Avtomatizirana analiza

Uvod

IUPAC ločuje med dvema pojmoma

- Avtomatski sistemi
- Avtomatizirani sistemi

Avtomatski sistemi

Avtomatski sistemi ne modificirajo svojega delovanja glede na povratno zanko iz analitskega senzorja.

Avtomatski titratorji le dodajajo reagent in sočasno določajo pH ali potencial v titracijski celici kot funkcijo dodanega volumna.

Avtomatizirani sistemi

Avtomatizirani sistemi vsebujejo eno ali več povratnih regulacijskih zank, ki kontrolirajo potek kemijske analize.

Nekateri titratorji glede na meritve potenciala in izračuna končne točke titracije spreminjajo količino dodanega reagenta.

Ostre meje meje med sistemoma ni in jo večina avtorjev izpušča.

Prednosti in slabosti avtomatizirane analize

- Zmanjšujejo strošek delovne sile
  - Avtomatski instrumenti omogočajo cenejše analize, vendar le v primeru, da je število vzorcev veliko in na ta način kompenziramo visoke začetne stroške investicije.
  - Ponavadi zahtevajo manj usposobljenega oziroma cenejšega operaterja.
- So hitrejši od neavtomatiziranih intrumentov – omogočajo nepretrgane meritve (monitoring).

Prednosti in slabosti avtomatizirane analize

- Dobro načrtovani analizatorji lahko producirajo bolj ponovljive rezultate skozi daljše časovno obdobje.

  Tudi samo delovanje instrumenta je bolj ponovljivo – uporabljamo lahko nepopolne kolorimetrične reakcije.

Avtomatski analizatorji so dveh tipov:

- *Diskretni analizatorji (ni kroskontaminacije)*
- *Pretočni analizatorji (kroskontaminacija vedno problem)*

Stopnje analiznega postopka

- Vse analizne postopke lahko razdelimo na osem faz (stopnje analiznega postopka). Vsaka od njih se lahko avtomatizira. Kar je prikazano v naslednji tabeli.

TABLE 33-1 Unit Operations in a Chemical Analysis

Operation	Typical Examples	Typical Type Automation[a]
1. Sample preparation	Grinding, homogenizing, drying	D
2. Sample definition	Determining sample weight or volume	D
3. Sample dissolution	Treating with solvent and diluting	C, D
	Heating, igniting, fusing	D
4. Separation	Precipitating and filtering	D
	Extracting, dialyzing, and chromatographing	C, D
5. Measurement	Determining absorbance, emission intensity, potential, current, and conductivity	C, D
	Titrating and weighing	D
6. Calibration	Running standards	C, D
7. Data reduction	Calculating result, analyzing data for accuracy and precision	C, D
8. Data presentation	Printing out numerical results, plotting data	C, D

[a] D = discrete; C = continuous flow

Diskretni analizatorji

A discrete analyzer automatically adds sample and reagent to a small cell, i.e. cuvette. It measures a reaction product while still in the cell or transfers it into a flow cell. It processes the sample in batches or individually.

Key advantages include speed and use of only microliter amounts of sample and reagent. It exactly mimics the operations of traditional manual wet chemistry methods.

Diskretni analizatorji

The DA 3500 Discrete Analyzer is a versatile, random access, colorimetric, automated chemistry analyzer. Using microliter amounts of sample and reagent in a reaction cuvette

Advantages of Using Discrete Automatic Chemistry Analysis for Wet Chemistry Analysis

- Much less sample volume than any other method, benefiting laboratories with small sample volumes (soil paste extracts)
- Low reagent consumption (about 3,000 tests per 25 mL for the nitrite method); only uses the exact reagent amount required for each test compared to a continuously-flowing system; generates less waste
- Automatic dilutions without added hardware
- No baselines to watch, no air bubbles to add, no peak shapes or flows to monitor
- No bubble formation in the flow cell
- No pump tubes to change or maintain
- Switch methods automatically without changing hardware
- True “walk away” capability
- Enormous improvements in setup, operational time, and ease of use
- Stable calibration curves over long periods of time

Disadvantages of Using Discrete Automatic Chemistry Analysis for Wet Chemistry Analysis

- Presently, discrete analyzers can only do simple colorimetric chemistries
- Cannot achieve ultralow detection limits
- Time-consuming sample preparation steps such as distillations, digestions, and matrix removal or enhancement performed manually before testing by a discrete analyzer.
- Cannot perform complex chemistries such as on-line gas diffusion, dialysis, distillations, extractions, and digestions

Kontinuirni analizatorji

Vse faze analize se izvajajo v toku nosilne tekočine (kontinuirnem ali segmentiranem)

- Analizatorji s segmentiranim tokom tekočine – SFA
- Pretočni injekcijski analizatorji – FIA
- Sekvenčni injekcijski analizatorji – SIA
- Laboratorij na ventilu - LOV

Segmented-Flow Analysis (SFA)

- The reaction stream is segmented with bubbles of air or nitrogen to reduce inter-sample dispersion.
- Faster analysis time and lower reagents consumption
- Complete reaction
- Sample concentration in the detector reaches a constant, maximum value (Steady State)

The output from a SFA system is a peak with a flat plateau. The plateau represents a constant, steady state value in the flowcell, at maximum concentration.

Segmented flow analysis

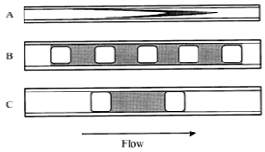
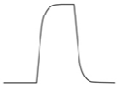


Figure 1. Sample profiles assumed in: A, Flow injection systems; B, Multisegmented systems and C, Monosegmented systems. The grey areas represent the regions occupied by the sample. The distinct flow patterns impart unique characteristics to the different systems. The scale for the transporting tubing reflects the practical reported values (0.5 to 1.0 mm for FI and 1.5 to 2.5 mm for the segmented systems).

The steady state SFA peaks maximize sensitivity in two ways



- The sample concentration in the flowcell reaches its maximum value, undiluted by wash or carrier solution.

- Maximum concentration is maintained for long enough to obtain an accurate reading. In contrast, the sample peak from a FIA system only reaches maximum concentration for an instant.

SFA System

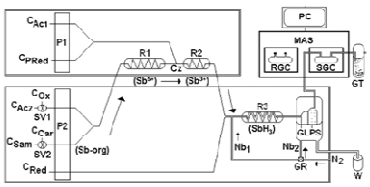
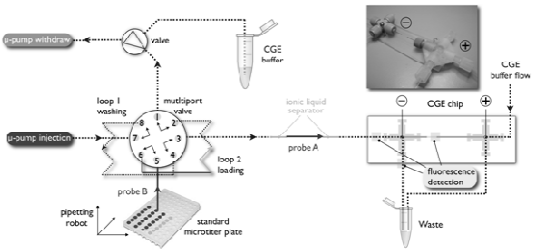


Figure 15. Schematic diagram of the 7A-HC-G7MAS coupled system proposed. C_{Ac}, acid agent; C_{PRed} pre-reducing agent; C_{Cx}, oxidizing agent; C_{Car}, carrier; C_{Sam}, sample/standard; C_{Red}, final reducing agent; P1, independent peristaltic pump; P2, peristaltic pump from the Varian GLPS system; SV, manual selecting valve; R1, oxidation/mineralization reaction coil; R2, pre-reducing reaction coil; R3, hydride generation coil; ⊡, confluence point; GLPS, gas-liquid phase separator; VGA-77; N_2, nitrogen gas entry; Nb, nitrogen branch; GR, regulated supply of nitrogen; MAS, molecular absorption spectrophotometer; RGC, reference gas cell; SGC, sample gas cell; PC, Computer; GT, gas trapper; W, waste; Sb-org, organic antimony. Further details are given in Table 15

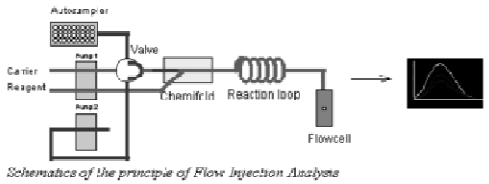
Primer kapilarne gelske elektroktroforeze



FLOW-INJECTION ANALYSIS...

Flow-injection methods, in their present form, were first described in the mid 70s. Flow-injection methods are and outgrowth of segmented-flow procedures, which were widely used in clinical laboratories in the 1960s and 1970s for automatic routine determination of a variety of species in blood and urine samples for medical diagnostic purposes.

Principles of Flow-Injection Analysis



Schematics of the principle of Flow Injection Analysis

Instrumentation...

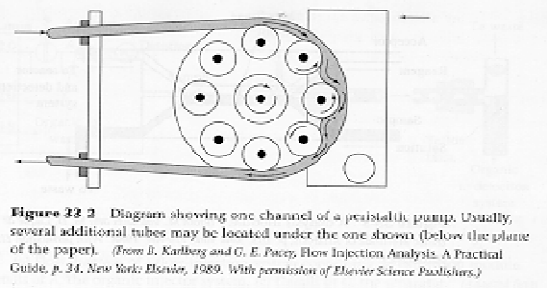


Figure 22.2 Diagram showing one channel of a peristaltic pump. Usually, several additional tubes may be located under the one shown (below the plane of the paper). *(From B. Karlberg and G. E. Pacey, Flow Injection Analysis. A Practical Guide, p. 34. New York: Elsevier, 1989. With permission of Elsevier Science Publishers.)*

Sample and Reagent Transport System...

- Ordinarily, the solution in a flow-injection analysis is moved through the system by a peristaltic pump, a device in which a fluid (liquid or gas) is squeezed through plastic tubing by rollers.

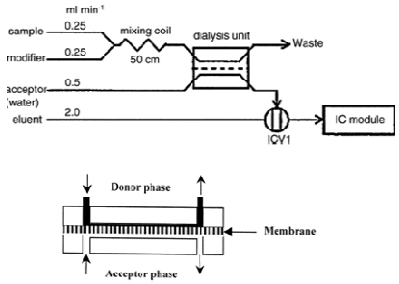
Sample Injectors and Detectors...

- The injectors and detectors employed in flow-injection analysis are similar in kind and performance requirements to those used in HPLC. For successful analysis, it is vital that the sample solution be infected rapidly as a pulse or plug of liquid

Separations in FIA...

- Separations by dialysis, by liquid/liquid extraction, and by gaseous diffusion are readily carried out automatically with flow-injection systems.

Dialysis



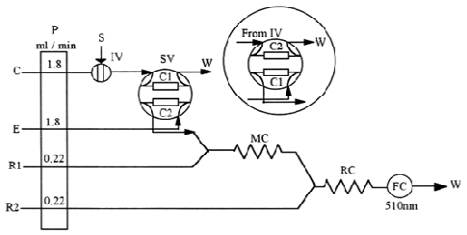
Dialysis and Gas Diffusion...

- Dialysis is often used continuous-flow methods to separate inorganic ions, such as chloride or sodium or small organic molecules, such as glucose, from high-molecular-weight species such as proteins.

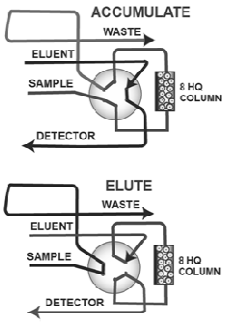
Extraction...

- Another common separation technique readily adapted to continuous-flow methods is extraction. It is important to reiterate that none of the separation procedures in FIA methods is ever complete. The lack of completeness is of no consequence, however, because unknowns and standards are treated an identical way.

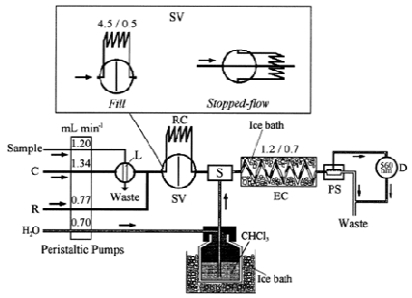
Protitočna ekstrakcija



Solid phase extraction



Liquid-liquid extraction



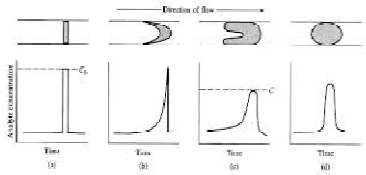
Dispersion...

Dispersion D is defined by the equation

$$D = c_o/c$$

where c_o is the analyte concentration of the injected sample and c is the peak concentration at the detector. Dispersion is influenced by three interrelated and controllable variables: sample volume, tube length, and pumping rate.

Dispersion



Applications of Flow-Injection Analysis

- In the flow-injection literature, the terms limited dispersion, medium dispersion, and large dispersion are frequently encountered where they refer to dispersions of 1 to 3, 3 to 10, and greater than 10, respectively.

Limited-Dispersion Applications…

- Limited-dispersion flow-injection techniques have found considerable application for high-speed feeding of such detector systems as flame atomic absorption and emission as well as inductively coupled plasma.

Application of Flow-Injection Analysis

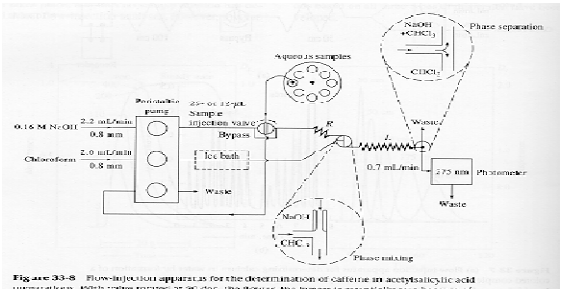
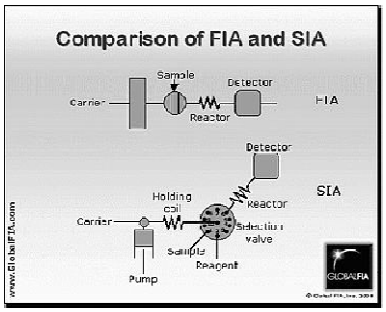
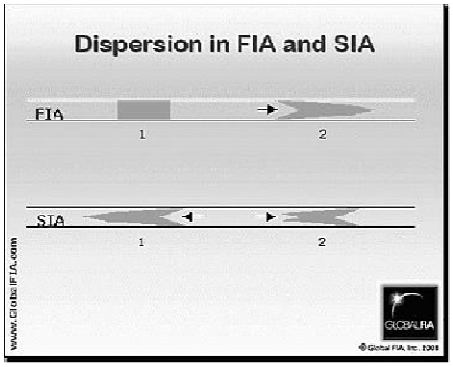


Figure 33-8 Flow-injection apparatus for the determination of caffeine in acetylsalicylic acid preparations. With valve mainly at 90°C, the flow in the bypass is essentially zero because of its small diameter. *b* and *L* are Teflon coils with 0.8-mm inside diameters; *L* has a length of 2 m, while the distance from the injection point through *B* to the mixing point is 0.15 m. [*Adapted from B. Karlberg and S. Thelander, Anal. Chim. Acta* **1978**, *98*, 1. With permission.]

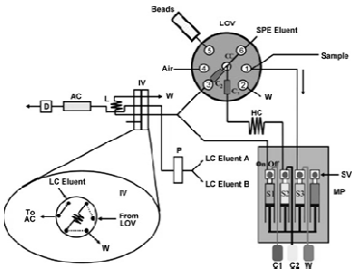
Sekvenčna injekcijska analiza (SIA)

- **Analizne operacije** se izvajajo v zaporedju-sekvenc. Njihovo delovanje in trajanje uravnava računalnik.
- **Osnovne komponente**: injekcijska batna črpalka, večporni izbirni ventil, detektor, mešalne tuljave, računalnik.
- **Potek operacij**
  - Injeciranje vzorca
  - Kontrolirano mešanje
  - Detekcija
  - Izpiranje





Laboratorij na ventilu



Težnja po miniaturizaciji

Automatic Sampling and Sample Definition of Liquids and Gases...

- This device consists of a movable probe, which is a syringe needle or a piece of fine plastic tubing supported by an arm that periodically lifts the tip of the needle or tube form the sample container and positions it over asecond container in which the analysis is performed.

Robotics...

- The robotic system is controlled by a microprocessor that can be instructed to bring samples to the master laboratory station where they can be diluted, filtered, partitioned, ground, centrifuged, extracted, and treated with reagents.

Useful Websites Dealing With Instrumental Analysis...

- http://www.cas.org
- http://www.chemcenter/org
- http://www.kerouac.pharm.uky.edu/asrg/wave/wavehp.html
- http://www.anachem.umu.se/jumpstation.htm
- http://www.lplc.com/
- http://www.zirchrom.com/
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- http://www.chrom.com/