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IMPURITY MEASUREMENTS BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS ON PALLADIUM, NICKEL AND COPPER THIN-FILMS

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INTRODUCTION

Unexpected excess heat.

Fleischmann and Pons, 1989: the possibility of obtaining excess heat greater than that generated by electrochemical reactions.

BACKGROUND OF THE WORK

Literature data reporting:

- Random and sporadic production of neutrons and/or tritium.
- Extreme difficulty for measuring ^{4}He.

➢ X-ray emission and production of new atomic species during experiments.

AIM OF THE WORK

Series of experiments analyzing the materials and substances with the Instrumental Neutron Activation Analysis (INAA) for both choosing the purest materials and discarding the others, and checking the blanks, and investigating elements present in electrodes after the test.

Preliminarily, some candidate materials to be used in the experiments were analyzed by INAA; after, electrode blanks and electrolyte solutions were analyzed, and finally, the electrodes used and the electrolyte solutions exhausted as well.

Electrolysis experiments on mono- and multi-layered thin-films of Pd and Ni; possibility of observation of new atomic species; some species could be produced by nuclear transmutation in condensed matter.

Why INAA?

- ✓ INAA is a no-destructive analytical method.
- ✓ No chemical-physical pre-treatment of samples.
- ✓ Determination up to 50-60 elements.
- ✓ Analytical characteristics: very low limit of detection (LOD); high sensibility; high precision.
- ✓ Bulk method.
- ✓ The main used technique in literature.

In this work: **Ag**, **Al**, **As**, **Au**, **Br**, **Cl**, **Cr**, **Co**, **Cu**, **Eu**, **Fe**, **Ga**, **Hf**, **Mg**, **Mn**, **Mo**, **Na**, **Ni**, **Pd**, **Sb**, **Se**, **Sm**, **Ta**, **V**, **W**, **Zn**.

EXPERIMENTAL APPARATUS

Experiment cells: 15 ml^{-1}, pure polyethylene containers, very low level of impurities.

Anode: Platinum wire, 99.99 % pure Pt.

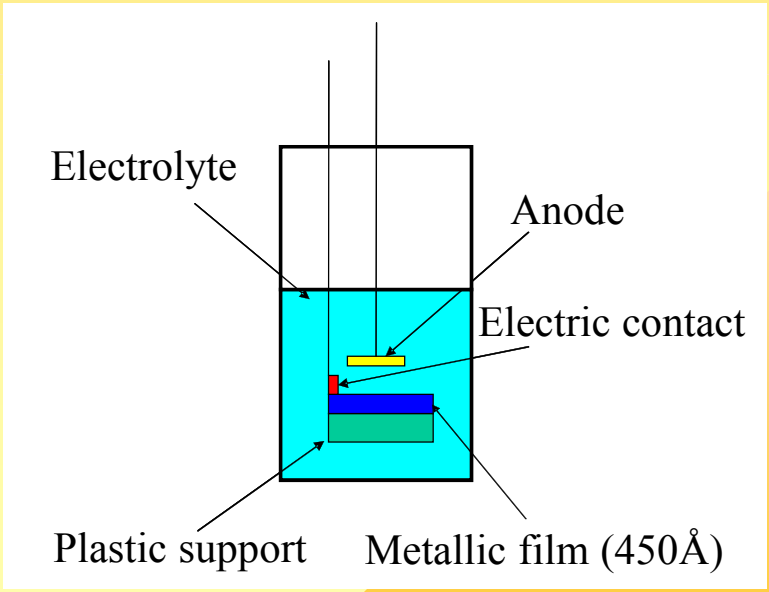
Cathode: metallic thin-film containing Cu, or Ni, or Pd, deposited onto a polyethylene disk (12 mm diameter and 1 mm thickness).

Cathode contact: “C” shape Pt wire inserted into a polyethylene support to prevent the electrolysis between anode and cathode connections.

HYDROGEN LOADING

- ✓ Pure Polyethylene (Kartell)
- ✓ Pure Pt (99.99%) wire
- ✓ Light water (18MΩ) $LiSO_4$ solution
- ✓ Electrolysis time: 3-40 hours
- ✓ Current: 5-190 mA
- ✓ Voltage: 3-7 V

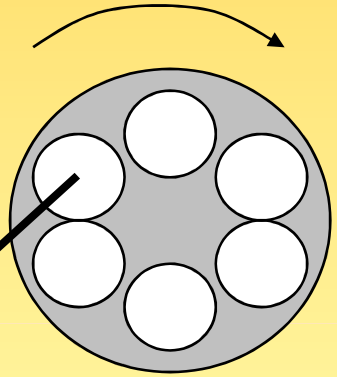
Photo of the electrodes

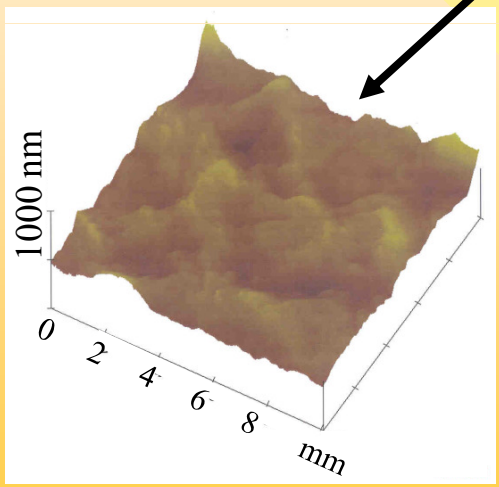


Electrolytic cell

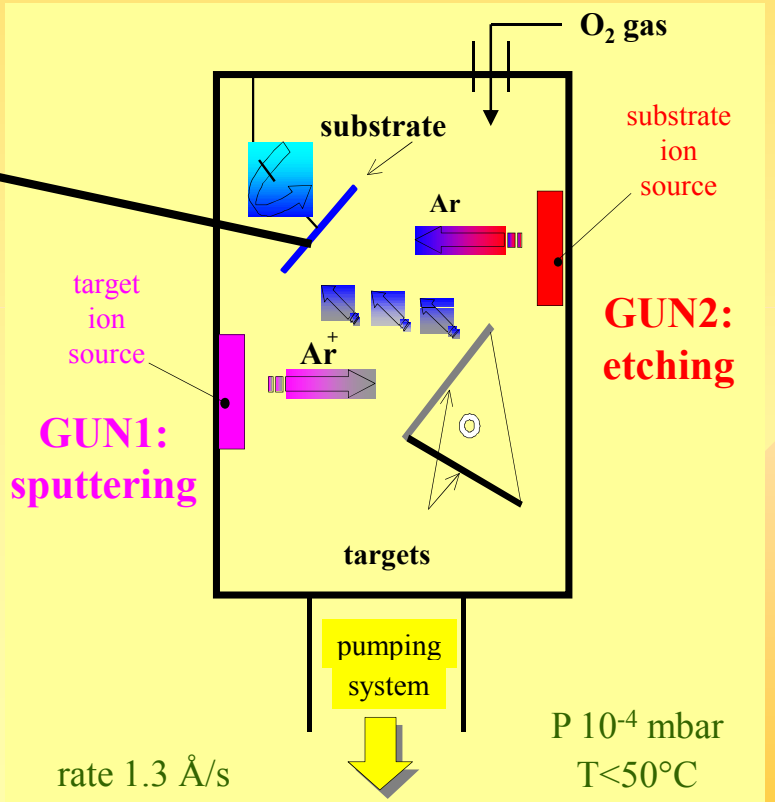
Film Deposition Details

Rotating Sample Holder
(6 identical locations)





Film surface morphology
(by Atomic Force Microscopy)



Dual Ion beam Sputtering plant

PROCEDURE PREPARATION

Cleaning procedure: first washing with 18 $M\Omega \times cm^{-1}$ ultrapure distilled deionized water; washing with HNO_3 65% for 1 minute; rinsing with 18 $M\Omega \times cm^{-1}$ ultrapure distilled deionized water; rinsing with solution 20% KOH in ethanol; rinsing with ethanol; rinsing several times with 18 $M\Omega \times cm^{-1}$ ultrapure distilled deionized water; drying at room temperature.

Pt wire: supplementary step cleaning using acetone and ethylene.

All the procedures and the experiments performed in a class 100 clean room.

EXPERIMENTS

Three series of experiments:

1. Mono-, double- (e.g. Cu/Ni) and multi-layer thin-film (e.g. Cu/Ni/Pd/Ni/Pd) electrodes and electrolyzing Li_2SO_4 10^{-4} M and $SrSO_4$ 1 M;
2. same type of electrodes excluding Cu mono-layer, and electrolytes;
3. X-rays emission measurements during electrolysis, using mono and double layers electrodes (Cu; Ni; Cu/Ni and Cu/Pd) and Li_2SO4 10^{-3} M and 1 M.

After electrolysis: both spent cathodes with relative blanks and solutions with relative standards were irradiated.

NEUTRON IRRADIATION - INAA

Electrolytical solutions and electrodes: 2 neutron irradiations in Rabbit of TRIGA MARK II Casaccia reactor for 1 and 10 min at $\Phi=1.25\times10^{13}$ $n\times cm^{-2}\times s^{-1}$.

Electrolytical solutions and electrodes: 3 neutron irradiations in Lazy Susan of TRIGA MARK II Casaccia reactor for 24, 30 and 30 hrs at $\Phi=2.6\times10^{12}$ $n\times cm^{-2}\times s^{-1}$.

γ-Spectrometry: HPGe detector ORTEC, FWHM 1.70 keV at 1332.5 keV, efficiency 23%, peak/Compton ratio 58:3.

NUCLEAR DATA

Element	Product nuclide	Cross Section (barn)	Half life		γ-Ray used (keV)	LOD (ng)
Ag	^{108}Ag	35	2.41	m	632.9	0.1
Ag	^{110m}Ag	37.2	250.4	d	657.7	
Al	^{28}Al	0.232	2.246	m	1778.8	30
As	^{76}As	4.3	26.3	h	559.2	0.001
Au	^{198}Au	98.8	2.70	d	411.8	6×10^{-5}
Br	^{80}Br	8.5	17.4	m	617.0	0.002
Br	^{82}Br	2.69	1.47	d	776.5	
Cl	^{38}Cl	0.428	37.2	m	1642.4	2
Co	^{60}Co	37.2	5.272	y	1332.5	0.06
Cr	^{51}Cr	15.9	27.7	d	320.0	0.1
Cu	^{64}Cu	4.5	12.74	h	1345.8	
Cu	^{66}Cu	2.17	5.1	m	1039.0	0.4
Eu	^{152}Eu	5900	12.7	y	1408.0	2
Fe	^{59}Fe	1.15	45.1	d	1099.2	20
Ga	^{72}Ga	4.71	14.1	h	834.0	0.002
Hf	^{181}Hf	12.6	42.4	d	482.2	0.02
Mg	^{27}Mg	0.038	9.45	m	1014.4	20
Mn	^{56}Mn	13.3	2.58	h	846.6	8×10^{-5}
Mo	^{99}Mo	0.45	2.75	d	141.0	0.03
Na	^{24}Na	0.53	15.02	h	1368.6	0.004
Ni	^{58}Co	0.113	70.78	d	810.7	6
Pd	^{109}Pd	12	13.46	h	88.1	
Pd	^{109m}Pd	0.2	4.69	m	188.9	
Sb	^{122}Sb	6.25	2.70	d	564.0	0.001
Se	^{75}Se	51.8	120.4	d	264.6	0.1
Sm	^{153}Sm	206	1.948	d	103.1	5
Ta	^{182}Ta	21	115	d	1221.3	0.01
V	^{52}V	4.88	3.75	m	1434.2	0.9
W	^{187}W	37.8	24.0	h	685.7	0.001
Zn	^{65}Zn	0.78	243.8	d	1115.5	0.1

RESULTS AND DISCUSSION

Element	Mono Cu	Mono Ni	Mono Pd	Double Cu/Ni	Multi Cu/Ni/Pd/Ni/Pd
Na	< 8	< 3	< 4	< 3	< 7
Mn	56±17	66±4	109±5	118±8	143±10
Br	< 391	< 29	145±30	404±111	< 133
Mg	< 89	< 21	< 26	< 51	< 39
Cl	< 32	< 30	111±16	168±18	78±15
Al	< 62	209±1	468±8	2223±12	558±14
V	< 19	< 13	205±7	609±10	130±13
As	< 41	< 2	< 5	< 13	< 12
Ag	< 5840	< 1500	< 2200	< 2790	< 1660
Au	< 13	2±1	< 3	< 5	< 3
Cu	298000±2490	2330±105	< 166	259140±1308	163560±1742
Pd	1093±348	7±1	27869±178	337±6	43933±421
Ni	46±16	322±8	< 13	318±26	698±36

Blank electrodes, Rabbit irradiation: levels (Bq) of elements

Blank solutions, Rabbit irradiation, Li_2SO_4 and $SrSO_4$ solutions: levels (Bq mL^{-1}) of elements

Element	$SrSO_4$ 10^{-4} M	Li_2SO_4 1 M
Na	99±12	1217±80
Mn	74±11	< 94
Br	< 243	8920±662
Mg	< 56	< 252
Cl	348±41	< 81
Al	657±20	3954±50
V	< 23	< 520
As	< 24	< 123
Au	< 8,3	< 114

First series of experiments, Rabbit irradiation, Li_2SO_4 solution (1×10^{-4}M): levels (Bq) of elements

Element	Mono Cu	Mono Ni	Mono Pd	Double Cu/Ni	Multi Cu/Ni/Pd/Ni/Pd
Na	< 9	18±7	< 6	< 12	< 10
Mn	94±13	99±7	< 13	113±11	29±10
Br	< 200	< 98	< 70	390±138	< 156
Mg	< 57	< 37	< 16	< 55	< 49
Cl	< 7	< 28	< 34	< 29	< 35
Al	446±8	< 137	< 39	< 167	< 145
V	**12766±81**	**12733±81**	**1507±29**	**13795±102**	**17424±425**
As	< 27	< 5.2	< 2.4	< 16	< 8.8
Ag	< 4150			< 3750	< 3430
Au	< 9	38±4	< 3.4	15±7	16±7
Cu	n.d.	< 360	< 153		
Cu		< 1180	< 500		
Ni			< 8		

First series of experiments, Lazy Susan irradiation, Li_2SO_4 solution (1×10^{-4}M): levels (Bq) of elements

Element	Mono Ni	Mono Pd	Double Cu/Ni	Multi Cu/Ni/Pd/Ni/Pd
Zn	82±2	71±1	11.8±1.4	92±4
Ag	42±1	< 0.5	< 0.6	< 0.6
Mo	9.3±0.5	< 0.8	1.4±0.2	32.4±0.4
W	578±2	< 42	< 50	112±3
Au	8490±33	1423±8	592±3	1481±11
Cr	129±4	< 7.4	64±3	< 11
Co	2.5±0.5	< 0.4	< 0.6	2.3±0.4
Sb	34±1	5.7±0.4	8.4±0.6	21.2±0.9
Fe	< 1.3	< 1.2	4.5±0.4	< 1.6
Br	66±1	< 8	27.3±0.6	< 8

Second series of experiments, Lazy Susan irradiation, polyethylene support after etching, Pt wire, lab gloves and paper, Li_2SO_4 solutions (10^{-3}M and 1M): levels (Bq) of elements

Element	PET support after etching	Pt wire	Lab gloves	Lab paper	Li2SO4 10-3 M	Li2SO4 1M
	Bq	*Bq/g*	*Bq*	*Bq*	*Bq/mlL*	*Bq/mL*
Zn	1.14±0.11	**148±52**	**3919700±47784**	**820±12**	0.59±0.10	1.76±0.29
Ag	6.19±0.12	**1986±46**	< 238	< 0.75	< 0.05	< 0.2
Cr	9.43±0.35	< 15000	< 4430	115±6	4.8±0.2	< 10
Co	0.27±0.07	< 33	52±21	18.1±0.6	0.26±0.03	< 0.2
Fe	< 0.35	< 229	< 500	7.8±1.6	0.79±0.07	< 0.7
Se	< 0.1	< 249	< 213	< 2	< 0.07	1.1±0.4
Eu	<0.08	< 503	< 224	< 1.6	< 0.05	< 1.6
Sb	< 0.06	< 553	< 185	46±1	0.16±0.03	1.7±0.2
Ni	< 0.13	< 44	< 410	< 2	< 0.07	< 0.4
Hf	4.42±0.05	< 239	< 407	37±1	< 0.11	< 0.7
Ta	0.59±0.11	**1510±61**	< 374	**629±8**	0.64±0.10	0.98±0.29
Ir	0.16±0.03	**3020100±18138**	< 239	<1.1	< 0.05	< 0.4

Third series of experiments, Lazy Susan irradiation, cathodes: levels (Bq) of elements

Element	Mono Cu	Mono Ni	Double Cu/Ni	Double Cu/Ni	Double Cu/Pd
Zn	61.4±0.9	33.6±0.7	14.4±0.6	23.1±0.7	61.4±1.0
Ag	3.6±0.3	144±2	8.89±0.24	39.1±0.63	6.03±0.30
Cr	598±3	341±2	69±2	733±3	475±3
Co	< 0.37	< 0.39	< 0.50	1.33±0.39	8.9±0.3
Fe	7.26±0.28	5.31±0.36	6.51±0.54	8.50±0.52	10.19±0.45
Se	5.88±0.32	4.15±0.32	< 0.59	2.36±0.33	<0.88
Eu	1.85±0.83	< 1.07	< 0.81	< 1.46	<1.24
Sb	< 0.82	< 0.82	< 0.73	< 1.04	< 1.34
Ni	< 1.2	< 1.34	< 1.67	< 1.70	2.08±0.20
Hf	< 0.94	< 1.2	< 1.1	< 1.3	< 1.2
Ta	9.75±0.44	6.46±0.48	< 2.1	6.75±0.61	21.3±1.3
Ir	76±6	451±3	156±1	407±3	154±1

Third series of experiments, Lazy Susan irradiation, cathodes: levels (ng) of some elements

Element	Mono Cu	Mono Ni	Double Cu/Ni	Double Cu/Ni	Double Cu/Pd
Zn	1509±78	825±3	354±24	567±33	920±50
Ag	27±2	1083±28	67±2	294±8	45±3
Cr	1020±9	582±3	117±3	1250±9	810±7
Co	< 0.66	< 0.70	< 0.89	2.4±0.7	15.9±0.6
Fe	3410±160	2500±180	3060±270	3990±270	4790±25

CONCLUSION

- Au and Ir levels: due to contamination problem from platinum anode because of the erosion occurring during the electrolysis process.

- Cr, Hf, Mo, W and Zn: their presence can be attributed from mould during the etching process and to their participation to the thin-film preparation.

- Presence of Ag, Ir, Ta and Zn: possible contamination from Pt wire.

- Levels (ng) of Ag, Co, Cr, Fe and Zn: very low levels of contaminants (detectable only by INAA); can be attributed to the cathode deposition during electrolysis. Actually, this is an “apparent” enrichment and not due to transmutation phenomena in the condensed matter.

- The only anomaly concerning the V levels (ranging between 25-280 ng) may be explained by considering that the cap of the cell was made by tools containing V.

- Suitable markers may be appropriate for this analysis.

Thanks for your kind attention