Inovace vzdělávání v chemii na PřF MU
Projekt CZ.1.07/2.2.00/07.0436 v rámci OP Vzdělávání pro konkurenceschopnost
předmět „*Trendy v analytické chemii*“

Přímá analýza pevných vzorků atomovou absorpční spektrometrií s elektrotermickou atomizací

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

Why ?

elimination of sample preparation step
(sample handling can be minimized only to weighing procedure)

- ***reduction of contamination risk, blank fluctuation, detection limits***
- ***elimination of troublesome, time consuming digestion, decomposition***

Trace / Ultra-trace element analysis
of modern, advanced, High-Tech materials

chemical resistance, hardness, electrical properties …..

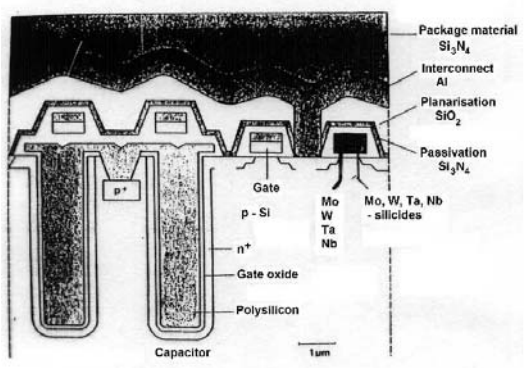
Ceramics

oxides - Al_2O_3, TiO_2, SiO_2, MgO, ZrO_2 …..
nitrides - BN, Si_3N_4 , Ti_3N_4 …….
carbides - SiC, B_4C_3 , TiC, WC ……..

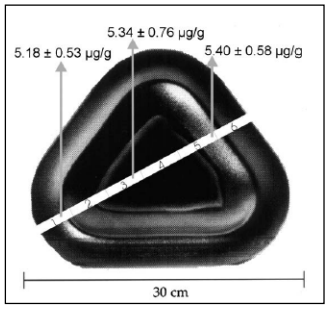
Microelectronics

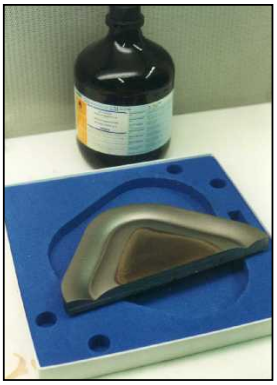
refractory metals - Mo,W, Ta, Nb, Ti ……..
silicides - $MoSi_2$, $CoSi_2$ …….
:
:

Microelectronic cell and its materials



6N Titanium sputtering target for VLSI-technology





Example

refractory metals in VLSI-technology *(gate material)*
6N high purity grade molybdenum (99.9999 %)
(sputtering targets for plasma technology)

requirements:

- ***heavy metals*** *(Cu, Fe, Mn, Ni, Pb, Zn ….)* ***- max. 10^2 ppb***
  (juction 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)

Why ?

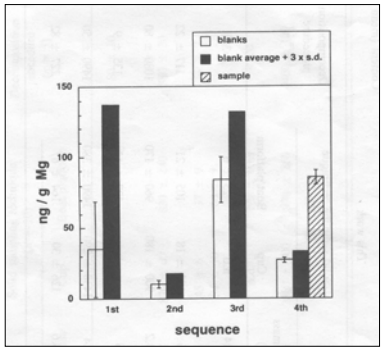
elimination of sample preparation step

- **reduction of contamination risk in order to achieve the desired detection limits** *(Na, K, Mg, Ca)*

Example - determination of Mg in hp Mo, hp MO_3

wet decomposition in HNO_3 + H_2O_2 under clean-bench conditions - class 100, n = 5

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



B.Dočekal, V.Krivan: *JAAS 8*, 637 (1993)
B.Dočekal, V.Krivan: *Spectrochim.Acta 50B*, 517 (1995)

Why ?

- **elimination of troublesome, time consuming digestion, decomposition procedures**

most of the advanced materials are chemically resistant

extreme temperature and chemical treatment is necessary to decompose the sample

example:

decomposition of powdered silicon carbide (HC Starck Berlin, grain size 0.2-0.5 µm)

0.2 g + high purity concentrated HNO_3, HF, H_2SO_4 with 30% of SO_3

10 h, PTFE-lined bomb, DB4 Berghof (250 bar)

B.Dočekal, P.Tschöpel, J.A.C.Broekaert, et al.: Determination of impurities in silicon carbide powders. - *Fresenius J.Anal.Chem. 342*, 113-117 (1992).

Comment:

Decomposition of sample with modern MW - digestion technology

(ranking list showing the decreasing difficulty of decomposition)

SiC
ceramics, graphite
sediments, soils
coal, plastic material
cocoa, chocolate, milk
crud oil, fuel, plant oil, fat, butter, margarine
biological tissue (liver, muscle, kidney)
plant material (leaves, grain, shoot, root, needless…)
environmental samples (sewage sludge, waste water…)

Purity requirements for TiO_2 samples

food-, pharma-grade
additives to cigarette paper and viscose fibers, etc.

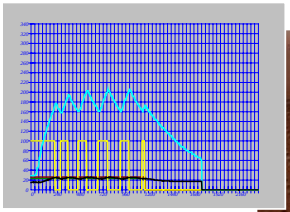
maximum permitted content of trace elements according to European standards

concentration of impurities in mg/kg (ppm)

Product type	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_2O_3	50

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



T, p, P - chart

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

Corrosion of graphite parts due to sulfuric 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: 10µl

sample boat

fume escaping the atomizer

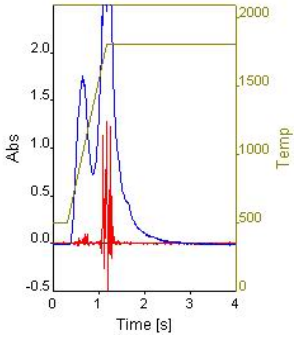
Spectral interference effects due to sulfuric and hydrofluoric acids

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

Sb 217.6 nm
sample aliquots: 2.5µl
(LOD > 5 ppm)

similar results for
As 193.7 nm
sample aliquots: 5µl
(LOD = 25 ppm



How ?

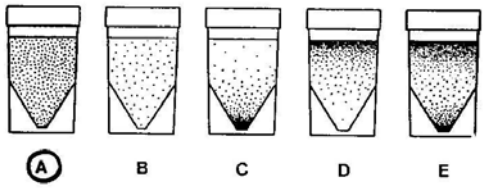
- ***slurry sampling***
  - *powdered samples*
  - *preparation of representative suspension (1-5%)*
  - *disintegration of agglomerates by ulrasonication*
  - *slurry homogenization and stabilization during taking aliquotes*
  - *dispensing by micropipettes or by conventional autosamplers*
- ***true direct sampling of solids***
  - *various types of sample carriers (miniature sample boats, cups, platforms)*
  - *sample weighing*
  - *insertion to the atomizer (manually, robotized)*

How ?

- ***slurry sampling***
  - *powdered samples - useful for powdered products*
    - *additional grinding can cause contamination/loss*
    - *inconvenient for biological materials (disintegration in liquid nitrogen is applicable)*
  - *slurry homogenization and stabilization*
    - *dispersion medium - high purity water, alcohol, ...*
    - *addition of surfactants (Triton), stabilization agents (density control), leaching with acids (homogeneity)*
    - *limited to materials of low density (1-2 g cm^{-3})*
    - *plastic vessels, laboratory magnetic stirring devices, PTFE-lined magnetic bars*
    - *ultrasonic probe, bath*

How ?

- ***slurry homogenization and stabilization***



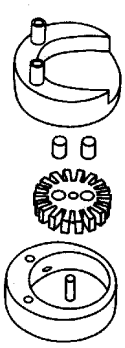
How ?

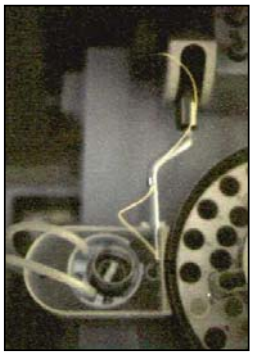
- ***slurry homogenization and stabilization***

turbine driven by air or water

magnetic pieces

modification of sample cup tray

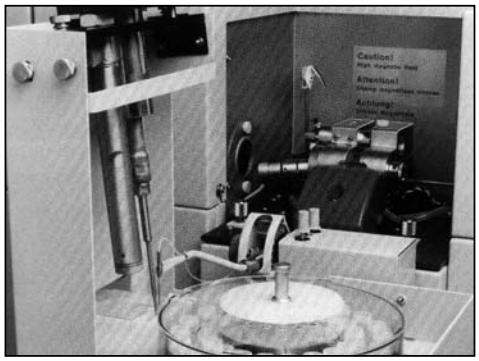




B.Docekal, A simple stirring device for slurry sampling technique in electrothermal atomic absorption spectrometry - *J.Anal.Atom.Spectrom.*, 8, 763-764 (1993)

How ?

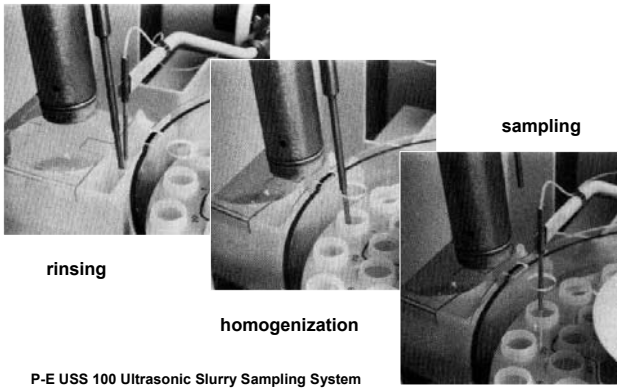
- *slurry homogenization - ultrasonication*



P-E USS 100 Ultrasonic Slurry Sampling System

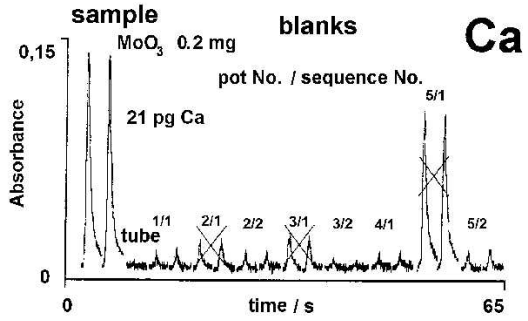
How ?

- *slurry homogenization - ultrasonication*



P-E USS 100 Ultrasonic Slurry Sampling System

- *slurry sampling*
  - *control and measurement of real blanks in dispersion medium*



- *slurry sampling*
  - *control and measurement of real blanks in dispersion medium*
  - *detection limits can be significantly reduced*

Example - analysis of hp MoO_3

LODs (ppb)		
Analyte	*wet*	*slurry*
Ca	500	2
K	200	1
Mg	100	0.5
Na	200	1

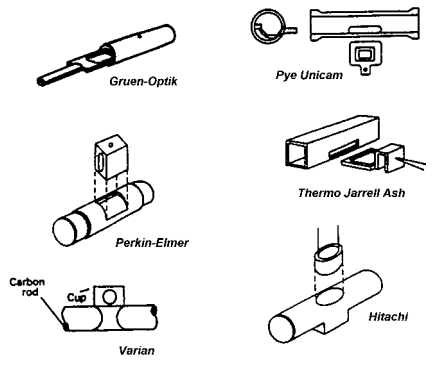
B.Docekal, V.Krivan: Determination of trace elements in high purity molybdenum trioxide by slurry sampling ET AAS. - *J.Anal.Atom.Spectrom.*, 8, 637-641 (1993).

How ?

- *true direct sampling of solids*
  - *various types of sample carriers (miniature sample <u>boats</u>, cups, platforms)*
  - *sample weighing*
  - *insertion to the atomizer (manually, robotized)*

How ?

- *true insertion of solid samples - history*



boats
platforms
cups

How ?
• *true insertion of solid samples* - www.analytikjena.de

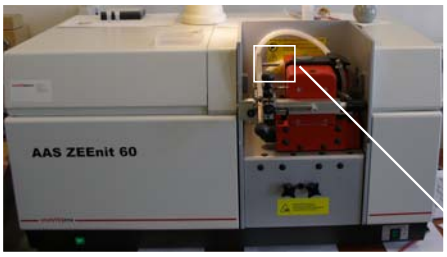
sample boat

full-automatic sample changer equipped with micro-balance and data transmission

How ?
• *true insertion of solid samples*

3-field mode Zeeman-effect BG-correction system

direct solid sampling introduction technique for the determination of trace impurities in titanium dioxide powder by ETAAS



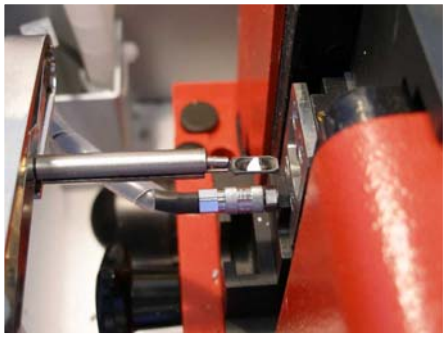
manual solid sampling

How ?
• *true insertion of solid samples*

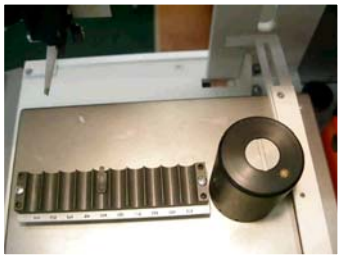
Detail of the manual insertion device in stand - by position

How ?
• *true insertion of solid samples*

Boat with the sample

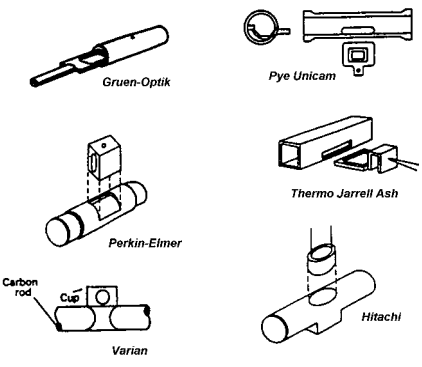


How ?
• *robotized true insertion of solid samples*



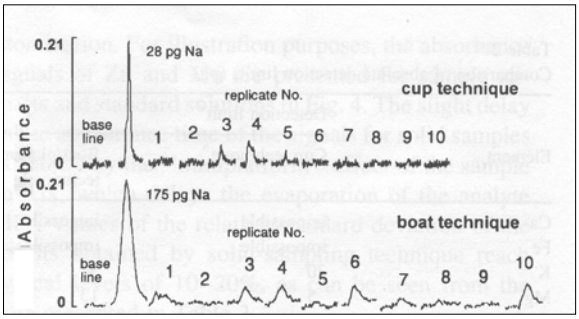
microbalance with robotized tweezers

How ?
• *true insertion of solid samples – blanks ?*



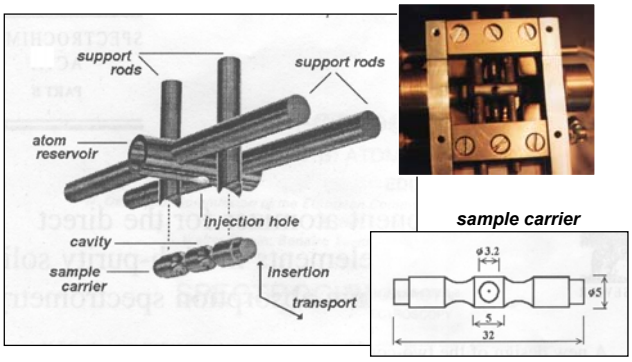
How ?

- ***true insertion of solid samples***
  - *various types of sample carriers (boats, cups, platforms, probes)*
  - *contamination problems in ultratrace analysis ??*



How ?

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

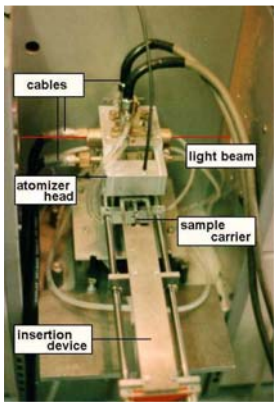


B.Docekal: A new design of the two-component atomizer for the direct determination of medium and volatile elements in high-purity solid refractory metals by electrothermal atomic absorption spectrometry. - *Spectrochim. Acta, Part B,* 53B, (1998) 427-435.

Direct Solid Sampling AAS

How ?

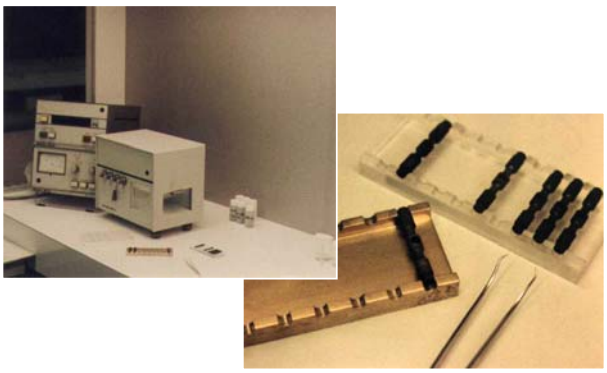
New design of the two-component atomizer for solid sample analysis



B.Docekal: *Spectrochim. Acta, Part B,* 53B, (1998) 427-435

How ?

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

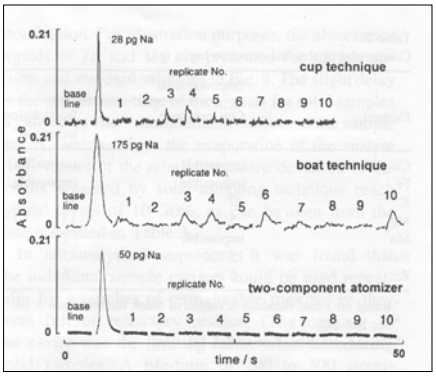


B.Docekal: *Spectrochim. Acta, Part B,* 53B, (1998) 427-435

How ?

- *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*

B.Docekal: *Spectrochim. Acta, Part B,* 53B, (1998) 427-435.

"Problems" of direct solid sampling AAS ?

Any method is accompanied by its inherent "problems" !
It is just to pay for advantages of direct solid sampling !

- ***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, ...)*

"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*

How to manage,
how to overcome these "problems" ??

"Problems" of direct solid sampling AAS ?

- *refractory matrix*

build up of residue ***TiO_2 samples***

vs clean out temperature
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

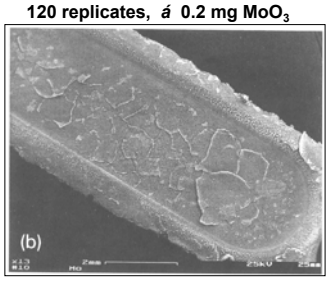
"Problems" of direct solid sampling AAS ?

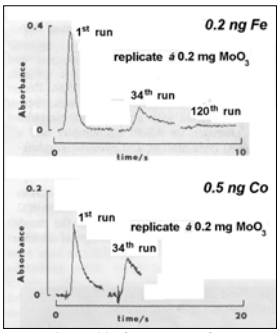
- *refractory matrix*

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





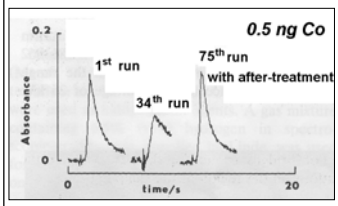
B.Docekal, V.Krivan: Halogen assisted cleaning after-treatment in graphite furnace a.a.s. for analysis of molybdenum based materials. - *Anal.Chim.Acta 279*, 253-260 (1993)

"Problems" of direct solid sampling AAS ?

- *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	argon + Freone
temperature	(CCl_4, CF_4, …)
blow-out	argon + hydrogen
clean-out	argon
cool-down	argon



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)

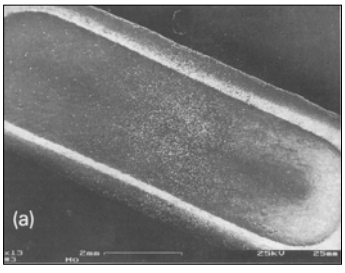
"Problems" of direct solid sampling AAS ?

- *refractory matrix*

removal of matrix *- atomizer should be cleaned*
chemical modification in gaseous phase
utilization of alternate gas implemented in modern instrumentation

SEM of graphite platform

after 72 atomization runs
with 0.2 mg MoO_3
employing
CF_4-assisted after-treatment



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)

"Problems" of direct solid sampling AAS ?

- *refractory matrix*

Is it possible to vaporize / atomize the analyte from the refractory matrix ?!!

boiling , decomposition points are very high

Example

molybdenum - radiotracer study

MoO_3 spiked with tracers
reduced in hydrogen atmosphere
vaporization efficiency

some of the analytes are excluded from the crystal lattice to the surface and can be 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).

"Problems" of direct solid sampling AAS ?

- ***refractory matrix***

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

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

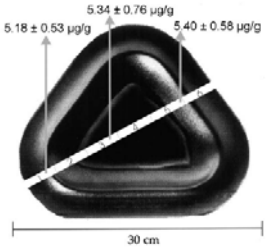
Example

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



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).

Problems of direct solid sampling AAS ?

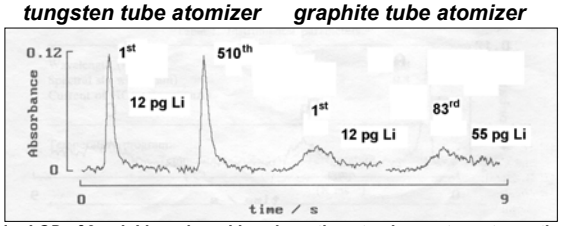
- ***refractory matrix***

interaction with the atomizer - analytical tube lifetime is significantly reduced

Example

determination of Li in molybdenum based materials (MoO_3)

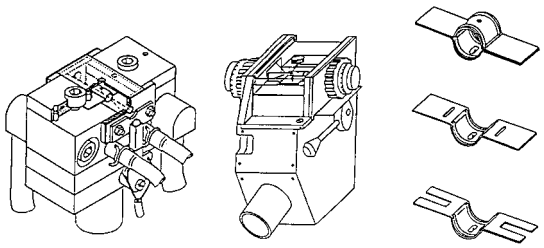
tungsten tube atomizer graphite tube atomizer



superior LOD of 2 ppb Li can be achieved vs other atomic spectrometry methods

B.Docekal, V.Krivan: An improved electrothermal atomic absorption spectroscopy method for the determination of lithium in molybdenum oxide using slurry sampling and a tungsten atomizer. - *Spectrochim. Acta, Part B*, 48B, 1645-1649 (1993).

tungsten tube atomizer WETA 80, 82, 93



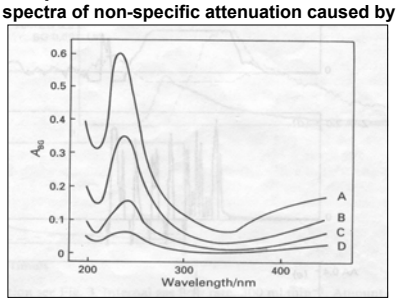
"Problems" of direct solid sampling AAS ?

- ***refractory matrix***

spectral interference - high background attenuation, structured spectra of background

Example

spectra of non-specific attenuation caused by 0.1 mg SiC matrix



A, B, C and D

0, 50, 100 and 300 ml/min Ar, resp.

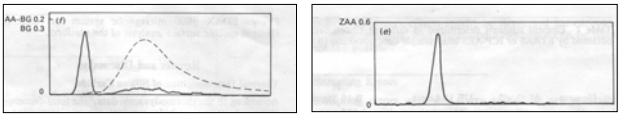
B.Docekal, V.Krivan: Direct determination of impurities in powdered silicon carbide by GF AAS using slurry sampling technique. - *J.Anal.Atom.Spectrom.* 7, 521-528 (1992)

"Problems" of direct solid sampling AAS ?

- ***spectral interference***

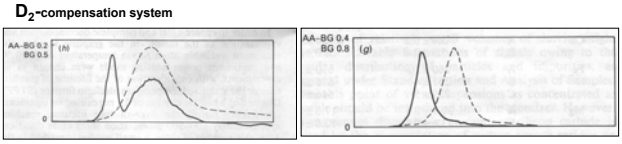
Zn 213.8 nm **0.5 mg SiC matrix**

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

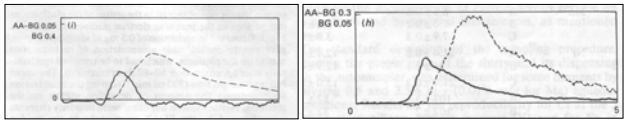


"Problems" of direct solid sampling AAS ?

- ***spectral interference***

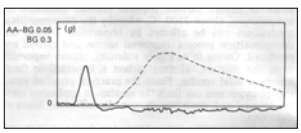
Ni 232.0 nm **0.5 mg SiC matrix** **Ni 352.5 nm**

D_2-compensation system

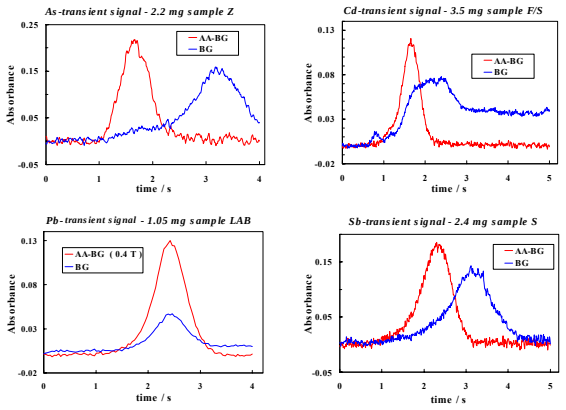


Cd 228.8 nm **0.1 mg SiC matrix**

D_2-compensation system - signal separation in time



Analytical signals *for TiO_2 samples, Zeeman-effect compensation*



"Problems" of direct solid sampling AAS ?

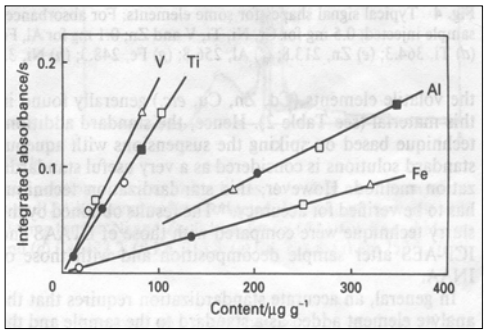
- ***calibration***
  lack of standards, RMs, CRMs

solution:

- ***preparation of standards based on the same matrix when possible (Al_2O_3 ….)***
  Z.Slovák, B.Docekal: *Anal.Chim.Acta 129*, 263-267 (1981).
- ***standard addition method***
  (spiking of the sample with aqueous standard solution - validation by independent method) (Mo, $MoSi_x$ …..)
  B.Docekal, V.Krivan: *Spectrochim. Acta 50B*, 517-526 (1995).
- ***utilization of analyzed samples** (one / more) - "laboratory RM "*
  one - introduction of various amounts of sample
  more - introduction of aliquots of various samples
  (SiC, TiO_2 ….)
  B.Docekal, V.Krivan: *J.Anal.Atom.Spectrom. 7*, 521-528 (1992)

"Problems" of direct solid sampling AAS ?

- ***calibration***
  utilization of analyzed samples of SiC - "laboratory RM s"

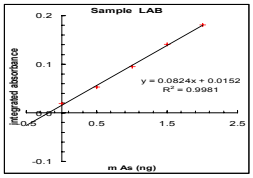


B.Docekal, V.Krivan: Direct determination of impurities in powdered silicon carbide by GF AAS using slurry sampling technique. - *J.Anal.Atom.Spectrom. 7*, 521-528 (1992)

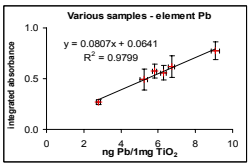
Calibration

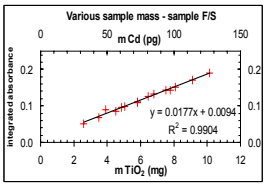
TiO_2 samples

standard addition method



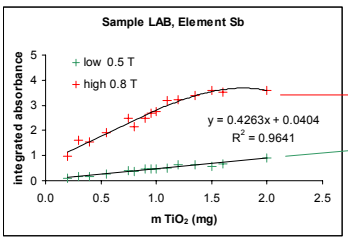
method of internal laboratory reference samples



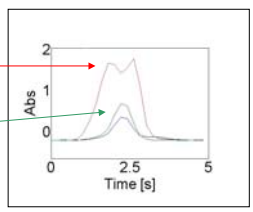


Calibration

3-field dynamic mode ***high value 0.8 T***
low value 0.5 T



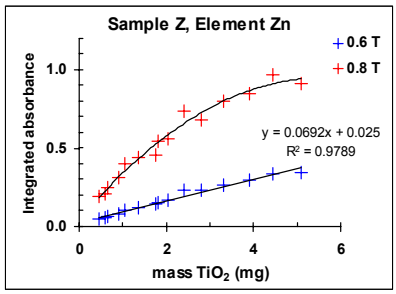
TiO_2 LAB 1.4 mg



Calibration

» ***3-field dynamic mode*** high value 0.8 T
low value 0.6 T

TiO_2 - sample Z , 0.4 - 4.5 mg



"Problems" of direct solid sampling AAS ?

- ***homogeneity***

Example

Analysis of SiC

Repeatability of dispensing in determination of Fe, Cr

dispensing: 20 µl-aliquots of 0.5% m/v SiC ≅ 0.1 mg SiC

Sample	*RSD (%)* (n=6)	*concentration* (ppm)
I	3.7	250 Fe
II	5.1	650 Fe
IV	8.3	130 Fe
IV	3.4	5.6 Cr
V	6.8	320 Fe

B.Docekal, V.Krivan: Direct determination of impurities in powdered silicon carbide by GF AAS using slurry sampling technique. - *J.Anal.Atom.Spectrom.* 7, 521-528 (1992)

"Problems" of direct solid sampling AAS ?

- ***homogeneity***

Example

Analysis of hp MoO_3

Repeatability of dispensing and sampling procedures

slurry preparation: 1% m/v MoO_3 , 100 mg MoO_3 / 10 ml water

dispensing: 20 µl-aliquots ≅ 0.2 mg MoO_3

Element	*RSD (%)* dispensing (n=8)	sampling (n=5)
Ca	1.8	14
Fe	85	59
K	9.6	12
Mg	34	32
Na	8.5	20

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).

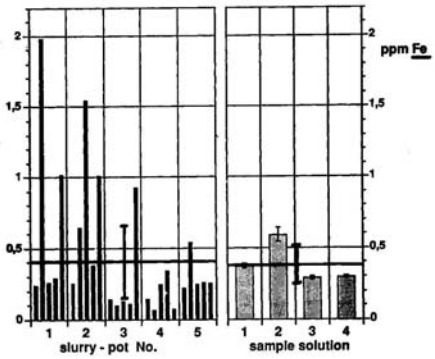
"Problems" of direct solid sampling AAS ?

- ***homogeneity***

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).

iac brno

Bohumil Dočekal
Institute of Analytical Chemistry, Czech Academy of Sciences v.v.i.
Veveří 97, CZ 60200 Brno, Czech Republic
e-mail: docekal@iach.cz