

# ***Minerals and trace elements analysis in food***

## **Definition:**

- constituents of ash of the food sample  
(a residue remaining after total oxidation of organic matter)
- major mineral elements: K, Na, Mg, Ca, P, Cl
- trace elements: Fe, Zn, Cu, Mn, Ni, Co, Mo, Cr, V, Se, I, F, B, Si, Pb, Cd, Hg, As, Al, Sn...

## **Why these elements are determined?**

- to know and evaluate the composition of food or agricultural products or another raw material from nutritional point of view
  - natural content of essential elements
  - fortification of food product by compounds of Fe, Ca...
- to check food safety – content of toxic elements (Pb, Cd, Hg, As etc.)
- to control some technologically important properties of raw material or the final product

## ***Ash***

- a rough indicator of the total content of mineral elements
- gravimetric determination of sample ash after sample charring and flameless combustion (ignition in a porcelain crucible at 500-600°C)
- insoluble ash (= a portion of ash insoluble in 10 % HCl – it contains mostly silicates) – determined gravimetrically
- conductometric determination of ash

## ***Analytical procedure applied for element's determination***

- sample preparation, preparation of blank samples (mostly sample decomposition)
- (separation and preconcentration of the element)
- measurement of element's concentrations in treated samples and blanks
- data treatment
  - calculation of detection and quantification limits
  - calculation of the element content in the samples

## ***Ways of sample preparation***

**when a conventional (destructive) method is to be used**

- decomposition
- extraction by diluted acids (HCl, HNO<sub>3</sub>, EDTA)
- dilution of liquid samples by diluted HNO<sub>3</sub>, or a surfactant solution
- preparation of slurry of the powdered sample  
→ ET AAS

**when a non-destructive method\* is to be used**

- freeze drying and sealing into an ampoule
- \* **Some non-destructive methods:**  
INAA (*instrumental neutron activation analysis*)  
XRF (*X-ray fluorescence spectrometry*)

## ***Sample decomposition***

Aim: – removal of the organic matrix of the sample (oxidation)  
– transfer of analytes into a solution

Decomp.: total (mineralization) or partial (solubilization)

- **dry decomposition**
  - a classical one (dry ashing)
  - modern versions of dry decomposition
- **wet decomposition**
  - under normal pressure – in open vessels
  - under high pressure – in closed vessels

## Classical dry ashing

- it takes place in an open vessel (silica crucible, Pt crucible or dish, borosilicate glass beaker) under atmospheric pressure and high temperature (max. 450-550°C);  
the sample is oxidised by air oxygen → ash  
→ ash solution (extract)
- sample weight 1-25 g of dry matter
- additional reagents (ashing aids):  $\text{HNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4$
- application: unsuitable for determination of volatile elements (Hg)
- for As, Se or P determination an addition of  $\text{Mg}(\text{NO}_3)_2$  is necessary

## Dry ashing

Step	Temp., time	Device	Remark
1. drying	<110°C 1-2 h	drying oven or programmable furnace	optional addition of ashing aid*
2. charring	<350°C 8-20 h	hot plate or program. furnace	slow rise of temperature
3. combustion	450-500°C 12-20 h	programmable furnace	addition of ashing aid ** at the end of the step
4. ash dissolution	20-100°C 0,5-1 h	hot plate	final concentration of an acid (HCl or $\text{HNO}_3$ ): 0,1-1 M

\* mostly  $\text{Mg}(\text{NO}_3)_2$

\*\* addition of  $\text{HNO}_3$ , evaporation to dryness, ignition in the furnace at 450-500°C for 1-4 h

## Advantages and disadvantages of dry ashing

- high efficiency of decomposition
- large sample weights
- low consumption of reagents
- low cost
- low safety risks
- losses of some analytes (volatile elements Hg, Tl, Se, As, P...)\* → cannot be used for detn. of all elements
- sample contamination
- inconvenient for liquid samples
- time-consuming procedure

\* losses of P, As, Se are negligible if  $\text{Mg}(\text{NO}_3)_2$  is added as an ashing aid  
– convenient for As or Se determination by HG-AAS method

## *Classical wet decomposition*

i.e. decomposition by mixture of inorganic acids under normal pressure and high temperature

- in general more versatile than dry ashing (but unsuitable for determination of halogenides  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ )
- duration of decomposition: several hours
- sample weight 0.5-3 g of dry matter, or less (0.2-1 g) when  $\text{HClO}_4$  is used (risk of explosion!)
- crucial parameter – time-temperature programme (it affects safety of the procedure and recovery of the elements)
- a semi-closed glass apparatus is necessary for determination of Hg

## Reagents for wet decomposition

Reagent	t (°C)	Remark
diluted HCl	60-120	sample hydrolysis only → solubilization
HCl+HNO <sub>3</sub> (3+1)	60-120	for decomposition of soil samples
HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub>	60-180	the most common mixture, losses of Se (As), insoluble Ca, Sr, Ba, Pb sulphates
HNO <sub>3</sub>	60-120	low efficiency, losses of Hg
HNO <sub>3</sub> +H <sub>2</sub> O <sub>2</sub>	60-120	low efficiency, losses of Hg
HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub>	60-180	losses of Se and As are lower
HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub> + HClO <sub>4</sub>	60-210	high efficiency, suitable for Se, As, Hg detn.; losses of Pb; risk of explosion!
HNO <sub>3</sub> + HClO <sub>4</sub>	60-200	no losses of Pb, higher losses of Hg; higher risk of explosion!

When decomposition is completed HNO<sub>3</sub> is normally evaporated from the mixture.

## *Wet decomposition under high pressure*

- a modern method used in analytical laboratories most often
- closed decomposition vessels
  - made of teflon (PTFE) – temp. limit approx. 240 °C
  - made of silica glass – used up to 320 °C
- sample weight 0.2-1 g of dry matter  
(a large sample weight → explosion!)
- reagents: HNO<sub>3</sub>, HNO<sub>3</sub>+H<sub>2</sub>O<sub>2</sub>,  
HNO<sub>3</sub>+HF (only in PTFE)
- heating
  - conventional heating of the whole vessel
  - microwave heating → easy control of the process

## Pressure decomposition

- safety: sample oxidation produce a lot of gaseous products (nitrogen oxides, CO<sub>2</sub>, water vapour)  
→ pressure increases (units to tens of MPa); vessels are placed in massive jackets made of steel or PEEK; sensors monitor pressure and optionally both pressure and temperature inside the vessels; when pressure exceeds the chosen limit microwave heating is stopped; in the case of explosive reaction a controlled expansion occurs
- efficiency of decomposition: at  $t < 200$  °C partial decomp. only (pressure solubilization); final  $t > 280$  °C is needed to achieve the complete destruction of organic matter (necessary when a voltammetric method of determination is to be used)
- duration (decomposition and cooling): 20 min to 2 h

## Advantages and disadvantages of pressure decomposition

- |                                                                             |                                                                                                                             |
|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|
| • almost no losses of analytes                                              | • expensive equipment                                                                                                       |
| • minimal contamination                                                     | • low sample weight<br>→ a sample has to be homogenous                                                                      |
| • much safer than decomp. using an HClO <sub>4</sub> containing mixture     | • lower efficiency at $t < 200$ °C                                                                                          |
| • no difficulties associated with the use of H <sub>2</sub> SO <sub>4</sub> | • resulting solution contains HNO <sub>3</sub><br>→ interference in hydride generation determination of As, Se, Sb, Sn etc. |
| • low consumption of acids                                                  |                                                                                                                             |
| • fast decomposition (microwave)<br>→ automation                            |                                                                                                                             |

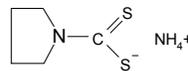
## **Analytes' separation and enrichment**

- mostly done in one step
- **separation** – needed when analytical method is not selective enough (some spectrophotometric measurements) or in the case of strong interference caused by sample matrix (ET AAS analysis of some difficult samples)
- **enrichment (pre-concentration)** – for trace element analysis; applied when analytical method is not sensitive enough; prerequisite: a large amount of sample has to be available

Whenever separation and/or enrichment steps are not absolutely necessary leave them out of the procedure to keep the analysis as simple as possible. Highly sensitive and selective methods that do not require a separation step should be used preferentially.

## **Separation and enrichment methods**

- **extraction of metal chelates** – formation of the metal complex with a suitable (mostly organic) reagent and its extraction from aqueous phase to organic solvent  
example: metal chelates with APDC – extraction into MIBK (methylisobutylketone)



→ increased sensitivity of F AAS analysis

- **sorption at ion-exchangers** – e.g. preconcentration of transition metal ions on chelating ion-exchangers and separation from alkali elements and anions

## Separation and enrichment methods

- **analyte's conversion into a volatile species and its transfer to a gaseous state** – applied e.g. in the hydride generation technique of AAS or ICP-OES for detn. of As, Se, Sb, Te, Sn... (formation of hydrides such as  $\text{AsH}_3$ ...); or in the cold vapour technique of AAS for Hg determination
- **electrolysis**
  - the first step of determination of metals and some metalloids by electrochemical stripping analysis (e.g. stripping voltammetry)
  - electrodeposition of the analyte in the graphite furnace before its determination by ET AAS

## *List of analytical method*

- classical chemical methods – gravimetric and titrimetric
- spectrophotometric methods
- fluorometry (determination of Se)
- atomic absorption spectrometry
- atomic emission spectrometry
  - flame atomic (optical) emission spectrometry  
F AES, F OES (flame photometry)
  - inductively coupled plasma atomic (optical) emission spectrometry ICP-AES, ICP-OES
- mass spectrometry (namely ICP-MS)
- electrochemical methods: potentiometry, polarography and voltammetry

## List of analytical methods

- other methods
  - HPLC: determination of anions  
( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{I}^-$ ...)
  - GC: determination of Se,  
determination of Hg and Sn compounds
  - isotachopheresis
  - NAA
  - XRF
  - PIXE

## ***Gravimetric and titrimetric determinations of elements***

Limitation: applicable for major elements only

### **Gravimetric determination of calcium**

- $\text{CaC}_2\text{O}_4$  precipitation by ammonium oxalate
- substance weighed  $\text{CaSO}_4$

### **Gravimetric determination of magnesium and phosphorus**

- both  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  can be precipitated as  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$  with a solution of ammonium phosphate or that of magnesium chloride, ammonium chloride and ammonia, respectively
- substance weighed  $\text{Mg}_2\text{P}_2\text{O}_7$

## Complexometric determination of calcium and magnesium

two back titrations

1. determination of Ca + Mg sum  
an aliquot of sample + ammonia buffer solution (pH=10)  
+ excessive amount of Na<sub>2</sub>EDTA, titration of the excess with standard solution of Mg<sup>2+</sup> using EBT as an indicator  
(blue → violet colour)
2. determination of Ca  
an aliquot of sample + KOH (pH=12 → Mg(OH)<sub>2</sub> precipitation)  
+ excessive amount of Na<sub>2</sub>EDTA, titration of the excess with standard solution of Ca<sup>2+</sup> using fluorexon as an indicator  
(pink colour → yellow-green fluorescence)

## Titrimetric determination of chlorides

- Sample preparation:
  - dry ashing, ash leaching in hot water (+HNO<sub>3</sub>)
  - hot water extraction of Cl<sup>-</sup> from a sample, clarification of the extract (Carrez reagent)
- Argentometric determination
  - Mohr's method:  $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$   
indicator K<sub>2</sub>CrO<sub>4</sub> (excess AgNO<sub>3</sub> → red-brownish Ag<sub>2</sub>CrO<sub>4</sub>)  
potentiometric indication also possible
  - Volhard's method: back titration of Ag<sup>+</sup> excess with thiocyanate using NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub> as an indicator
- Mercurimetric determination:  
Votoček's method:  $\text{Hg}^{2+} + 2 \text{Cl}^- \rightarrow \text{HgCl}_2$   
indicator: Na<sub>2</sub>[Fe(CN)<sub>5</sub>NO]  
(excess of Hg(NO<sub>3</sub>)<sub>2</sub> → white mist of Hg[Fe(CN)<sub>5</sub>NO])

## Determination of elements by spectrophotometric methods

### Principle

- chelate-forming reactions:  
metal cation + (organic) reagent  
→ coloured product
  - oxidation-reduction reactions:  
→ coloured product
- } absorbance measurement

### Typical features of the methods

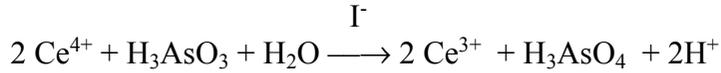
- complex procedures → time-consuming analysis  
(limited selectivity of analytical reactions in some cases)
- sensitivity is given by  $b \cdot \epsilon$  value

## Spectrophotometric determination of phosphorus

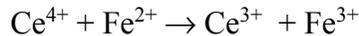
- after wet digestion a sample contains  $\text{H}_3\text{PO}_4$
- in acidic solution  $\text{H}_3\text{PO}_4$  forms with an excess of molybdate a weakly yellow-coloured molybdophosphoric acid  $\text{H}_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$  strongly absorbing UV light ( $\lambda_{\text{max}} = 310 \text{ nm}$ ).
- so called molybdenum blue is then formed by reduction of molybdophosphoric acid (using e.g. hydrazine, ascorbic acid, or ferrous ions etc.);  
molybdenum blue is a mixture of heteropolyacids of Mo in oxidation state V and VI;  $\lambda_{\text{max}}$  value is 660-820 nm (it depends on the reaction conditions);  
absorbance of the solution is proportional to P concentration (As, Si and Ge yield analogous products under similar conditions)

## Spectrophotometric determination of iodine

- it utilizes catalytic action of  $I^-$  on Sandell-Kolthoff reaction
- an aliquot of the sample + arsenious acid + cerium (IV) sulphate



after a specific period of time (e.g. exactly 20 min) the drop of  $Ce^{4+}$  concentration is measured e.g. based on subsequent reaction of  $Ce^{4+}$  ions:



formation of ferric ions is detected with thiocyanates

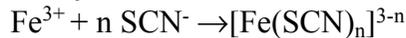
( $\rightarrow$  red-coloured product,  $\lambda=480$  nm);

calibration within the interval of 0 to 50 ng I

calibration line ( $A$  vs.  $m_1$ ) has a negative slope

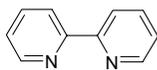
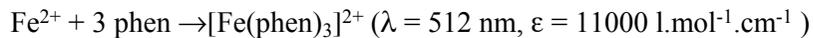
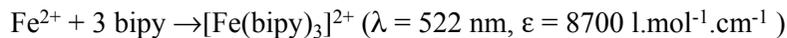
## Spectrophotometric determination of iron

- in an acidic solution (HCl)  $Fe^{3+}$  gives a red complex with thiocyanate

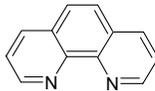


- in weakly acidic solutions (pH 3-6)  $Fe^{2+}$  gives red or red-orange complexes with 2,2'-bipyridine (formula I) or 1,10-phenanthroline (formula II)

$Fe^{3+}$  is firstly reduced to  $Fe^{2+}$  with  $NH_2OH.HCl$



I



II

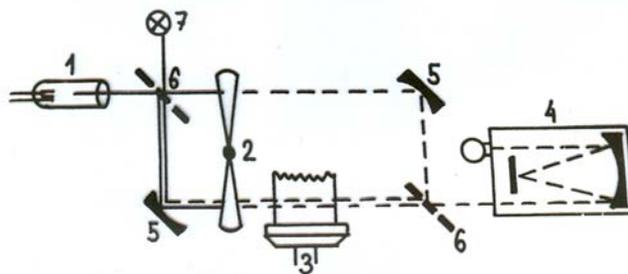
# ***Determination of elements by atomic absorption spectrometry***

## **Techniques of AAS**

- flame (F AAS)
- electrothermal (ET AAS), graphite furnace (GF AAS)
- hydride generation (HG AAS)
- cold vapour (CV AAS)

Note: hydride generation and cold vapour techniques are sometimes designated as *vapour generation technique* – VG AAS

## **Scheme of AAS**



- 1 – hollow cathode lamp
- 2 – beam modulator
- 3 – absorbing area (flame, electrothermal atomizer)
- 4 – monochromator and detector
- 5 – concave mirrors
- 6 – semipermeable mirrors
- 7 – deuterium lamp

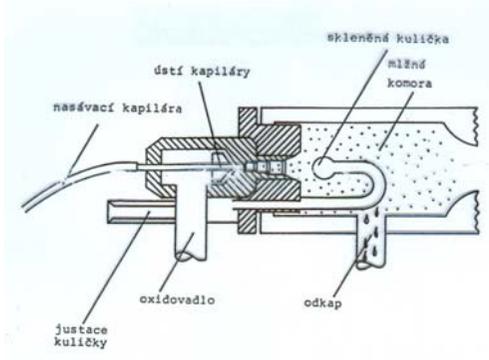
## Flame AAS

- determination of metals, boron and silicon at conc. approx.  $10^{-2}$ - $10^2$  mg/l
- sample solution in diluted mineral acid → aerosol → → flame (evaporation and atomization) → → absorbance measurement
- flames
  - $C_2H_2$ -air: atomization of Na, K, Mg, Ca, Mn, Fe, Ni, Cu, Zn, (Co, Cd, Pb – high concentrations only)
  - $C_2H_2$ - $N_2O$ : atomization of Al, Ca, Mg, Sr, Ba, Sn, (Mo, V, Cr...)
- fast, cheap analysis, easy automation possible

## F AAS

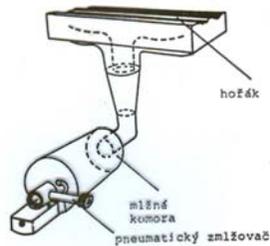
Sensitivity of F AAS measurement is expressed indirectly as so called *characteristic concentration* = the conc. of the element (in mg/l) resulting in absorbance  $A = 0.0044$ .

Element	$\lambda$ (nm)	Flame	Characteristic concentration (mg/l)
Zn	213.9	air- $C_2H_2$	0.007-0.010
Pb	217.0	air- $C_2H_2$	0.07-0.10
Al	309.3	$N_2O$ - $C_2H_2$	0.75
Mo	313.3	$N_2O$ - $C_2H_2$	0.50



## F AAS

Nebulizer  
and spray chamber



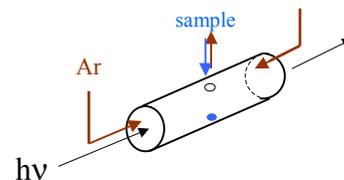
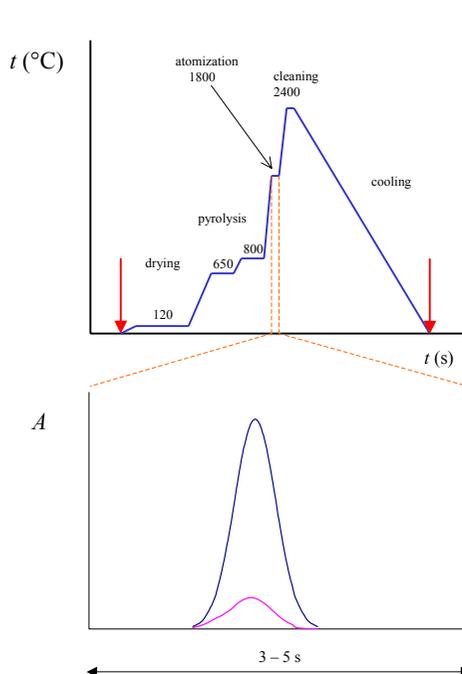
Nebulizer – burner system

## Application of F AAS

- determination of Na, K –  $C_2H_2$ -air flame  
addition of deionisation agent CsCl
- determination of Mg, Ca
  - $C_2H_2$ -air flame – addition of releasing agent (typically  $LaCl_3$ ) is necessary
  - $C_2H_2-N_2O$  flame – addition of deionisation agent (CsCl or KCl) is necessary
- determination of Mn, Fe, Ni, Cu, Zn –  $C_2H_2$ -air flame  
(Fe, Ni:  $C_2H_2-N_2O$  is also possible)

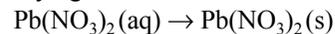
## Electrothermal AAS

- highly sensitive method for determination of elements at  $10^{-2}$ - $10^2$   $\mu\text{g/l}$  concentrations
- atomizer: mostly graphite furnace (tube)
- injection of a single volume of sample (5-50  $\mu\text{l}$ ) into the tube
- steps of analysis:
  - injection
  - drying
  - pyrolysis (thermal decomp., „ashing“)
  - atomization
  - cleaning of atomizer
  - cooling
- temp. programme is chosen according to properties of the element, sample composition and the type of atomizer
- slow analysis (1.5-4 min), expensive instruments

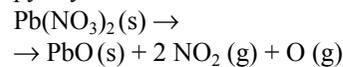


Processes taking place in the tube during determination of Pb

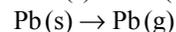
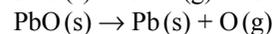
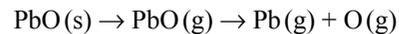
drying:



pyrolysis:



atomization:



## Application of ET AAS

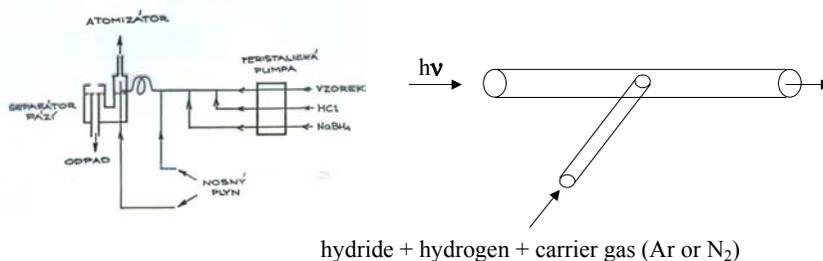
- determination of trace amounts of Pb, Cd, Tl, Al, Cr, V, Mo, Co, Cu, Sn, (As, Se, Sb) etc.
- samples:
  - decomposed samples (mostly in  $\text{HNO}_3$ )
  - biol. fluids (blood, plasma, milk, urine...)
  - and beverages – with or without decomposition
  - slurries of powdered solids
- addition of matrix modifiers (e.g.  $\text{NH}_4\text{H}_2\text{PO}_4 + \text{Mg}(\text{NO}_3)_2$ , Pd comp.) → optimum course of pyrolysis and atomization

	$\lambda$ (nm)	$t_{\text{pyrol.}}$ (°C)	$t_{\text{atom.}}$ (°C)	characteristic mass (pg)	detection limit (20 $\mu\text{l}$ injection)
Cd	228.8	300-800	1400-1600	0.35	approx. 0,01 $\mu\text{g/l}$
Pb	283.3	400-850	1600-1800	12	approx. 0.25 $\mu\text{g/l}$

\* it depends on the type of atomizer, kind of sample and matrix modifier

## Hydride generation AAS

- applied for detn. of As, Se, Sb, Te, Bi, Ge, Sn, Pb (metals and metalloids forming gaseous hydrides i.e. binary compounds with hydrogen)
- hydride formation takes place in so called *hydride generator* (continuum type is shown) mostly in HCl solution by sample reaction with  $\text{NaBH}_4$ ; analyte is then transferred to a gaseous state and delivered to an *atomizer* (mostly heated quartz T-tube)



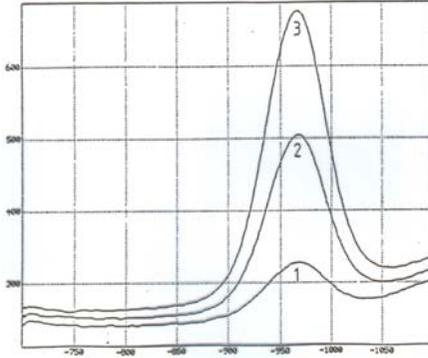
## Chemistry of As and Se determination by HG AAS

- sample decomposition (wet digestion  $\text{HNO}_3 + \text{H}_2\text{SO}_4 (+\text{HClO}_4)$  or dry ashing with  $\text{Mg}(\text{NO}_3)_2$  and dissolution in  $\text{HCl}$ ) is accompanied by oxidation of the analytes to high or the highest oxidation state  $\Rightarrow$  reduction to lower ox. state ( $\text{As}^{\text{V}} \rightarrow \text{As}^{\text{III}}$ ,  $\text{Se}^{\text{VI}} \rightarrow \text{Se}^{\text{IV}}$ ) is needed:  
$$\text{H}_3\text{AsO}_4 + 2 \text{I}^- + 2 \text{H}^+ \rightarrow \text{H}_3\text{AsO}_3 + \text{I}_2 + \text{H}_2\text{O}$$
$$\text{H}_2\text{SeO}_4 + 2 \text{Cl}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{SeO}_3 + \text{Cl}_2 + \text{H}_2\text{O}$$
- reaction of the reduced compound with sodium borohydride ( $\text{NaBH}_4$ ) in acidic solution (most often  $\text{HCl}$ ):  
$$\text{BH}_4^- + \text{H}^+ + 3 \text{H}_2\text{O} \rightarrow \text{H}_3\text{BO}_3 + 8 \text{H}$$
$$\text{H}_3\text{AsO}_3 + 6 \text{H} \rightarrow \text{AsH}_3 + 3 \text{H}_2\text{O}$$
$$\text{H}_2\text{SeO}_3 + 6 \text{H} \rightarrow \text{H}_2\text{Se} + 3 \text{H}_2\text{O}$$
- the hydride ( $\text{AsH}_3$  or  $\text{H}_2\text{Se}$ ) yields atoms of analyte under high temperature in the atomizer via thermal dissociation and radical reactions; trace of oxygen is necessary to be present
- absorbance at 193.7 nm (As) or at 196.0 nm (Se) is measured  
– detection limit approx. 0.1-0.3  $\mu\text{g/l}$

## Electrochemical methods

- potentiometry with ISE:  
determination of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$
- classical polarography (DC)  
determination of Zn, Cu, Sn:  
$$\text{M}^{2+} + 2 \text{e}^- \rightarrow \text{M} \quad (\text{M} = \text{Zn}, \text{Cu})$$
$$\text{Sn}^{4+} + 4 \text{e}^- \rightarrow \text{Sn} \quad (\text{only in HCl solution})$$
  
determination of  $\text{I}^-$ :  
$$\text{I}^- + 3 \text{BrO}^- \rightarrow \text{IO}_3^- + 3 \text{Br}^-$$
$$\text{IO}_3^- + 3 \text{H}_2\text{O} + 6 \text{e}^- \rightarrow \text{I}^- + 6 \text{OH}^-$$
- differential pulse polarography (DPP) and voltammetry (DPV) – peak-shaped curves,  
much lower detection limits in comparison with classical polarography

## Voltammetric determination of Zn



DPV

$E_p = -700 \text{ mV}$

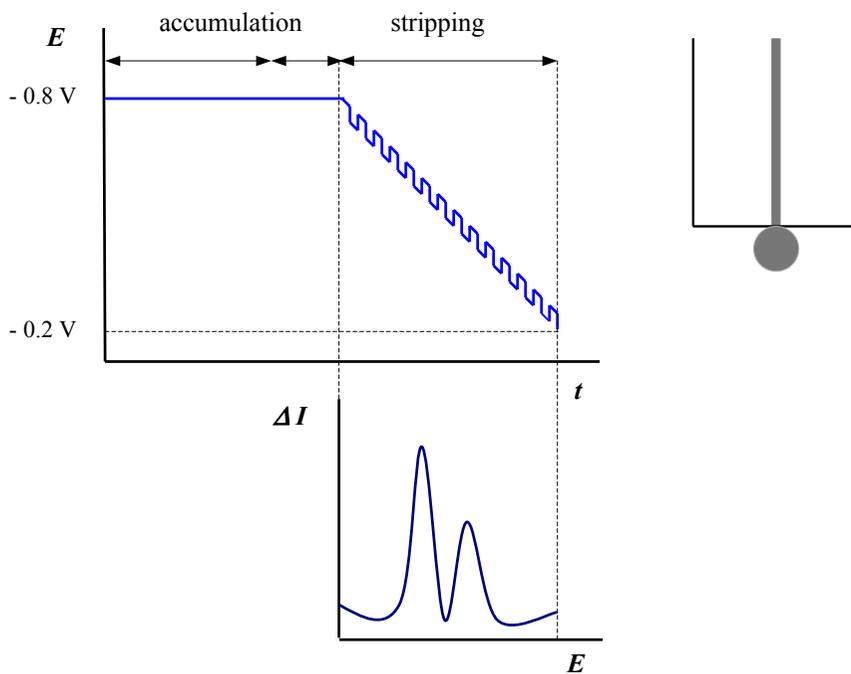
(1) : 5 ml sample in 0.1 M  $\text{HNO}_3$   
+ 1.5 ml 1M  $\text{CH}_3\text{COONa}$

(2) : (1) + 5  $\mu\text{g}$  Zn, V = 6.75 ml

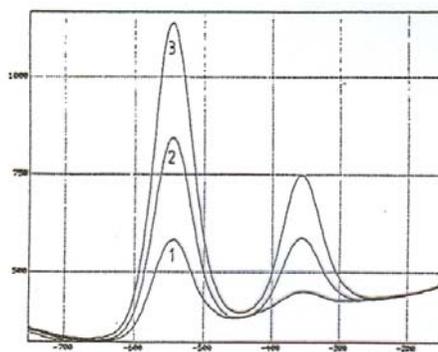
(3) : (1) + 10  $\mu\text{g}$  Zn, V = 7.0 ml

## Electrochemical methods

- stripping voltammetry  
intended for trace and ultratrace analysis
  - anodic stripping voltammetry (ASV, DPASV)
    - using Hg electrodes: detn. of Cd, Pb, Cu, Zn, Tl, Bi...  
(see the scheme at the following page)
    - using Au electrodes: detn. of Hg, Se, As
  - cathodic stripping voltammetry (CSV, DPCSV):  
determination of Se, As, I...
- main features of stripping voltammetry  
(compared with and spectrometric methods):
  - very low detection limits (comparable with ET AAS or lower)
  - time-consuming analysis
  - relatively cheap instruments
  - sample decomposition has to be absolutely complete



## Voltammetric determination of Cd and Pb



DPASV

$E_d = -750\text{ mV}$

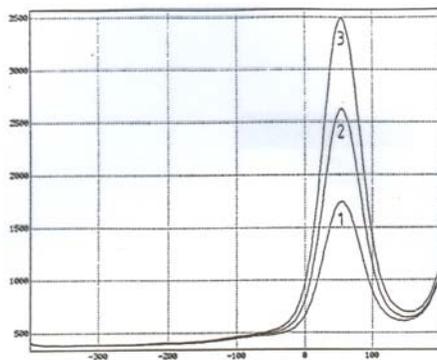
$t_d = 90 + 20\text{ s}$

(1) :  $5\text{ ml}$  sample in  $0.1\text{M HNO}_3$

(2) : (1) +  $100\text{ ng Cd, Pb}$ ,  
 $V = 5.1\text{ ml}$

(3) : (1) +  $200\text{ ng Cd, Pb}$ ,  
 $V = 5.2\text{ ml}$

## Voltammetric determination of Cu



DPASV

$E_d = -400 \text{ mV}$

$t_d = 10 \text{ s}$

(1) : 5 ml sample in 0.1M HNO<sub>3</sub>

(2) : (1) + 1  $\mu\text{g}$  Cu, V = 5.05 ml

(3) : (1) + 2  $\mu\text{g}$  Cu, V = 5.1 ml

## Other analytical methods

- ICP-OES:
  - multielement analysis
  - determination of all metals and some non-metals (S, P)
  - wide linear dynamic range
  - detection limits comparable with F AAS or lower
  - high-cost instruments (comparable with ET AAS)
  - high operating costs
- ICP-MS
  - multielement analysis
  - determination of all elements except of noble gases, H, C, N, O and F
  - very wide linear dynamic range
  - detection limits comparable with ET AAS or lower
  - cost of the instrument: high or extremely high
  - high operating costs