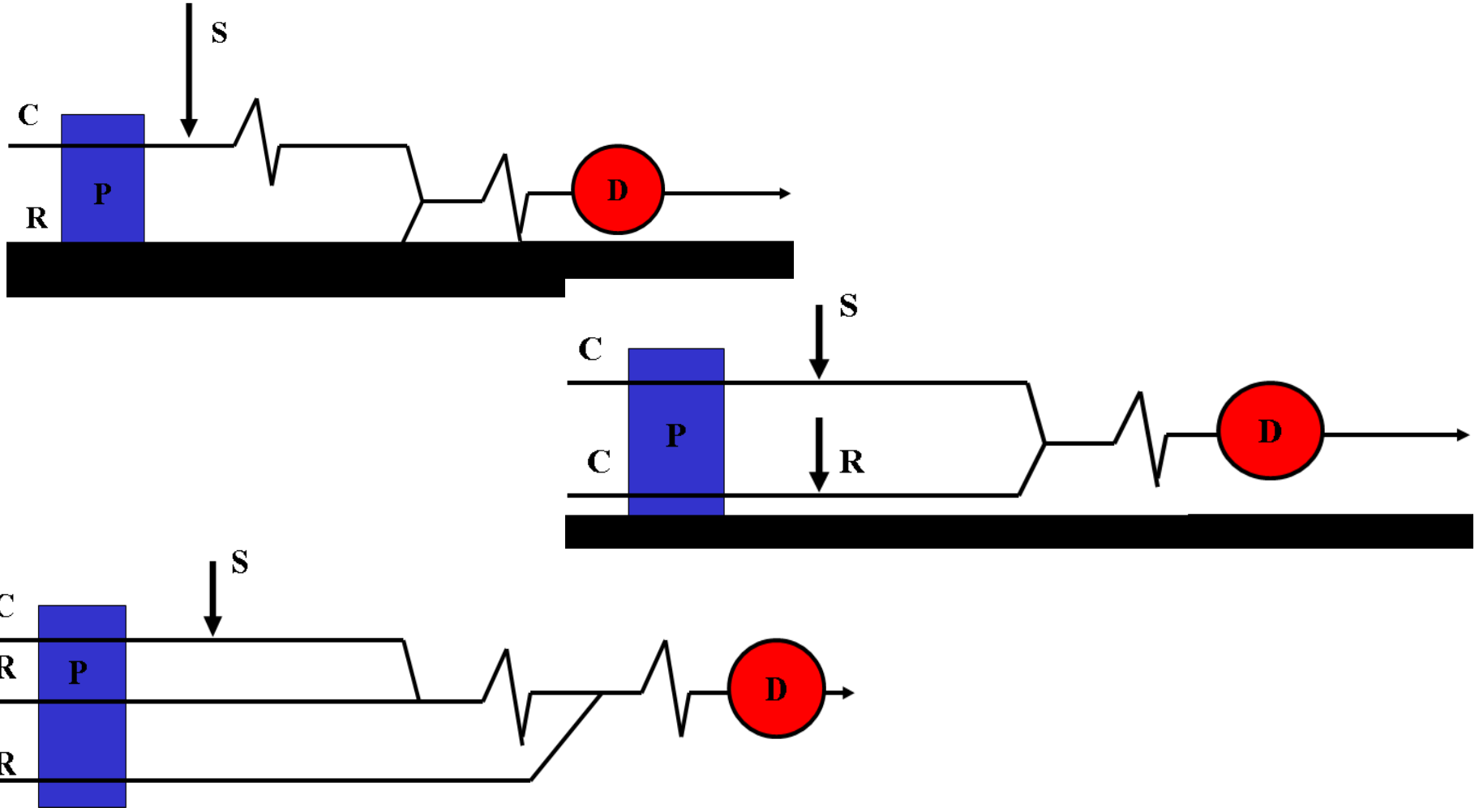
The answer to this question can be found on slide 28 and 33.

The essential component for sample pre-concentration in a FIA system is either (a) a phase separator for liquid-liquid extr



Continued on the next slide

The essential component for a colorimetric reaction in a FIA system is one of the following combinations. All three allow mixing of reagents with the sample prior to detection. The extent of the mixing can be controlled by the length and format of the mixing coil.



Outline answer to question 14.9

The answer to this question can be found on slides 33 - 39 and Chapter 7 of this teaching & learning programme.

At first consideration no difference is identified between a flow injection manifold and a high performance liquid chromatography system when illustrated in the form of a diagram. In practice a significant number of differences are observed relating to:

- solvent delivery system and type of solvents
- sample injection system
- nature, type and performance of columns
- detector types can be the same e.g. UV/Visible detector, but variation occurs in the size and scope of the sample cell that is used.
- connecting tubing, often stainless steel for HPLC and PEEK for FI.
- operating pressure of the system (lower pressure for FI)
- sophistication of the PC-based operating systems and level of automation.

Outline answer to question 14.10

The answer to this question can be found on slides 46 - 53.

The use of spectroscopic techniques offers PAC the possibility of non-invasive, in-line and continuous real time measurements of the process stream. The range of spectroscopic techniques that have been and are being used for PAC is extensive and includes:

• Infrared spectroscopy. Examples include the use of IR in industry, construction and manufactured materials, consumer products and finished goods, speciality manufacturing and fabrication applications

•Mass spectrometry. Examples include the use of MS in biotechnology, petrochemical, semiconductor and environmental industries.

• UV/Visible spectroscopy. Examples include the use of UV/Visible spectroscopy in environmental, petroleum refining and gas production, petrochemical and chemical industries, pharmaceutical processing, and wood pulp production for the paper industry.