



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}Mo , ^{94}Nb (and ^{93}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}Zr ($t_{1/2} = 64$ days): 724 keV (44%) and 756 keV (54%) gamma-line
 - ^{95}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 „flourofil“ elements. [Anal Sci 25 (2009) 1181-1187]

„Fluorophil“ elements

1182

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

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

Ti	Fluorophile element
Os	Bromophile / Iodophile elements
U	Oxophile element

Ca	Insoluble fluoride forming element
Na	Bare cation / Aquaphile elements
#	See text.

Introduction 2

- ⁹⁴Nb can be measured by gamma-spectrometry.
 - Radionuclides causing the Compton continuum have to be removed.
- ⁹³Mo 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% HNO₃
 - 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

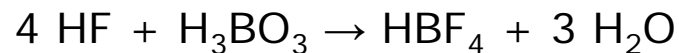
- Authors of some papers (for example: Prog Nucl En 93 (2016) 362-370) do not take care of presence of F^- when its concentration is below 0.005 M.
- So dilution might be used in certain cases.
 - Typically when HF concentration is not much higher than the given level (for example: 0.01 M or 0.02 M).
- 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 ≥ 1 M HF (for example 2 M, 4 M, 6 M etc.)
 - evaporation
 - taking up in 100 μ L cc. HF + 100 μ 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⁻, 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.

