

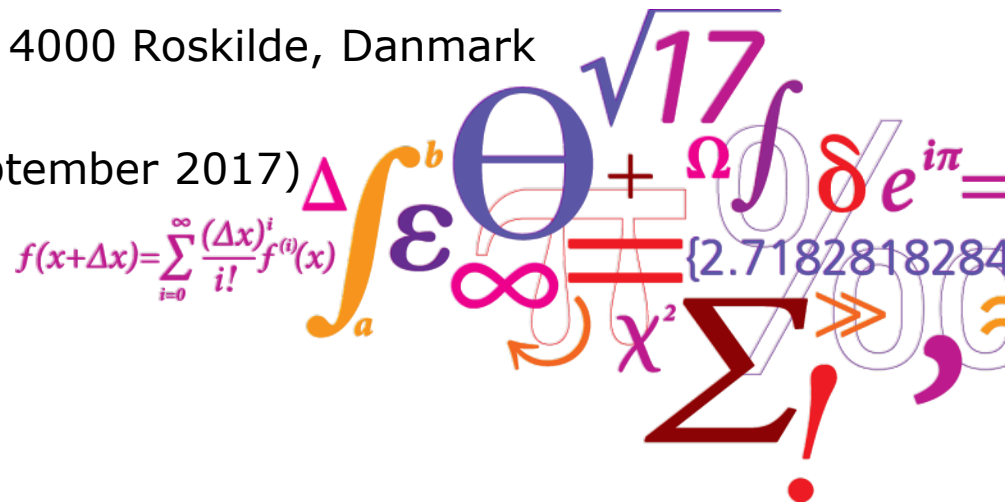
# ICP-OES measurement of some transition metals in HF acid media

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# Introduction 1

- Method has to be developed for determination of  $^{93}\text{Mo}$ ,  $^{94}\text{Nb}$  (and  $^{93}\text{Zr}$ ) from nuclear power plant wastes (for example steel samples).
- Many preliminary experiments for method development have to be performed: a relatively fast and easy technique is needed to understand the chemical behavior of Mo and Nb (and Zr).
- Easy-to-measure isotopes (gamma-emitters):  $^{95}\text{Zr} \rightarrow ^{95}\text{Nb}$ 
  - $^{95}\text{Zr}$  ( $t_{1/2} = 64$  days): 724 keV (44%) and 756 keV (54%) gamma-line
  - $^{95}\text{Nb}$  ( $t_{1/2} = 35$  days) : 765 keV (100%) gamma-line
  - No such isotope of Mo exists.
- No more working nuclear reactors at Risø! Without it the named radionuclides are very expensive to have (purchase).
- We have to rely on the stable isotopes of natural composition of these analytes. Their concentrations are measured using ICP-OES.
- Zr and Nb are „flouofil“ elements. [Anal Sci 25 (2009) 1181-1187]

# „Fluorophil“ elements

1182

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H																			He
Li <sup>I</sup>	Be <sup>II</sup>											B <sup>III</sup>	C <sup>IV</sup>	N <sup>V</sup>	O	F		Ne	
	#											#	CO <sub>3</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>					
Na <sup>I</sup>	Mg <sup>II</sup>											Al <sup>III</sup>	Si <sup>IV</sup>	P <sup>V</sup>	S <sup>VI</sup>	Cl		Ar	
												#	SiF <sub>6</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>				
K <sup>I</sup>	Ca <sup>II</sup>	Sc <sup>III</sup>	Ti <sup>IV</sup>	V <sup>III</sup>	Cr <sup>III</sup>	Mn <sup>II</sup>	Fe <sup>III</sup>	Co <sup>II</sup>	Ni <sup>II</sup>	Cu <sup>II</sup>	Zn <sup>II</sup>	Ga <sup>III</sup>	Ge <sup>IV</sup>	As <sup>III</sup>	Se <sup>IV</sup>	Br		Kr	
		#	TF <sub>6</sub> <sup>2-</sup>	VO <sub>2</sub>	#		#					#	GeF <sub>6</sub> <sup>2-</sup>	AsO <sub>3</sub> <sup>3-</sup>	SeO <sub>3</sub> <sup>2-</sup>				
Rb	Sr <sup>I</sup>	Y <sup>III</sup>	Zr <sup>IV</sup>	Nb <sup>V</sup>	Mo <sup>VI</sup>	Tc	Ru <sup>III</sup>	Rh <sup>III</sup>	Pd <sup>II</sup>	Ag <sup>I</sup>	Cd <sup>II</sup>	In <sup>III</sup>	Sn <sup>IV</sup>	Sb <sup>III</sup>	Te <sup>IV</sup>	I		Xe	
			ZrF <sub>6</sub> <sup>2-</sup>	NbOF <sub>5</sub> <sup>2-</sup>	MoO <sub>4</sub> <sup>2-</sup>		#	RhBr <sub>6</sub> <sup>2-</sup>	PdBr <sub>4</sub> <sup>2-</sup>		CdBr <sub>2</sub>	InBr <sub>3</sub>	SnF <sub>6</sub> <sup>2-</sup>	SbF <sub>6</sub> <sup>3-</sup>	TeO <sub>3</sub> <sup>2-</sup>				
Cs	Ba <sup>II</sup>	L	Hf <sup>IV</sup>	Ta <sup>V</sup>	W <sup>VI</sup>	Re <sup>VII</sup>	Os <sup>IV</sup>	Ir <sup>III</sup>	Pt <sup>IV</sup>	Au <sup>III</sup>	Hg <sup>II</sup>	Tl <sup>III</sup>	Pb <sup>II</sup>	Bi <sup>III</sup>	Po	At		Rn	
			HfF <sub>6</sub> <sup>2-</sup>	TaOF <sub>5</sub> <sup>3-</sup>	WO <sub>4</sub> <sup>2-</sup>	ReO <sub>4</sub>	OsBr <sub>6</sub> <sup>2-</sup>	IrBr <sub>6</sub> <sup>3-</sup>	PtBr <sub>4</sub> <sup>2-</sup>	AuBr <sub>3</sub>	HgBr <sub>2</sub> <sup>2-</sup>	TlBr <sub>3</sub>	PbBr <sub>4</sub> <sup>2-</sup>	BiBr <sub>3</sub>					
Fr	Ra	A	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg									

L	La <sup>III</sup>	Ce <sup>III</sup>	Pr <sup>III</sup>	Nd <sup>III</sup>	Pm	Sm <sup>III</sup>	Eu <sup>III</sup>	Gd <sup>III</sup>	Tb <sup>III</sup>	Dy <sup>III</sup>	Ho <sup>III</sup>	Er <sup>III</sup>	Tm <sup>III</sup>	Yb <sup>III</sup>	Lu <sup>III</sup>
A	Ac	Th <sup>IV</sup>	Pa	U <sup>VI</sup>	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
				UO <sub>2</sub> <sup>3+</sup>											

Ti	Fluorophile element
Os	Bromophile / Iodophile elements
U	Oxophile element

Ca	Insoluble fluoride forming element
Na	Bare cation / Aquaphile elements

#: See text.

## Introduction 2

- $^{94}\text{Nb}$  can be measured by gamma-spectrometry.
  - Radionuclides causing the Compton continuum have to be removed.
- $^{93}\text{Mo}$  can be measured by ICP-MS, LSC or X-ray spectrometry.
  - Each detection type needs a very pure source.
- A very effective method is needed. (Probably a several-steps method)
- Effectivity of each step has to be determined.
  - Decontamination factor (DF), separation factor
$$DF_{\text{component}} = A_{\text{component, before separation (step)}} / A_{\text{component, after separation (step)}}$$
$$DF_{\text{component}} = m_{\text{component, before separation (step)}} / m_{\text{component, after separation (step)}}$$
- To avoid the contamination of our laboratory, most preliminary experiments are performed using stable nuclides and ICP-OES as detection technique.

# Equipment 1



## Equipment 2

- Hardware: Varian Vista AX CCD Simultaneous ICP-AES
  - Software: ICP Expert II (Agilent Vista PRO Instrument Software, version 2.0)
  - Ca. 3 mL sample is needed (1 M alkali ... 1 M acid)
  - Blank: 3% HNO<sub>3</sub>
  - The main difficulty:
    - HF acid is practically always needed when dissolving and separating Nb and Zr, so it is present in all of the samples to be measured.
    - However, HF damages the glassware of the ICP-OES equipment.
- $$\text{SiO}_2 + 4 \text{HF} \rightarrow \text{SiF}_4 + 2 \text{H}_2\text{O}$$
- How to avoid this damage?
    - Dilution
    - Evaporation
    - Complexation

# Dilution

- Authors of some papers (for example: Prog Nucl En 93 (2016) 362-370) do not take care of presence of  $F^-$  when its concentration is below 0.005 M.
- So dilution might be used in certain cases.
  - Typically when HF concentration is not much higher than the given level (for example: 0.01 M or 0.02 M).
- But dilution also decreases the concentration of the analytes, so it cannot be widely used.
  - “Official” limits of detection: Mo: 4 ppb =  $\mu\text{g/L}$  = ng/mL  
Nb: 4 ppb  
Zr: 1.5 ppb

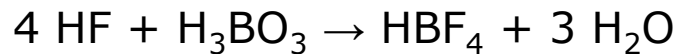
# Evaporation

- Avoiding HF is practically impossible, as Zr and Nb can practically not be (and do not remain) dissolved without  $F^-$ . (Remember, they are “fluorophile” elements.)
- But the concentration of  $F^-$  can be decreased significantly.
- For example: in case of 10 mL  $\geq 1$  M HF (for example 2 M, 4 M, 6 M etc.)
  - evaporation
  - taking up in 100  $\mu$ L cc. HF + 100  $\mu$ l cc.  $HNO_3$
  - dilution to 10 mL
  - Result: 0.28 M HF / 0.16 M  $HNO_3$
- Don't forget to protect the glass window of your fume hood!



# Complexation

- For complexation of excess F<sup>-</sup>, boric acid can be used (J Anal At Spectrom 11 (1996) 287-296):



- It has to be taken into account, that boric acid increases the number of false signals:
  - Mo: 201.512 nm line
  - Zr: 343.823 nm line
  - Fe: 234.830, 273.358 and 373.713 nm lines
  - Ni: 230.299 nm line
  - Mn: 344.199 nm line

## Further difficulties 1

- “Real time” analysis is not possible; results are produced some days after the experiment.
  - Correction of experiment’s parameters is mainly not possible.
  - A huge drawback compared to gamma-spectrometry.
- (But measurement of an individual sample is much faster.)

## Further difficulties 2

- A very wide range of concentrations has to be managed.
  - Composition of NIST Standard Reference Material 123c Stainless Steel (AISI 348) - a test material:
    - mainly (68.52%) Fe,
    - 17.40% Cr,
    - 11.34% Ni,
    - 1.75% Mn,
    - 0.65% Nb,
    - 0.22% Mo,
    - 0.12% Co.
  - Fe/Mo  $\approx$  311
  - If Mo  $\approx$  4 ppb (LOD)  $\Rightarrow$  Fe  $\approx$  1400 ppb
  - If Mo  $\approx$  100 ppb  $\Rightarrow$  Fe  $\approx$  30000 ppb
- Samples can be diluted; but isolation or separation are not possible, as we want to characterize the separation steps!

## Further difficulties 3

- Many other false signals arise, such as (for example):
  - Mo: 281.615 nm line           Al, Mn  
       284.824 line               Nb
  - Nb: 210.942 nm line         Fe, Mn  
       309.417 nm line         Cr, Mo
  - Zr: 256.889 nm line         Fe  
       343.823 nm line         Nb
  - Fe: 234.350 nm line         Cr  
       258.588 nm line         Mo  
       261.382 nm line         Cr
  - Cr: 286.674 nm line         Mo
  - Ni: 227.021 nm line         Cr  
       230.078 nm line         Nb
  - Mn: 261.815 nm line         Fe, Cr





# Conclusions

- ICP technique can be used for development of a radioanalytical method (determination of recoveries of analytes and decontamination factors of disturbing components); but some strange or unusual difficulties can arise.

# Thank you very much

for this challenging task, and  
for your kind attention.



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