# Clean rooms
# Clean laboratories
-
# Laboratory for trace element analysis
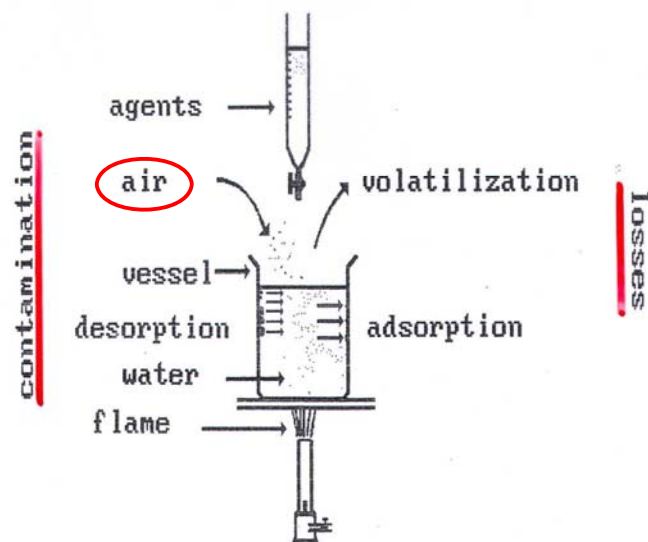
**jac brno**

**Bohumil Dočekal**
*Institute of analytical chemistry of the CAS, v.v.i., Brno*

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## Fundamental problems of trace and ultra-trace element analysis

- *major and minor components* $10^0 - 10^{-2}$ %

- *trace impurities* $\approx 10^{-4}$ % (ppm)

- *ultra-trace impurities* $\leq 10^{-7}$ % (ppb)

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## Sources of contamination and analyte losses



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## Sources of contamination

## Abundance of elements in earth crust

| Element | % | $10^{-2}$ % | | $10^{-3}$ % | | $10^{-4}$ % | | $10^{-5}$ % | |
|---------|------|------|----|------|-----|------|-----|------|------|
| O | 46,4 | Ti | 57 | Ni | 7 | Th | 9 | J | 5 |
| Si | 28,2 | H | 14 | Zn | 7 | Sm | 6 | Tl | 4,5 |
| Al | 8,2 | Mn | 10 | Ce | 6 | U | 2,7 | Cd | 2 |
| Fe | 5,6 | P | 10 | Co | 2,5 | Sn | 2 | Hg | 1,8 |
| Ca | 4,2 | S | 2,6 | Li | 2 | Ta | 2 | Bi | 1,7 |
| Na | 2,4 | C | 2,0 | N | 2 | As | 1,8 | Ag | 0,7 |
| Mg | 2,3 | Zr | 1,6 | Pb | 1,2 | Mo | 1,5 | Se | 0,5 |
| K | 2,1 | Cl | 1,3 | B | 1 | W | 1 | Au | 0,04 |

R. S. Taylor, Geochim. Cosmochim. Acta 28, 1273 (1964)

## Particle size of some types of aerosols
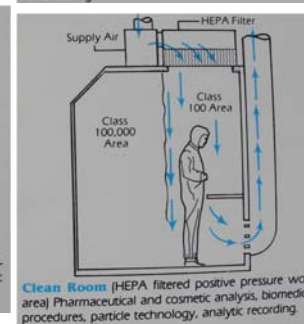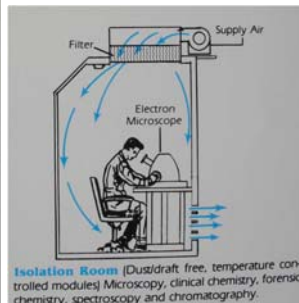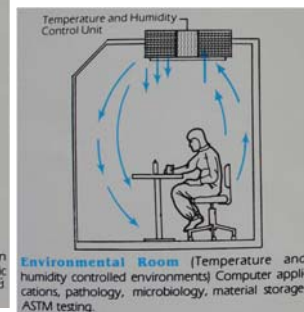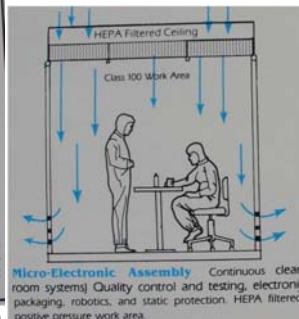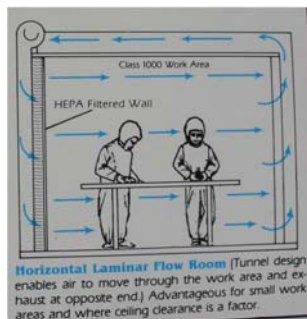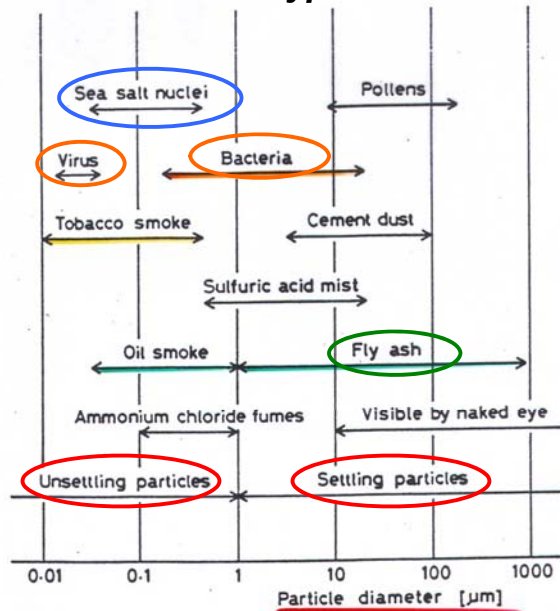






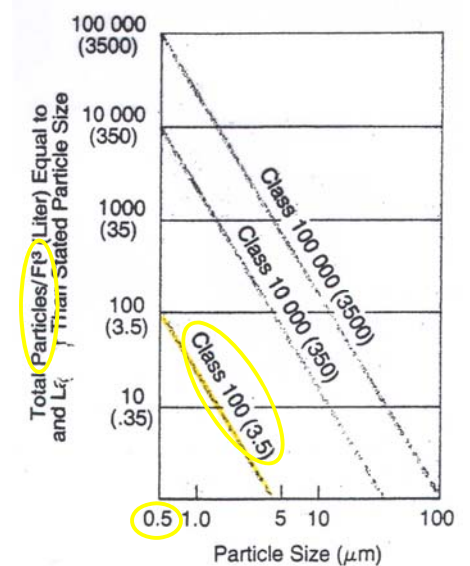**Relationship between the number of particles in contaminated air and their mass concentration**
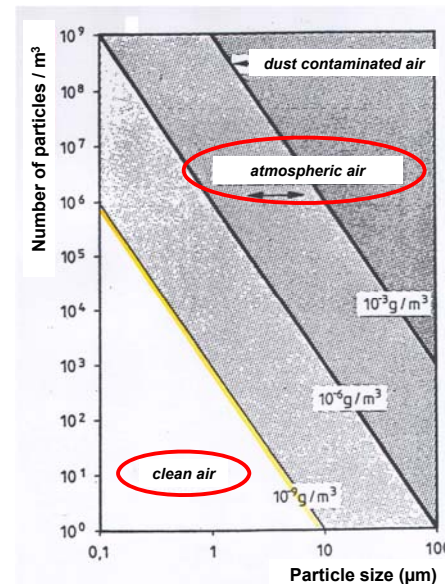


**Limits of particle size distribution according to US Federal Standard 209b**

**Classification of clean rooms according to US Federal Standard 209b and German VDI 2083**



Die Reinheitsklassen gemäss den Festlegungen des US Federal Standard 209b sowie von VDI 2083, Blatt 1.

| Reinheitsklasse | | maximal zulässiger Staubpegel | | | |
|---|---|---|---|---|---|
| US Fed. Std. 209b | VDI 2083 Bl. 1 | Teilchen pro ft³ Luft | | Teilchen pro m³ Luft | |
| | | ≥ 0,5 µm | ≥ 5 µm | ≥ 0,5 µm | ≥ 5 µm |
| 100 | 3 | 100 | < 10* | 4 × 10³ | – –* |
| 1 000 | 4 | 1 000 | < 10* | 4 × 10⁴ | 0,03 × 10⁴ |
| 10 000 | 5 | 10 000 | 70 | 4 × 10⁵ | 0,03 × 10⁵ |
| 100 000 | 6 | 100 000 | 700 | 4 × 10⁶ | 0,03 × 10⁶ |

\* aus statistischen Gründen nicht bewertet

Luwa-Vorschlag für einen erweiterten, den heutigen und den voraussehbaren Bedürfnissen der Reinraumtechnik entsprechen-den US Federal Standard 209b.
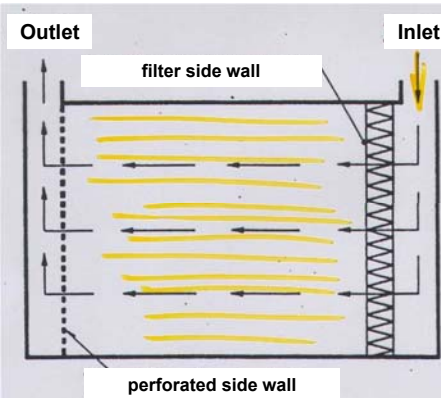
| Reinheitsklasse nach | | Partikel pro Kubikfuss | | | |
|---|---|---|---|---|---|
| VDI 2083 Blatt 1 | US. Fed. Std. 209b | ≥ 0,02 µm* | ≥ 0,1 µm* | ≥ 0,5 µm | ≥ 5 µm |
| 0* | 0,1* | 10² | 3 × 10⁰ | 10⁻¹** | *** |
| 1* | 1* | 10³ | 3 × 10¹ | 10⁰** | *** |
| 2* | 10* | 10⁴ | 3 × 10² | 10¹ | *** |
| 3 | 100 | **** | 3 × 10³ | 10² | *** |
| 4 | 1 000 | **** | **** | 10³ | 7 × 10⁰ |
| 5 | 10 000 | **** | **** | 10⁴ | 7 × 10¹ |
| 6 | 100 000 | **** | **** | 10⁵ | 7 × 10² |

\* Neue Reinheits- bzw. Partikelgrössenklassen
\*\* Angabe nur sinnvoll zum Zweck der Klassendefinition (siehe auch \*\*\*)
\*\*\* Angabe aus statistischen Gründen für Messzwecke nicht sinnvoll
\*\*\*\* Angabe nicht relevant für die Festlegung von Reinheitsanforderungen





## Air flow in clean rooms

**horizontal laminar flow**

**vertical laminar flow**



Outlet | Inlet | Outlet | Inlet
filter side wall
perforated side wall
filter top wall
perforated floor

*Filters are situated in the side wall, air is introduced forming air piston with horizontal laminar flow, afterwards air is returned through the perforated side wall for recirculation*
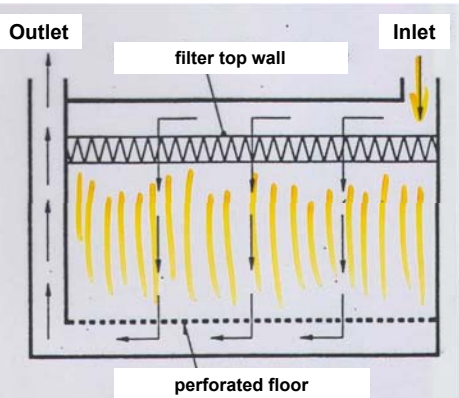
*Filters are situated in the top wall, air is introduced forming air shower with laminar flow, afterwards air is returned through the perforated floor for recirculation*

## Schematic air flow in the clean room
### equipped with laboratory furniture and instrumentation
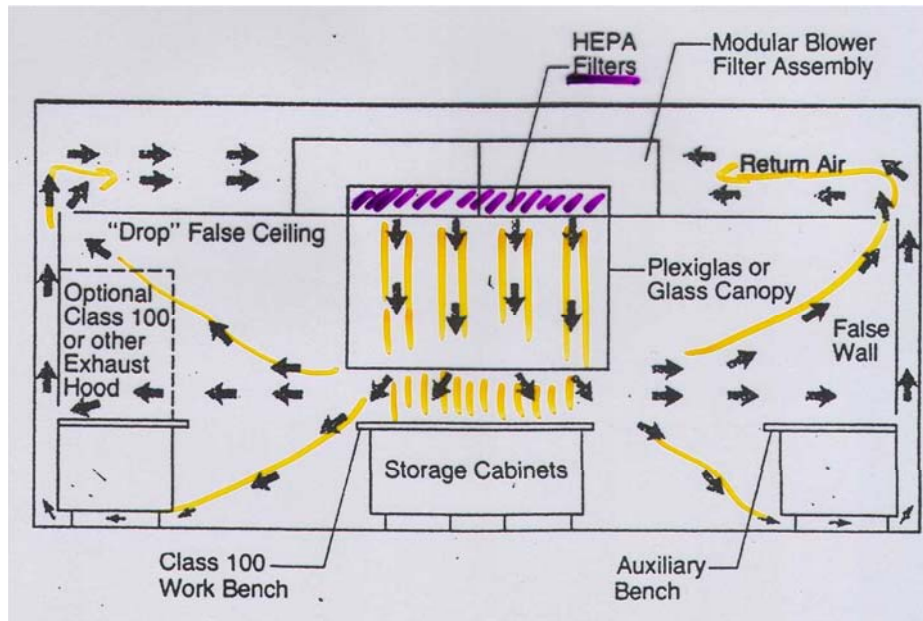


## Design - Concept of clean rooms

- *What is the purpose / task (protection of products / samples against contamination, safety protection of personnel, eventually both approaches – in microelectronics and pharmaceutical industry, special laboratories for trace analysis and clinical biochemistry, surgical operation spaces ……)*
- *Operations (weighing, sample preparation, sample decomposition, measurement, surgery ……)*
- *Individual work places (class of cleanliness, priority of operations, GLP/GMP, assessment of contamination risk, assessment of safety hazards for personnel …….)*
- *Economy - running costs (energy consumption for heating/cooling, control of air humidity, air recirculation, removal of ballast heat from instrumentation, extraction of toxic fumes ……….)*
- *Technology (air cleanliness, number of air exchanges in a room within a time period, air filtration, temperature and humidity control, minimization of ballast heat production from technological equipment, extraction hoods for dangerous fumes and gasses, space arrangement, service corridors and rooms, pressurized cabins in cascade regime)*
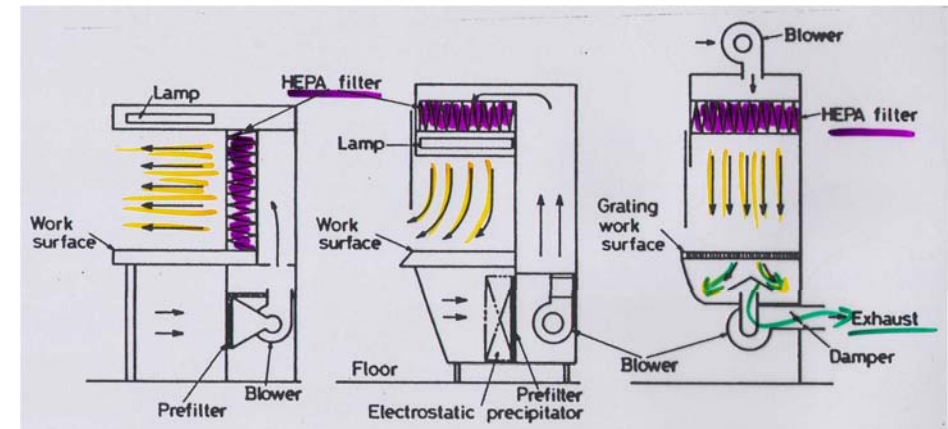
## Aerodynamic conditions in flow of streaming air

*Linear velocity and turbulence profiles below filters in various distances from filters without and with laminarization streamlining elements*
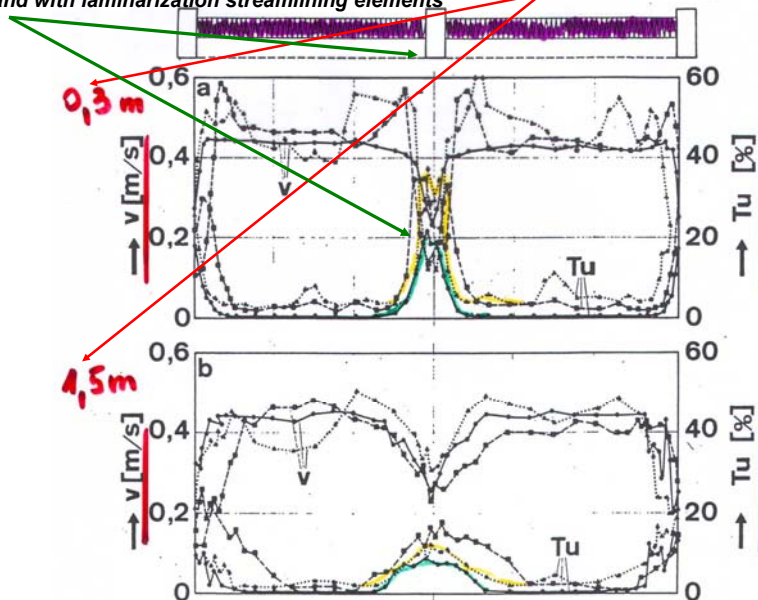


## Laminar boxes / fume hoods (flow box, clean bench)
### with integrated HEPA filters and hoods



*horizontal laminar box*

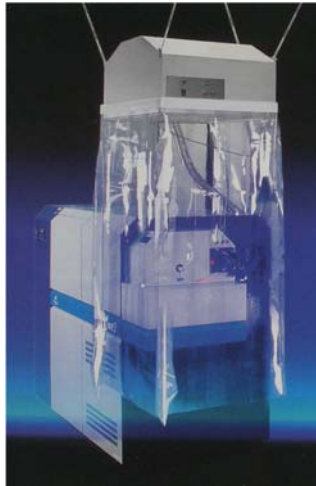*vertical laminar box without protection of personnel*

*vertical laminar box with extraction fume hood for protecting of personnel*

## Laminar boxes / hoods
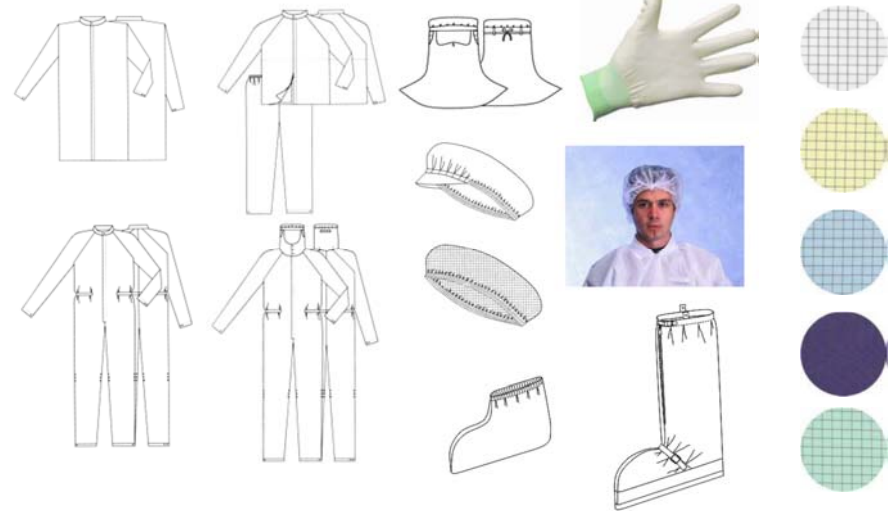


**BIOFUME HOOD™**

*vertical laminar box*

*vertical laminar box with plastic curtain*

## Clothing – *special clothes and protective components*

**CLEANTEX ®**

*coats, overalls, two piece suits (trousers + blouse), hoods, caps, facemasks, overshoos, gloves ..… (electrostatic dissipative material)*



## Sources of contamination and analyte losses



contamination

agents → 
air
vessel
desorption → volatilization
water
flame → adsorption

losses
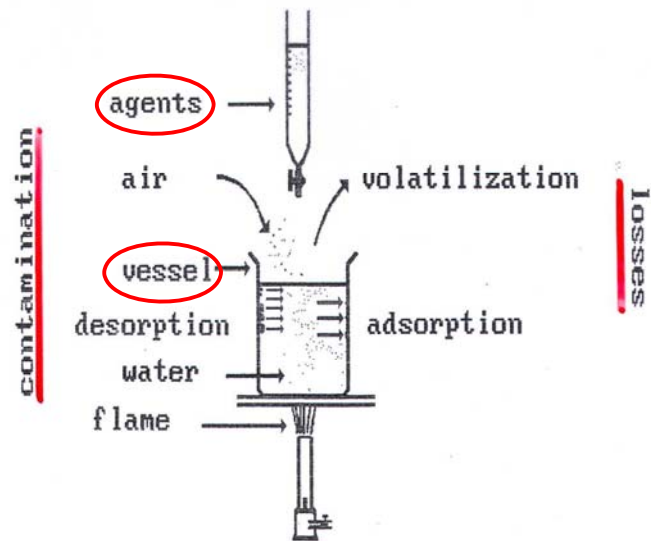
## Preparation and distribution of high purity water
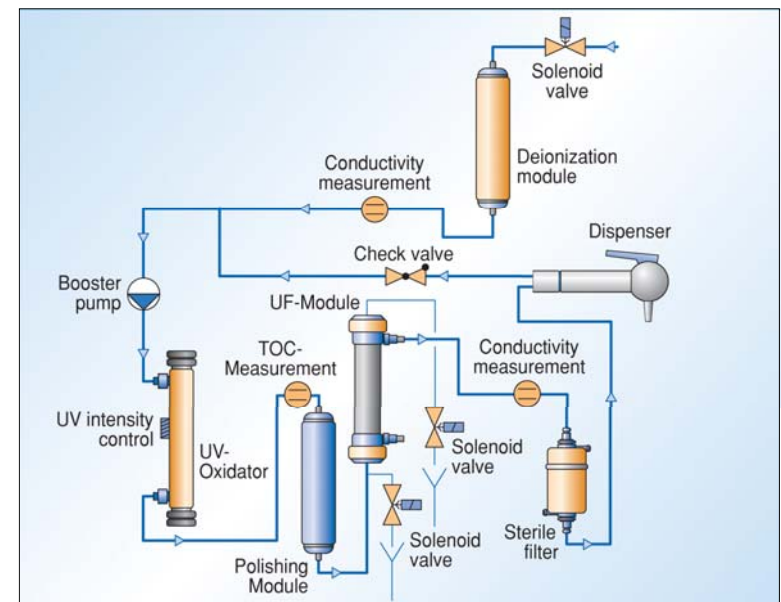
## Quality of high purity water



| Type* Ultra Clear ... | | – | UV | plus | UV plus | UV TM | UV plus TM |
|---|---|---|---|---|---|---|---|
| **Ultrapure water specifications** | | | | | | | |
| Output** up to | l/min | 2 | 2 | 2 | 2 | 2 | 2 |
| Conductivity at 25° C | µS/cm | 0.055 | 0.055 | 0.055 | 0.055 | 0.055 | 0.055 |
| Resistivity at 25° C | MΩ-cm | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 |
| TOC | ppb | 5 – 10 | <1 | 5 – 10 | <1 | <1 | <1 |
| DNase, RNase, DNA | | – | – | – | free | – | free |
| Bakteria | cfu/ml | <1 | <1 | <1 | <1 | <1 | <1 |
| Endotoxins | EU/ml | – | – | <0.001 | <0.001 | – | <0.001 |
| Particles > 0.1 µm | per ml | <1 | <1 | <1 | <1 | <1 | <1 |
| **Feed water specification** | | | | | | | |
| Feed water pressure | bar | 0.1 – 5 | 0.1 – 5 | 0.1 – 5 | 0.1 – 5 | 0.1 – 5 | 0.1 – 5 |
| Feed conductivity | µS/cm | < 20 | < 20 | < 20 | < 20 | < 20 | < 20 |
| TOC | ppb | < 50 | < 50 | < 50 | < 50 | < 50 | < 50 |

## Preparation of high purity acids and organic solvents by sub-boil distillation



input — cooling finger — cooling water — Siphon — IR radiator — purified liquid — trap vessel
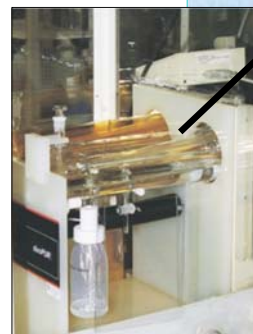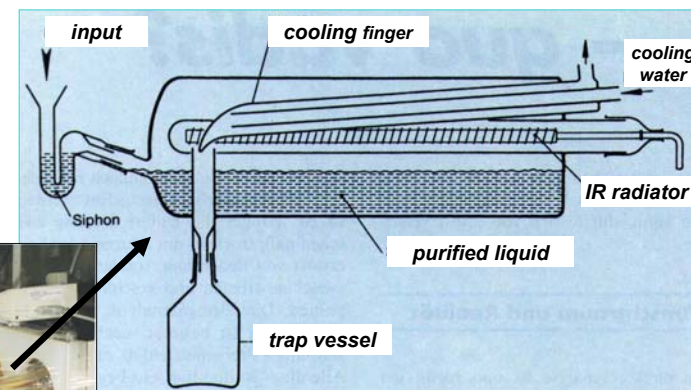
## Preparation of high purity acids (HF) by sub-boil distillation
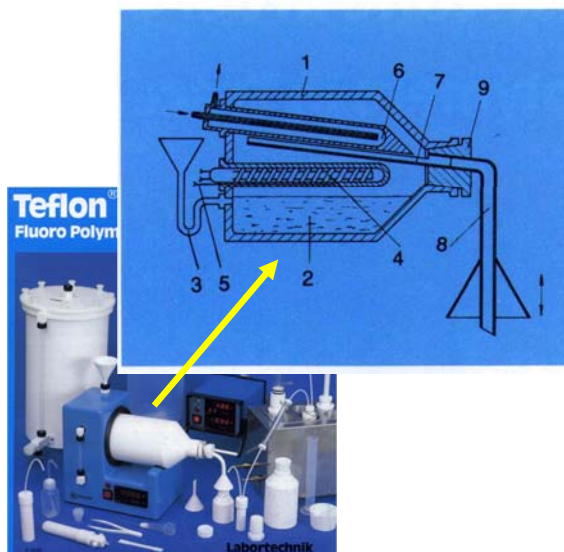


**Design**
1 Distillation vessel out of PTFE
2 Fluid to be distilled
3 Funnel tube with siphon
4 Heating radiator coated with PTFE
5 Thermosensor
6 Cooling bar with water connections
7 Outlet channel for distillate
8 Outlet tubing with dust protection
9 Locking stopper

**Technical Data:**
Volume: max. 600 ml
distilling performance depending on fluid and heating rate max. 20 – 40 ml/h
heating radiator: 0 – 300°C, 2 x 150 Watt
dimensions: h x w x d 320 x 450 x 180 mm

## Impurities in nitric acid (ppb)

| element | acid from sub-boiling still | A.C.S. reagent grade acid | commercial high purity |
|---|---|---|---|
| Pb | 0.02 | 0.2 | 0.3 |
| Tl | — | 0.2 | — |
| Ba | 0.01 | 8 | — |
| Te | 0.01 | 0.1 | — |
| Sn | 0.01 | 0.1 | 1 |
| In | 0.01 | — | — |
| Cd | 0.01 | 0.1 | 0.2 |
| Ag | 0.1 | 0.03 | 0.1 |
| Sr | 0.01 | 2 | — |
| Se | 0.09 | 0.2 | — |
| Zn | 0.04 | 4 | 8 |
| Cu | 0.04 | 20 | 4 |
| Ni | 0.05 | 20 | 3 |
| Fe | 0.3 | 24 | 55 |
| Cr | 0.05 | 6 | 130 |
| C | 0.2 | 30 | 30 |
| K | 0.2 | 10 | 11 |
| Mg | 0.1 | 13 | — |
| Na | 1 | 80 | — |

## Sources of contamination and analyte losses
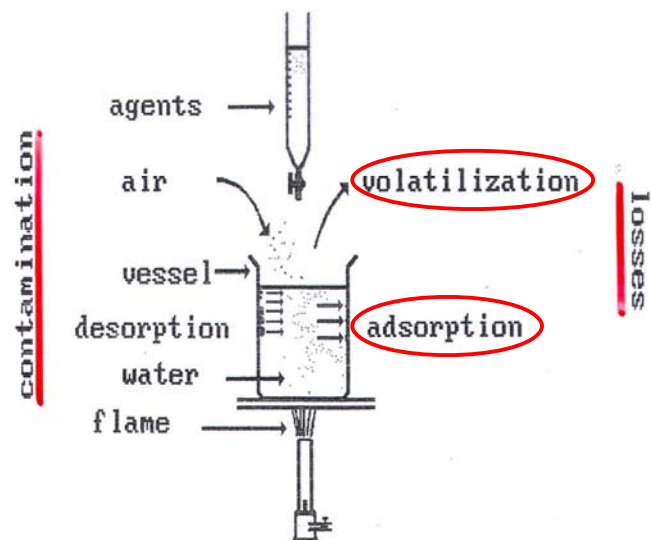


## Sample decomposition in pressurized systems
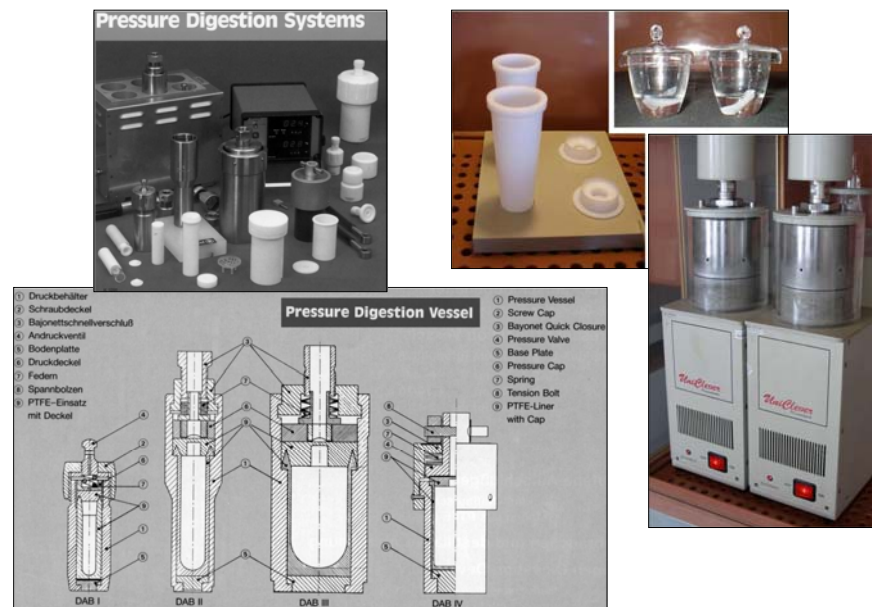


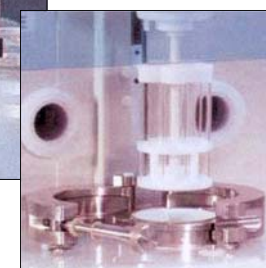## Sample decomposition in pressurized systems

*(Milestone s.r.l., Italy)*

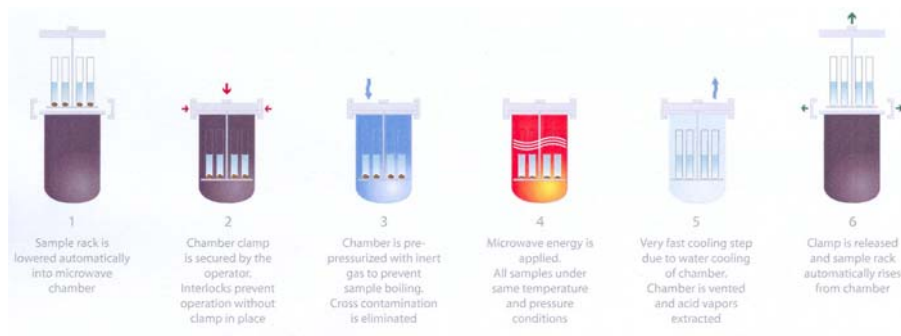

## Sample decomposition in autoclaves

*(Milestone, Italy)*



*reaction vessel TFM/PTFE
volume 990 ml
magnetron power 1500 W
max. pressure 199 bar
max. temperature 300°C
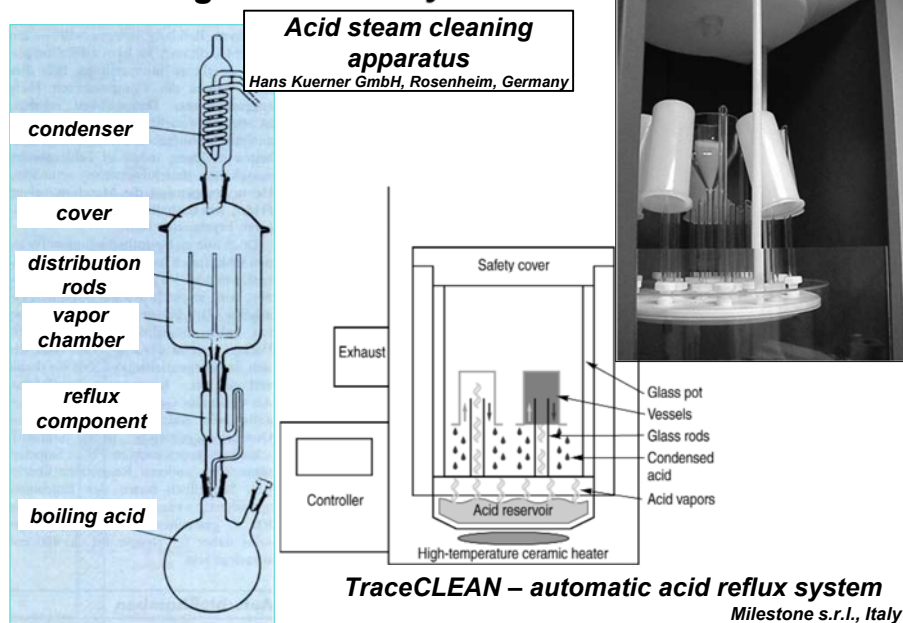water cooling*

## Sample decomposition in autoclaves
*(Milestone, Italy)*



| 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|
| Sample rack is lowered automatically into microwave chamber | Chamber clamp is secured by the operator. Interlocks prevent operation without clamp in place | Chamber is pre-pressurized with inert gas to prevent sample boiling. Cross contamination is eliminated | Microwave energy is applied. All samples under same temperature and pressure conditions | Very fast cooling step due to water cooling of chamber. Chamber is vented and acid vapors extracted | Clamp is released and sample rack automatically rises from chamber |

## Materials



| Material | Maximum service temperature (°C) | Poor chemical resistance [16] to | Permeability |
|---|---|---|---|
| Pyrex* (borosilicate glass) | 600 | Hydrofluoric acid, Conc. phosphoric acid, Sodium hydroxide solution | None |
| Vycor** (high-silica glass) | 900 | Hydrofluoric acid, Conc. phosphoric acid, Sodium hydroxide solution | None |
| Vitreous silica | 1100 | Hydrofluoric acid, Conc. phosphoric acid, Sodium hydroxide solution | None |
| Platinum | 1500 | Aqua regia | None |
| Glassy carbon [17] | 600 | None | None |
| Polyethylene | 80 (High-pressure process) 110 (Low-pressure process) | Organic solvents, Conc. nitric acid, Conc. sulfuric acid | Permeable |
| Polypropylene | 130 | Organic solvents, Conc. nitric acid, Conc. phosphoric acid, Sodium hydroxide solution | Permeable |
| Teflon (polyfluorocarbon) | 250 | None | Permeable |

## Cleaning of laboratory vessels

**Acid steam cleaning apparatus**
**Hans Kuerner GmbH, Rosenheim, Germany**



- condenser
- cover
- distribution rods
- vapor chamber
- reflux component
- boiling acid

Safety cover
Exhaust
Controller
Glass pot
Vessels
Glass rods
Condensed acid
Acid vapors
Acid reservoir
High-temperature ceramic heater

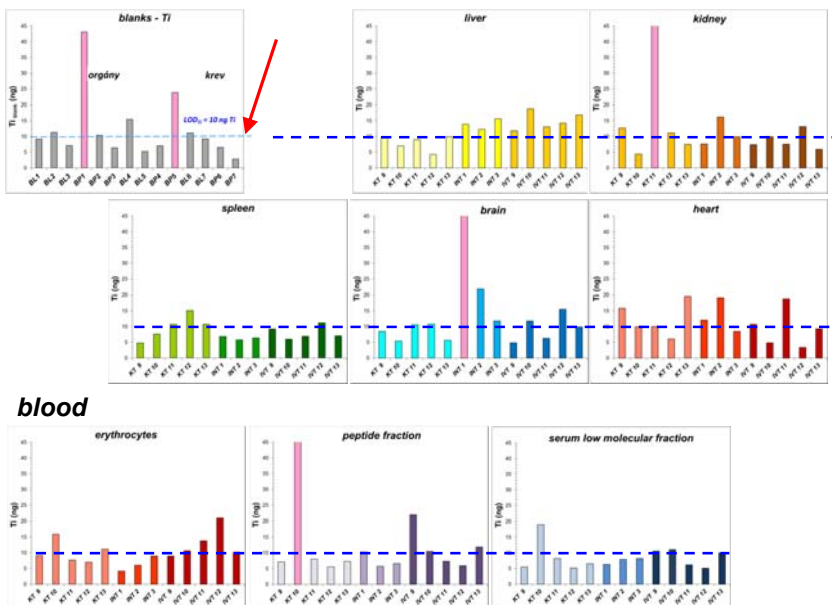*TraceCLEAN – automatic acid reflux system*
*Milestone s.r.l., Italy*

## Fluctuation of Cd blanks during microwave digestion of biological samples in closed pressurized PTFE autoclaves
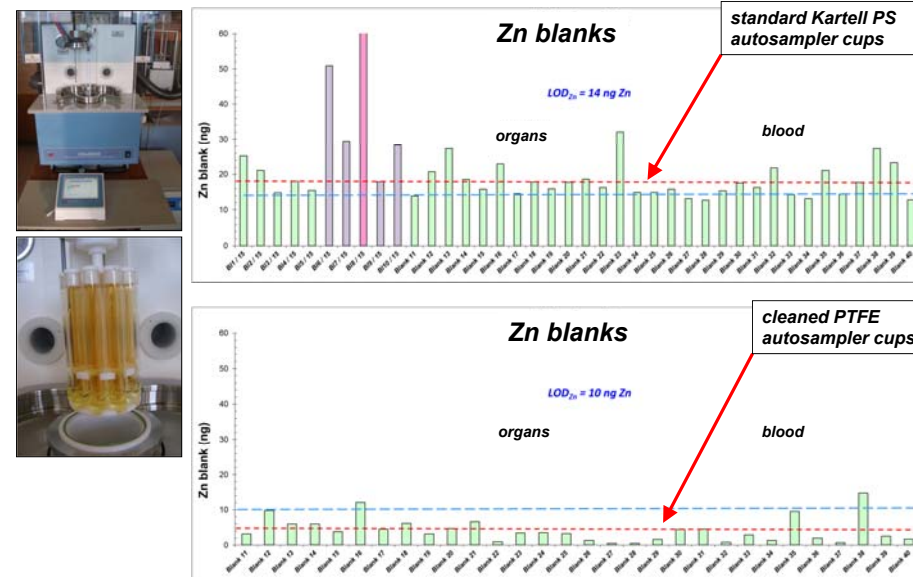- *3 ml HNO$_3$ subboiled*



ng Cd

LOD

LOD $_{instrumental}$
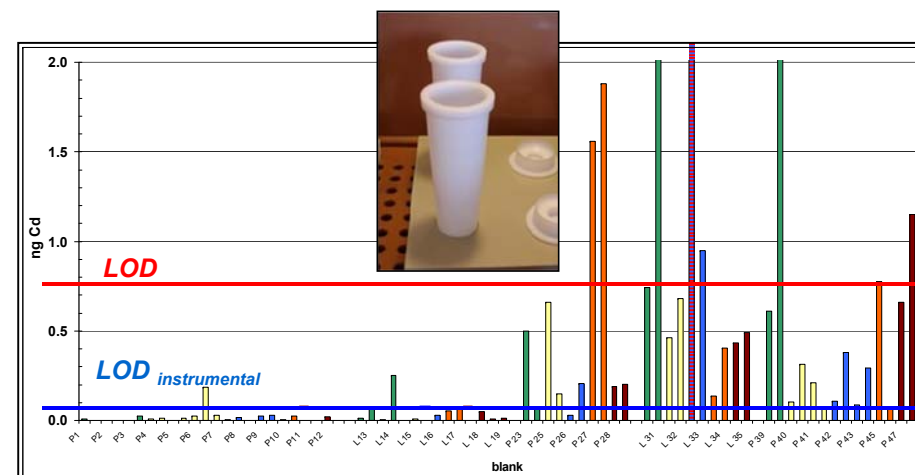
blank

## Inhalation of TiO₂ nanoparticles – Analysis of mice organs
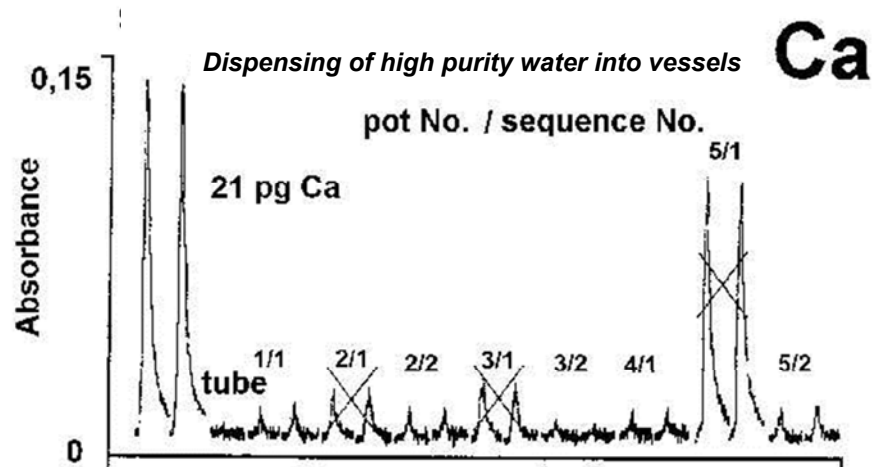


**blood**



## Inhalation of ZnO nanoparticles – Blank level and fluctuation using UltraWAVE decomposition system and TraceCLEAN acid steam cleaning



## Contamination – blanks



*Dispensing of high purity water into vessels*

*„Trends in Analytical Chemistry"*

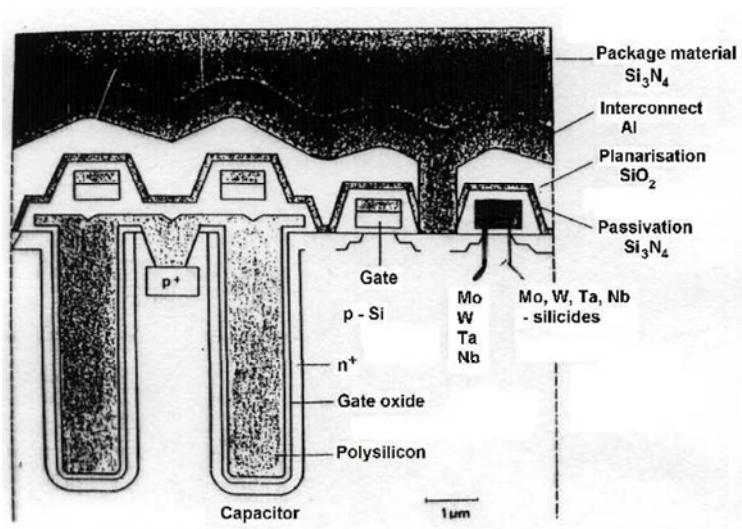# Direct analysis of solid samples by electrothermal Atomic Absorption Spectrometry



**Bohumil Dočekal**
*Ústav analytické chemie AVČR, v.v.i., Brno*

## Schematic view of microelectronic cell



- Package material Si₃N₄
- Interconnect Al
- Planarisation SiO₂
- Passivation Si₃N₄
- Gate
- Mo, W, Ta, Nb - silicides
- Mo W Ta Nb
- p⁺
- p - Si
- n⁺
- Gate oxide
- Polysilicon
- Capacitor
- 1 µm

## Metals in VLSI-technology (gate material)
### 6N high purity molybden (99.9999 %)
(sputtering targets for plasma technology)

### Requested purity:

- „heavy metals"(Cu, Fe, Mn, Ni, Pb, Zn ....) - max. $10^2$ ppb
  (junction leaks)

- mobile ions (Li, Na, K, Mg, Ca ...) - max. $10^1$ ppb
  (additional doping effects)

- radioactive species (U, Th ..) - below $10^0$ ppb
  (ionization effects)

## Example – determination of Mg in hp Mo, hp MO₃
wet decomposition in $HNO_3 + H_2O_2$ in laminar box class 100, n = 5

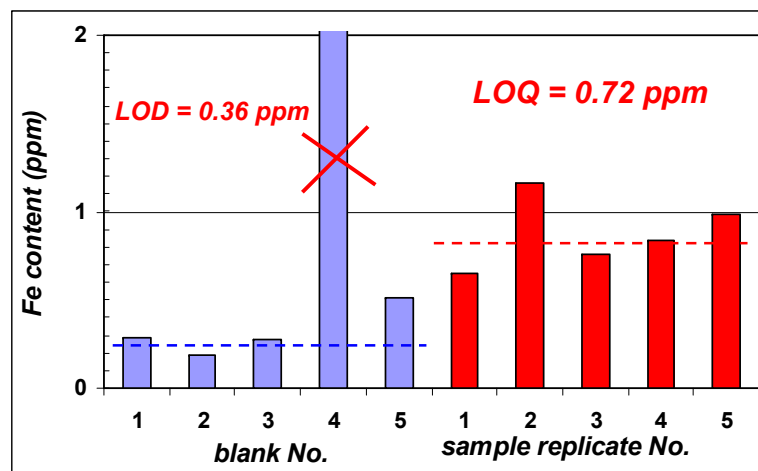| LODs (ppb) | |
|---|---|
| Ca | 500 |
| K | 200 |
| Mg | 100 |
| Na | 200 |
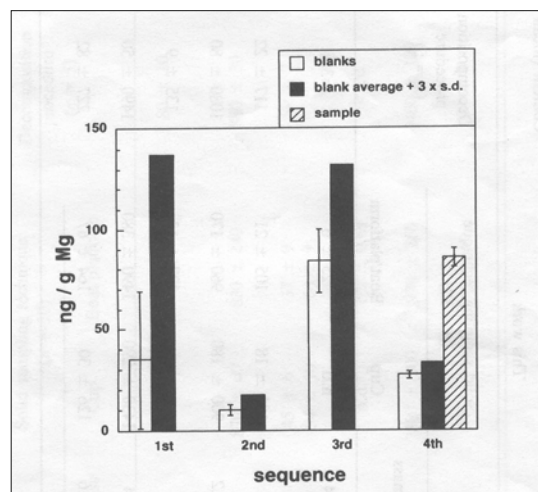


## Determination of detrimental impurities in terephtalic acid
(determination: 0.2 g sample + 3 ml conc. HNO₃ / 10 ml solution)

## Panel 1 (top-left)
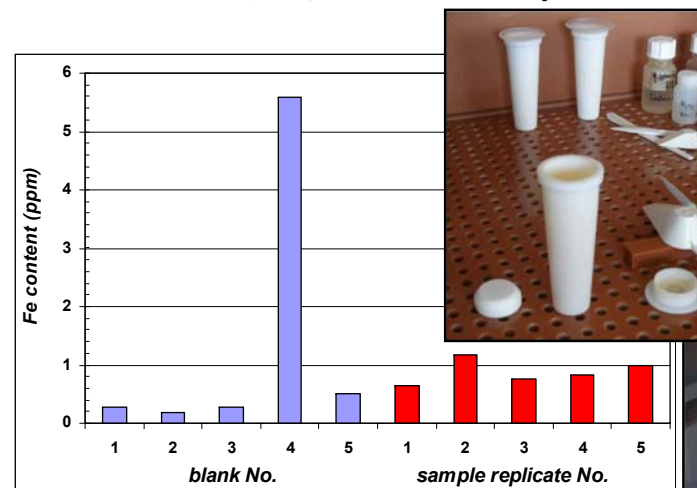
*Determination of detrimental impurities in terephtalic acid*
*excluding out-layers – result 0.56 ± 0.22 ppm Fe*

*blank: 0.32 ± 0.12 ppm*      *sample: 0.88 ± 0.18 ppm*



LOD = 0.36 ppm
LOQ = 0.72 ppm

Y-axis: Fe content (ppm)
X-axis: blank No. / sample replicate No.

## Panel 2 (top-right)

*Precheza a.s. Přerov*

# Requirements on purity of TiO$_2$

*Additive in food, pharmaceutic, cosmetic, textile technology, additive in cigarette paper, etc. (E175)*

*Maximální obsah stopových prvků podle Evropských norem*

*max. content of impurity in mg/kg (ppm)*

| Product | As | Cd | Cr | Hg | Pb | Sb | Zn |
|---|---|---|---|---|---|---|---|
| **food** | 3 | 1 | 20 | 1 | 10 | 50 | 50 |
| **pharma** | 3 | 0.5 | 10 | 0.5 | 10 | 50 | 5 |
| **paper** | 3 | 1 | 20 | 1 | 10 | 50 | 50 |
| **paper fine** | 3 | 1 | 20 | 1 | 10 | 50 | 50 |
| **fiber** | 3 | 1 | 20 | 1 | 10 | mod. Sb$_2$O$_3$ | 50 |

## Panel 3 (bottom-left)

## Sample decomposition

*0.2 g TiO$_2$ + concentrated acids*
*3 mL HF, 4 mL H$_2$SO$_4$, 1 mL H$_2$O$_2$*
*final volume:  10 mL*
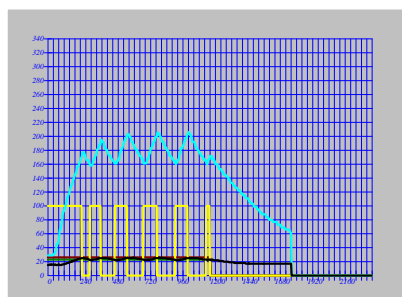


*T, p, P - chart*

*Uniclever microwave digestion unit*
*( Plazmatronika, Wroclaw, Poland )*
*20 min, power 100 W (max. 2.6 MPa, 250ºC)*

## Panel 4 (bottom-right)

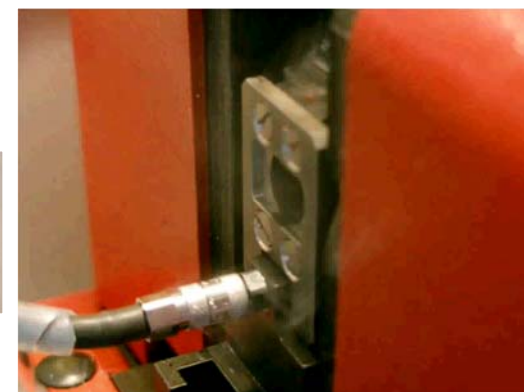## Corrosion of graphite parts of the atomizer by fumes of sulphuric and hydrofluoric acids

*Sample decomposition:*

*0.2 g TiO$_2$ + concentrated acids*
*3 mL HF, 4 mL H$_2$SO$_4$, 1 mL H$_2$O$_2$*
*final volume:  10 mL*
*sample aliquots: 10 μL*



*sample boat*

*fumes escaping atomizer*

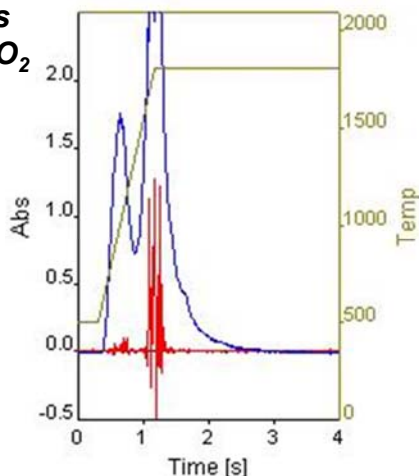## Spectral interference effects of sulphuric and hydrofluoric acids

**Sample decomposition:**

0.2 g $TiO_2$ + concentrated acids
3 mL HF, 4 mL $H_2SO_4$, 1 mL $H_2O_2$
final volume: 10 mL
sample aliquots: 10$\mu$L

**Sb  217.6 nm**
   injected: 2.5$\mu$L
   ( LOD > 5 ppm )

similar results for
**As 193.7 nm**
   injected: 5$\mu$L
   ( LOD = 25 ppm )



- **_slurry sampling_**
  - *powdered samples*
  - *preparation of representative suspension (1-5%)*
  - *disintegration of agglomerates by ultra-sonication*
  - *homogenization and stabilization of suspensions during sampling/injection of aliquots*
  - *introduction by means of micropipettes or* **_autosamplers_**

- **_true direct sampling_**
  - *various types of sample carriers (miniature __boats__, cups, platforms)*
  - *sample weighing*
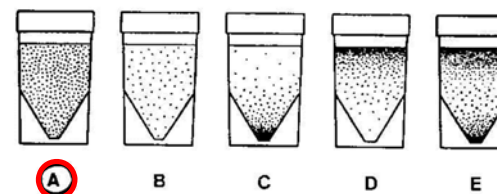  - *sample introduction into the atomizer (manual, robotized)*

- **Slurry sampling**
  - *measurement of real blanks in dispersion medium, control of blank level*
  - *reduction of detection limits*

**Example – analysis of hp $MoO_3$**

| analyte | LOD (ppb) | |
| --- | --- | --- |
| | wet | slurry |
| Ca | 500 | 2 |
| K | 200 | 1 |
| Mg | 100 | 0.5 |
| Na | 200 | 1 |

B.Docekal, V.Krivan: Determination of trace elements in high purity molybdenum trioxide by slurry sampling ETAAS.
- *J.Anal.Atom.Spectrom.*, 8, 637-641 (1993).

*homogenization and stabilization of suspensions*
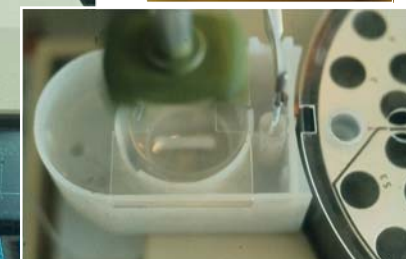
## Miniature stirring device

*turbine*
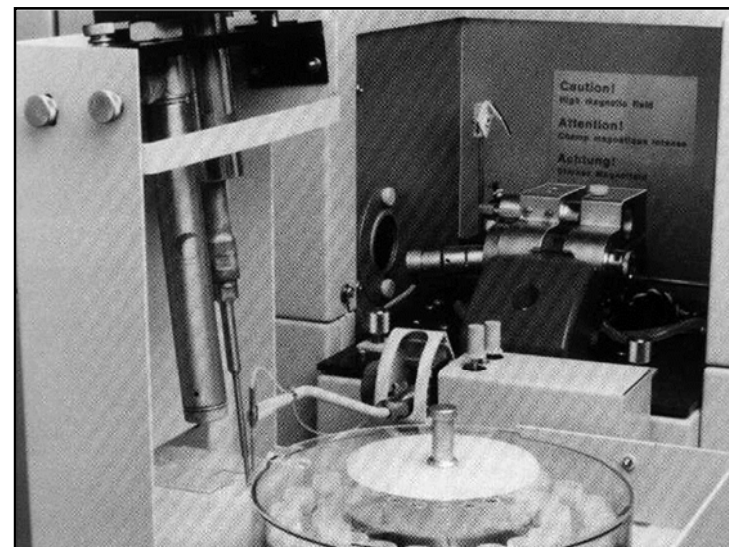
*driven by air or water*

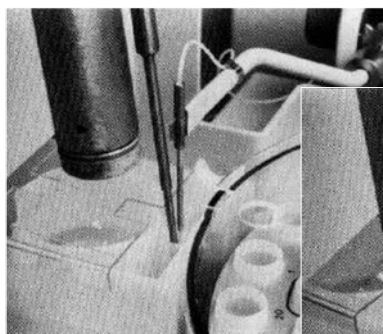*magnetic rods*

*modification of the sample tray*

B.Dočekal, A simple stirring device for slurry sampling technique in electrothermal atomic absorption spectrometry - *J.Anal.Atom.Spectrom.*, 8, 763-764 (1993)

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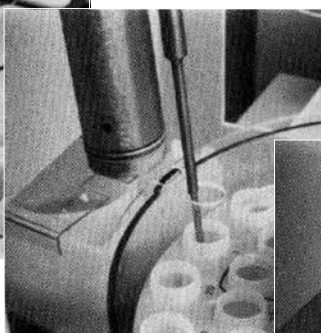*Slurry homogenization by using ultrasonic probe (ultra-sonication)*

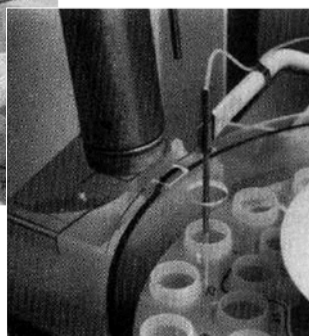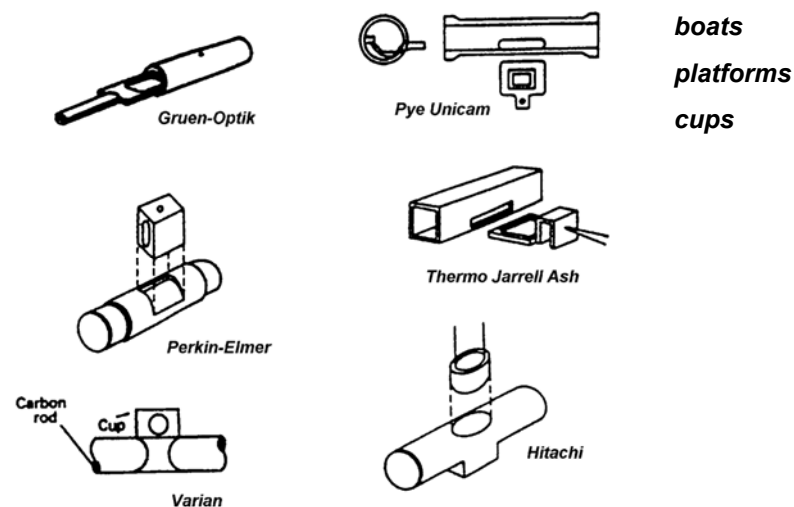P-E USS 100 Ultrasonic Slurry Sampling System

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## Ultra-sonication

*slurry sampling*

*probe rinsing*

*slurry homogenization*

P-E USS 100 Ultrasonic Slurry Sampling System

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## • Direct solid sample introduction - history
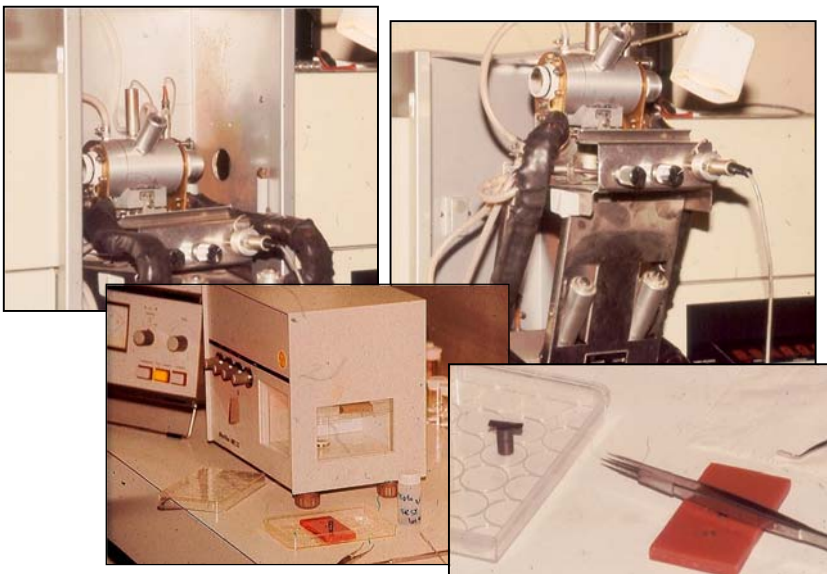
*boats*

*platforms*

*cups*

Gruen-Optik

Pye Unicam

Perkin-Elmer
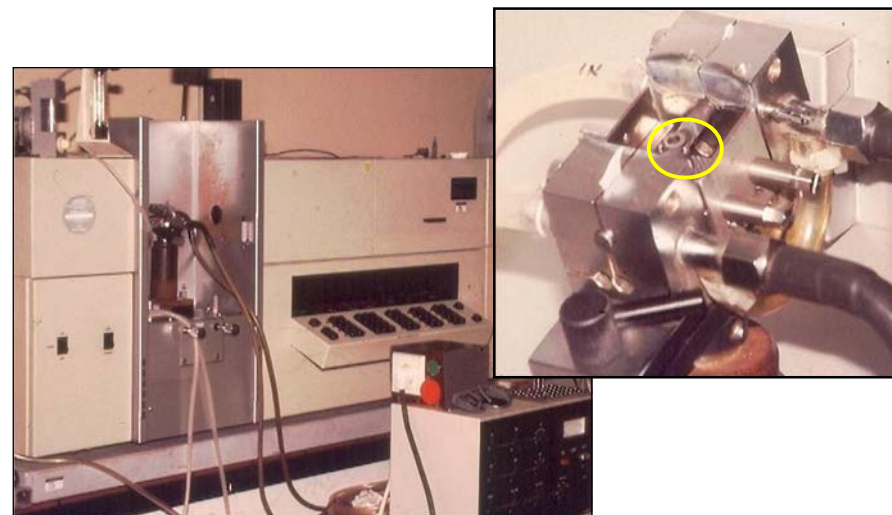
Thermo Jarrell Ash

Carbon rod    Cup

Varian

Hitachi

## • Direct solid sample introduction - history



B.Docekal, V.Krivan : Determination of trace impurities in powdered molybdenum metal and molybdenum silicides by solid sampling GFAAS. - *Spectrochim. Acta 50B*, 517-526 (1995).
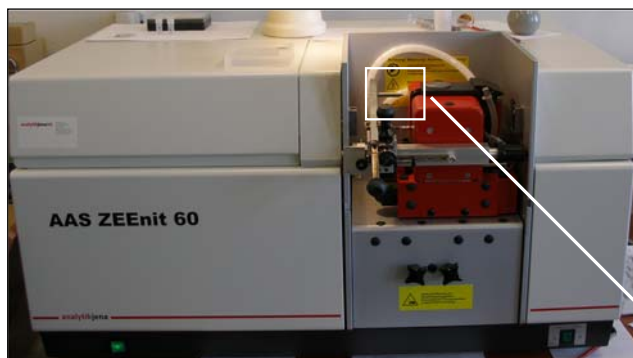
## • Direct solid sample introduction - history



B.Docekal, V.Krivan : Determination of trace impurities in powdered molybdenum metal and molybdenum silicides by solid sampling GFAAS. - *Spectrochim. Acta 50B*, 517-526 (1995).

## • Direct solid sample introduction

### 3-field mode Zeeman-effect BG-correction system



AAS ZEEnit 60

**manual solid sampling**

### Detail of the manual sample introduction system SSA 6

### (stand-by position)


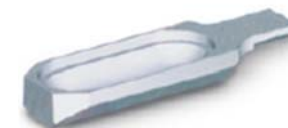
analytikjenaAG

**Sample in the boat**



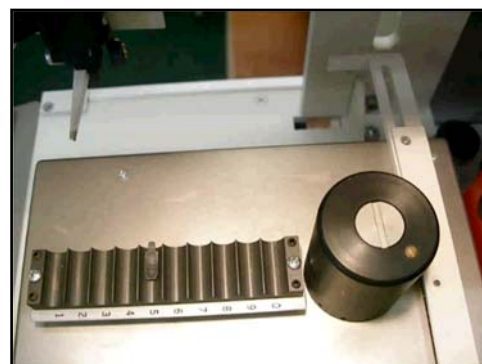**• Direct solid sample introduction**

analytikjenaAG



**sample carrier**

**robotic sample changer with integrated microbalance and data transmission**

**robotic sample changer with integrated microbalance and data transmission**
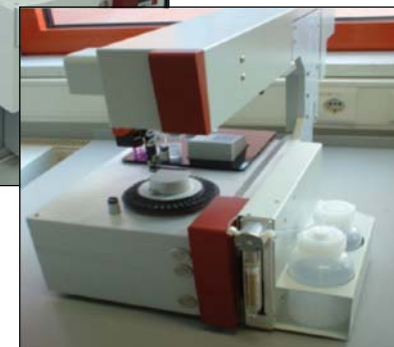
analytikjenaAG



**New robotized sample introduction system SSA 600**
with integrated sampler for chemical sample modification

analytikjenaAG



*Automatic system with 84 positions and integrated microbalance, automatic device for standard and modifier injection, integrated rinsing system*
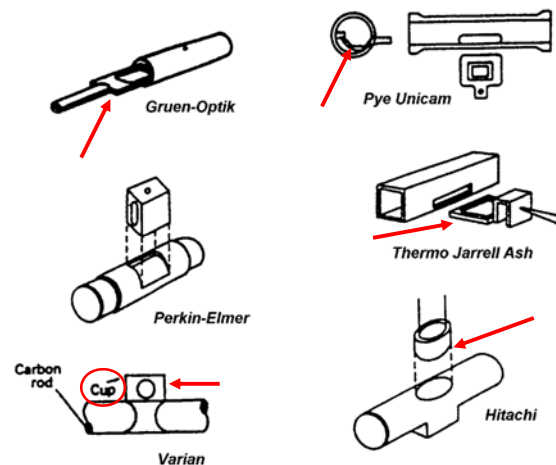
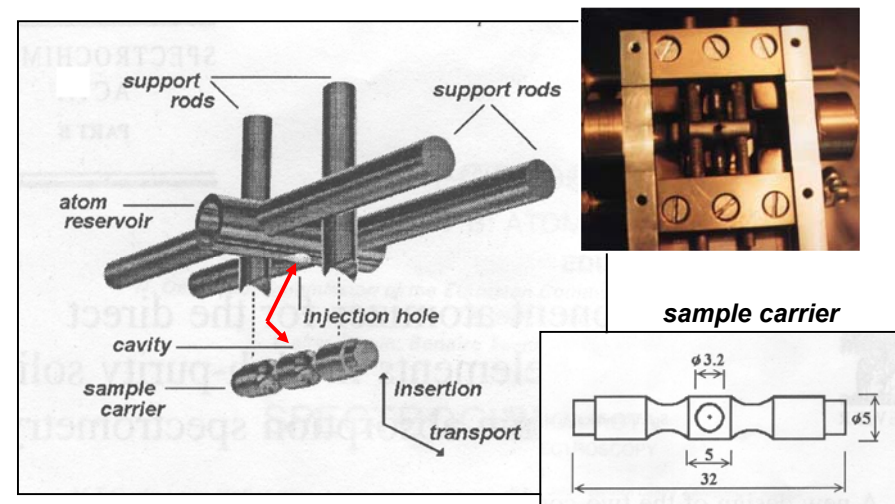## insertion of solid samples
### How to manage blanks ?

boats

platforms

cups



Gruen-Optik

Pye Unicam

Thermo Jarrell Ash

Perkin-Elmer

Carbon rod — Cup

Varian

Hitachi

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### New design of the two-component atomizer for solid sample analysis



support rods

support rods

atom reservoir

injection hole

cavity

sample carrier

insertion
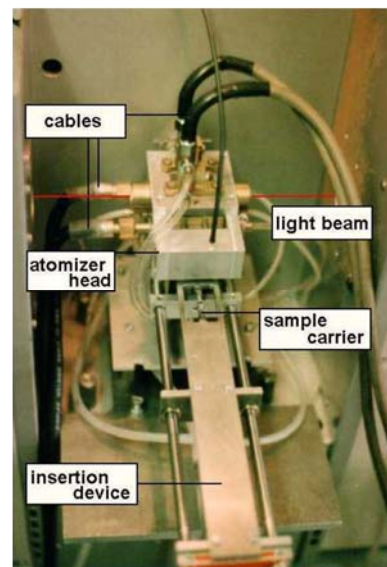
transport

sample carrier

ø 3.2

ø 5

5

32

B.Docekal: A new design of the two-component atomizer for the direct determination of medium and volatile elements in high-purity solid refractory metals by electrothermal atomic absorption spectrometry. - *Spectrochim. Acta, Part B,* **53B,** (1998) 427-435.
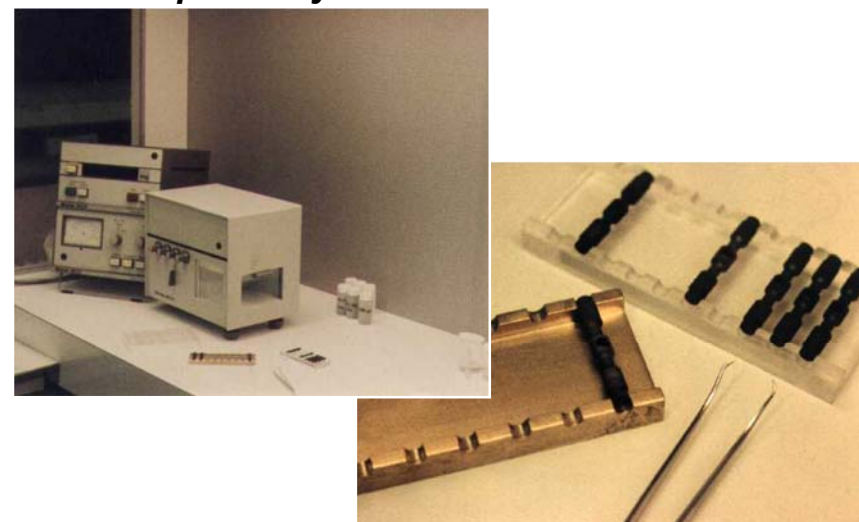
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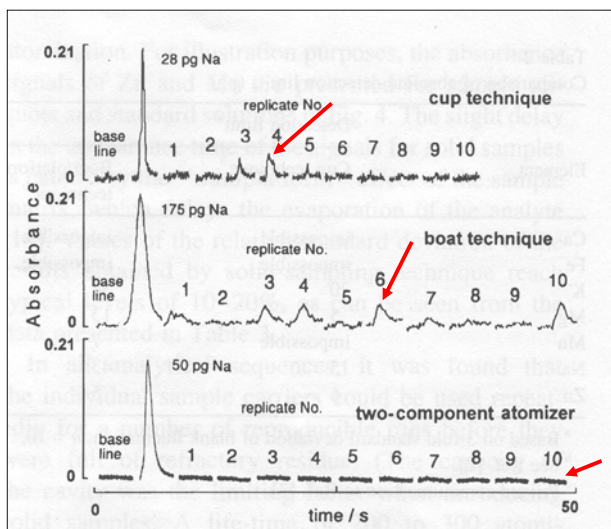### New design of the two-component atomizer for solid sample analysis

### Direct Solid Sampling AAS



cables

light beam

atomizer head

sample carrier

insertion device

---

### New design of the two-component  atomizer for solid sample analysis

## Quadrant 1 (top-left)

*true insertion of solid samples - contamination problems*

# two-component versus conventional atomizers



| LODs | | |
|---|---|---|
| Elem. | abs. (pg) | in Mo* (ppb) |
| Ca | 13 | 0.3 |
| K | 3.4 | 0.04 |
| Mg | 0.75 | 0.05 |
| Mn | 12 | 0.15 |
| Na | 1.8 | 0.03 |
| Zn | 6 | 0.06 |

*\* Max. sample portion of 50 mg*

## Quadrant 2 (top-right)

## *"Problems" of direct solid sampling AAS ?*

*refractory matrix, "heavy" matrix (Al, Si ...)*
*that cannot be removed during pyrolysis step or clean-out step*

*consequences:*
- *build up of residue - atomizer should be cleaned, exchanged, otherwise analytical tube lifetime is significantly reduced, interference in beam path, matrix modification is less efficient*
- *spectral interference - high background attenuation, structured spectra of background, occurrence of systematic errors, optimization procedure is more difficult, sophisticated instrumentation is necessary to obtain reliable data (Zeeman-effect BG-correction system, HR CS AAS)*



## Quadrant 3 (bottom-left)
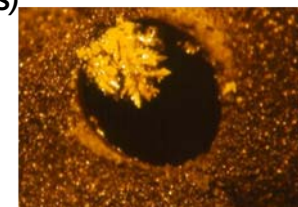
- **refractory matrix**
  **build up of residue**
  *vs.* **clean out temperature**

**TiO$_2$ samples**



### high temperature treatment

*above 2000°C*
*formation of Ti-carbide phase, maximum boat life time 30 runs due to creeping effect of the TiO$_2$-TiC-liquid phase (m.p. 1855°C)*
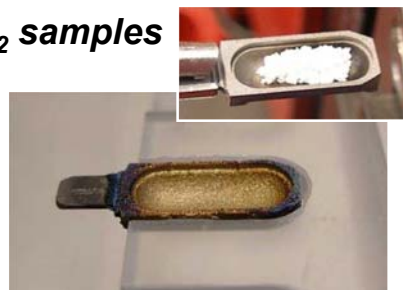
### low temperature treatment
*below 1900°C*
*tube and boat life time >1200 runs*

**B.Dočekal, B.Vojtková: Determination of trace impurities in titanium dioxide by direct solid sampling electrothermal atomic absorption spectrometry - Spectrochim. Acta, Part B., 62 /3/ 304-308 (2007).**

## Quadrant 4 (bottom-right)

- **refractory matrix**

*is it possible to vaporize/atomize the analyte from the refractory matrix ?!!*
*boiling , decomposition points are very high*

**Mo** - *radiotracer study*

*MoO$_3$ spiked with tracers reduced in hydrogen atmosphere*
*some of the analytes are excluded from the crystal lattice to the surface and can be subsequently atomized*
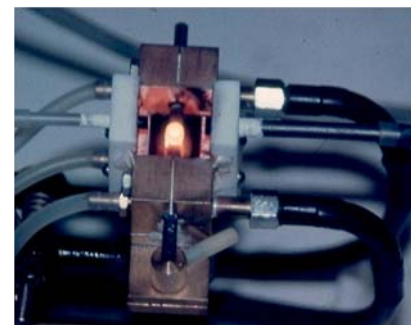


**Percentage of residual analyte**

| temp.°C | % | analytes |
|---|---|---|
| 2100 | < 2 | Na, K, Cu |
| 2300 | < 5 | Rb, Cs, Zn |
| 2500 | <10 | Sr |
| 2700 | <10 | Ba |
| | >10 | As,Co,Cr,Fe,Ni |

**B.Docekal, V.Krivan : Determination of trace impurities in powdered molybdenum metal and molybdenum silicides by solid sampling GFAAS. - Spectrochim. Acta 50B, 517-526 (1995).**
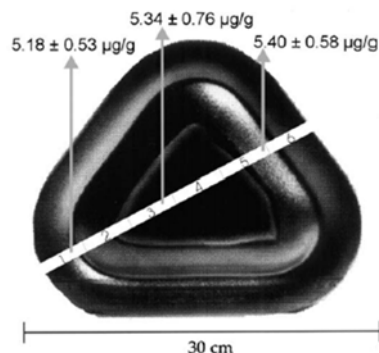
- *refractory matrix*

  *is it possible to analyze compact pieces of the refractory matrix ?!!*

*Interaction of the sample with additives (graphite …......)*

*Example*

  *titanium - sputtering target*

*sample is cut, etched, mixed with C,*

*titanium reacts during atomization step exothermally with graphite forming carbide,*
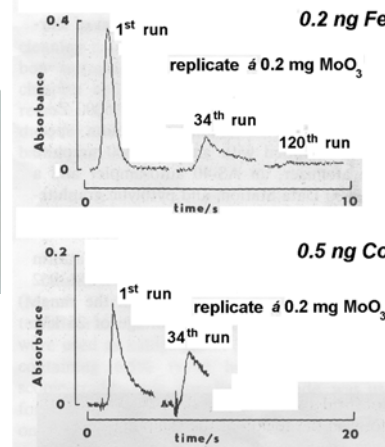
*analytes are released and measured*

5.34 ± 0.76 µg/g
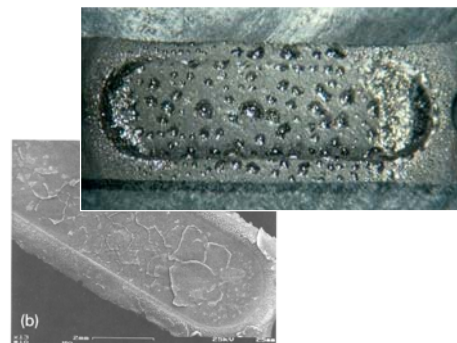5.18 ± 0.53 µg/g
5.40 ± 0.58 µg/g
30 cm

**H.M.Dong, V.Krivan : A solid sampling electrothermal atomic absorption spectrometry method for direct determination of silicon in titanium pieces - *J.Anal.Atom.Spectrom. 18*, 367-371 (2003).**

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- *refractory matrix*

  ***build up of residue** - atomizer should be cleaned, exchanged, otherwise analytical tube lifetime is significantly reduced, interference in beam path*

*Example*

  *120 replicates, á 0.2 mg MoO$_3$*

0.4  1st run  0.2 ng Fe
replicate á 0.2 mg MoO$_3$
34th run
120th run
time/s  10

0.2  0.5 ng Co
1st run  replicate á 0.2 mg MoO$_3$
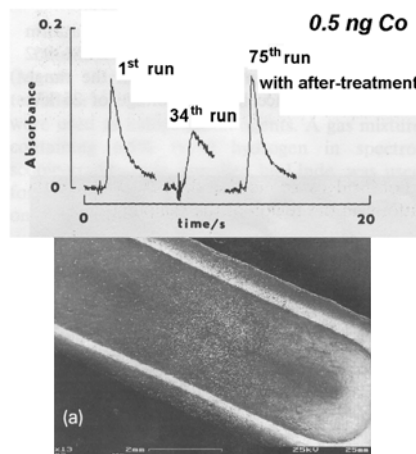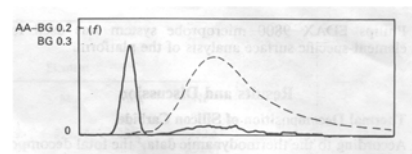34th run
time/s  20

**B.Docekal, V.Krivan: Halogen assisted cleaning after-treatment in graphite furnace a.a.s. for analysis of molybdenum based materials. - *Anal.Chim.Acta 279*, 253-260 (1993)**

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- *refractory matrix*

  ***removal of matrix** - atomizer should be cleaned / boat changed*
  *Freone - assisted after-treatment - volatilization of matrix residue chemical modification in gaseous phase*

### *Furnace & gas program*

| step | gas composition |
|---|---|
| drying | argon |
| pyrolysis | argon + hydrogen |
| atomization | argon + hydrogen |
| cool-down | argon |
| after-treatment | |
| at specific temperature | argon + Freone (CCl$_4$, CF$_4$, …) |
| blow-out | argon + hydrogen |
| clean-out | argon |
| cool-down | argon |

0.2  0.5 ng Co
1st run  75th run with after-treatment
34th run
time/s  20

**B.Docekal, V.Krivan: Halogen assisted cleaning after-treatment in graphite furnace a.a.s. for analysis of molybdenum based materials. - *Anal.Chim.Acta 279*, 253-260 (1993)**
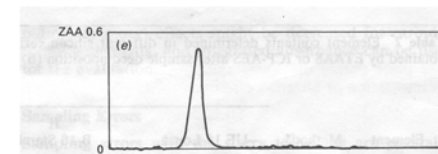
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- *spectral interference*

Zn 213.8 nm          0.5 mg SiC matrix
  D$_2$-compensation system          Zeeman-effect compensation system
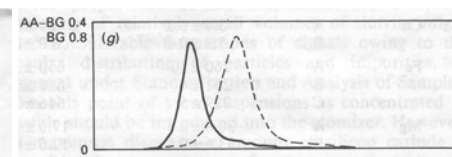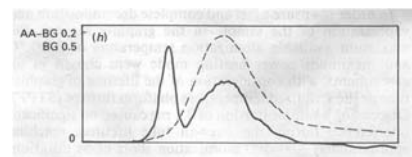
Fe 252.7 nm          0.1 mg SiC matrix          Fe 248.3 nm
  D$_2$-compensation system

## SSA 600 assisted insertion of solids & HR CS AAS



Fig. 6. Absorbance over time and wavelength for a biscuit sample in the vicinity of Cd resonance line at 228.802 nm; pyrolysis temperature: 700 °C; atomization temperature: 1700 °C for Cd and 2600 °C for Fe.
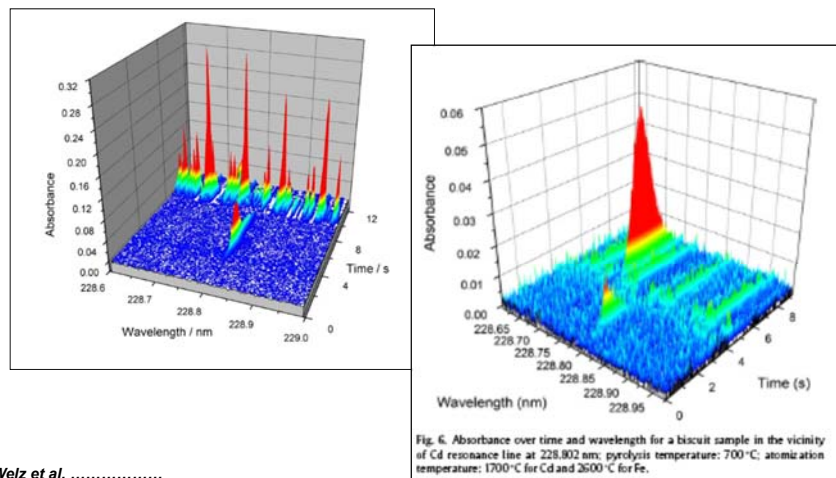
*B.Welz et al. ………………*

Lisia M.G. dos Santos, Rennan G.O. Araujo, Bernhard Welz, Silvana do C. Jacob,
Maria Goreti R. Vale, Helmut Becker-Ross: *Talanta* 78 (2009) 577–583

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## "Problems" of direct solid sampling AAS ?

- **calibration**
  lack of standards, RMs, CRMs, preparation of standards is complicated or even impossible

consequences:
- occurrence of systematic errors

- **homogeneity of the sample**
  lack of information about the homogeneity (distribution of the impurities in the sample), what portion of the sample is representative for the reality
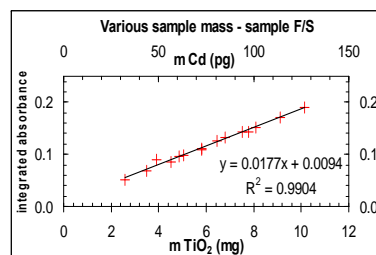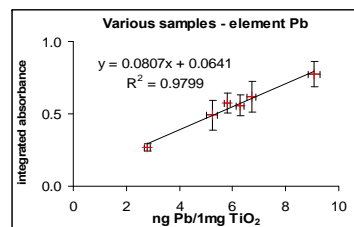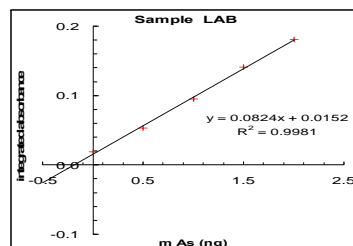
consequences:
- bad reproducibility, occurrence of systematic errors

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## Calibration

**TiO$_2$ samples**

**standard addition method**

**method of internal laboratory reference samples**



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## Calibration

Zeeman effect 3-field dynamic mode

high value 0.8 T
low value 0.5 T

analytik jena AG
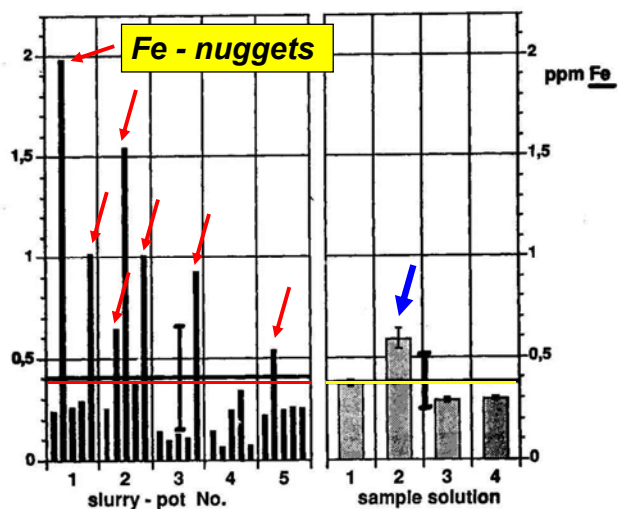
TiO$_2$ LAB 1.4 mg
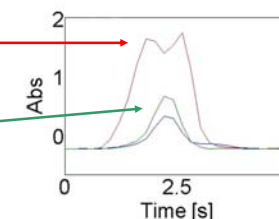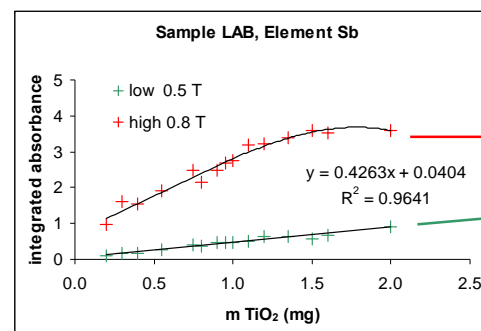
- *homogeneity – „fractionation" study*

**aliquots**

*slurry –*
     0.2 mg $MoO_3$

*dissolution –*
     0.5 g $MoO_3$



B.Docekal, V.Krivan: Determination of trace elements in high purity molybdenum trioxide by slurry sampling ET AAS. - *J.Anal.Atom.Spectrom. 8*, 637-641 (1993).

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