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**UNEXPECTED DETECTION OF NEW ELEMENTS IN ELECTROLYTIC  
EXPERIMENTS WITH DEUTERATED ETHYL-ALCOHOL, PD WIRE, SR AND HG  
SALTS**

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**Abstract**

The insoluble powder recovered at the bottom of our electrolytic cell, after several electrolytic deuterium loading/deloading cycles, was analysed by an ICP-MS analyser. The electrolyte was constituted of a deuterated hydro-alcoholic solution; Sr and Hg salts were added to such a solution at micromolar concentration; the cathode was a long and thin Pd wire. The ICP-MS analyses of the insoluble powder were motivated from the recent results of Y. Iwamura and collaborators at Mitsubishi Heavy Industries-Research Center (Yokohama, Japan) showing reproducible “transmutation” of Sr into Mo (isotopic composition different from natural one) and Cs into Pr, when a special multilayer Pd sheet was subjected to a prolonged Deuterium gas flowing. Some of our results look partially in agreement with Y. Iwamura report. Other unexpected elements were also detected with an isotopic distribution close to the natural one. The production of stable isotopes by *Selective Channel Photofission*, according to the model of A. Takahashi (Osaka University, Japan), can help for understanding. Further works, hopefully also from other Laboratories, are needed to clarify these kinds of results.

**Keywords:** PdDx, electrolytic hydro-alcoholic solution, Pd thin-long wire, Sr and Hg salts, “transmutation”.

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## 1. INTRODUCTION

Large and unexpected amounts of some foreign elements (Fe, Ti, Cu, Zn...) have been recently found on the surface of proper metallic cathodes (e.g. Pd) when electrolysis is performed with D<sub>2</sub>O based electrolytes<sup>1,2</sup>. The quantity of such foreign elements is in general too high to be considered as impurities galvanically deposited on the cathode. Furthermore, the isotopic mass ratios of these foreign elements are significantly different from the natural ones. This fact, in particular, has been explained by assuming that some nuclear reactions occur when Deuterium (D) is adsorbed on or absorbed into the Pd cathode, as pointed out from Akito Takahashi<sup>3</sup>.

At present, the electrolyte employed in our experiments is typically constituted by a solution of, both heavy, ethyl alcohol/water (93:7 by volume) containing very small amounts of specific inorganic ions. Our loading procedure is based on a series of D loading/deloading cycles (i.e. the Pd wire is alternatively set as cathode and anode). After a certain number of loading/deloading cycles a **black powder** appears at the bottom of the cell as a precipitate. The main component of this powder has shown to contain Pd, probably as PdO, which is produced during the deloading phase of the cycle when the Pd wire is anodic. If some *foreign elements* are formed during the cathodic phase of the cycle (D loading), it is very probable they are mainly present on the surface where the D/Pd ratio is higher. Therefore, when the Pd wire surface is subsequently oxidised, some of the *foreign elements* may remain entrained within the black powder. Taking into consideration the pioneering work by T. Mizuno<sup>1</sup>) and G.H.Miley<sup>2</sup>) and in particular the recent, very reliable and reproducible results obtained by Y. Iwamura<sup>4</sup>), we decided to check the presence of *foreign elements* in the black powder by means of a high resolution ICP-MS analyser.

## 2. EXPERIMENTAL CONDITIONS.

As reported in recent papers (ICCF8, JCF3, ICCF9), we adopt the following experimental conditions:

- a) **Electrolytic solution:** 750ml, heavy ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OD) and heavy water (D<sub>2</sub>O) mixture (93:7 by volume).  
The following salts and acids have been added to this kind of solution: SrCl<sub>2</sub>: 3–10\*10<sup>-5</sup> moles; HgCl<sub>2</sub>: 2–3\*10<sup>-5</sup> moles; D<sub>2</sub>SO<sub>4</sub>: 1–2\*10<sup>-5</sup> moles; DCl: 1–10\*10<sup>-5</sup> moles; Ba(OH)<sub>2</sub>: 0–1\*10<sup>-5</sup> moles.
- b) **Electrodes:** Cathode: Pd wire (l=60cm, φ=50μm), U-shaped so as to be contained into a borosilicate glass 3.3 (EU standard GH1), graduated cylinder (l=40cm, φ=5cm); Anode: U-shaped Pt wire (l=60cm, φ= 0.5mm);
- c) **Electrolysis** operating condition: DC@10mA, Anode-Cathode distance and Voltage: 5cm, 50—250V;
- d) **Loading measurement** (wire electrical resistance method): Pd wire electrical resistance measured through the voltage drop, along the Pd wire, produced by AC current (10kHz, square wave) of 18mA (J=1000A/cm<sup>2</sup>).
- e) **Solvent components** of the solution (C<sub>2</sub>H<sub>5</sub>OD, D<sub>2</sub>O) are vacuum distilled (45°C) and on line filtered (100nm, MILLIPORE type VVLP, PTFE filter): properly modified, by us, Rotavapor system (model R-134 BÜCHI). These operations allow for:

- 1) *control* over the composition of the electrolyte (necessary because of the very low concentrations of the electrolytes added, typical of our method) and strong reduction of all the impurities normally dissolved in the two liquids. Such impurities, even if present in very small amount, could be galvanically accumulated on the cathode and be mistaken for *foreign elements*. After the double distillation procedure the electrical conductivity of the two solvent components of the electrolytic solution was reduced from about 100 $\mu$ S to less than 1 $\mu$ S, for D<sub>2</sub>O, and from 2 $\mu$ S to 0.05 $\mu$ S, for C<sub>2</sub>H<sub>5</sub>OD, respectively. As a reference, typical distilled H<sub>2</sub>O, in the same specific experimental conditions of measurement, shows a conductivity of about 3 $\mu$ S. In particular, a strong reduction of KMnO<sub>4</sub> and Iron ions, usually present in heavy water, is required: the presence of such substances significantly inhibits the D-loading, ensuing in lower D/Pd ratios;
- 2) *elimination* of the two new species of bacteria (*Ralstonia* and *Stenotrophomonas detesculanense*), discovered by us in D<sub>2</sub>O in 1999<sup>5)</sup>. We experienced that such bacteria negatively affect the D/Pd loading<sup>6)</sup>.

### 3. EXPERIMENTAL RESULTS.

By adopting the above experimental conditions, during the D-loading phase (Pd is cathode) a thin coating containing Hg, Pt and Sr sulphate is formed on the Pd wire surface. Pt ions (a drawback because they lower the cathodic overvoltage) are produced because of the anodic corrosion of the Pt wire. Pt metal is galvanically deposited on the Pd wire, together with Hg. Sr ions, because of the local alkalinization due to the cathodic D<sup>+</sup> discharge, precipitate as SrSO<sub>4</sub> on the cathodic surface. Such a coating, which basically characterises our D loading method, significantly increases the cathodic overvoltage of the Pd wire. R/R<sub>0</sub> values < 1.7, at 25°C, (D/Pd > 0.93) can currently be achieved<sup>7)</sup>.

During the deloading phase of the cycle (Pd wire as an anode) the coating and a consistent amount of Pd (probably as PdO) detaches from the wire and precipitates as a black powder. Accordingly, it was found that Pd, Pt, Hg, and Sr are the main constituents of such a precipitate.

Y. Iwamura and co-workers reported<sup>4)</sup> that Sr, electrochemically applied on a multi-layer Pd sheet, was progressively and surprisingly “transmuted” into Mo when D gas was forced to flow through the multi-layer sheet. Taking into consideration that a thin layer of Sr is also present in our Pd cathodes, we thought that our procedure, even if consistently different from that of Y. Iwamura, might allow for a reproduction of their results.

In the Y. Iwamura experiment a low work-function material (e.g. CaO) is sputtered together with Pd on a Pd sheet so as to form a 1000Å layer. The presence of a low work-function material seems to be essential for the Sr→Mo “transmutation”. On the other hand, as pointed out by A. Takahashi and co-workers (**JCF4-22**, in press), such nuclear reactions in the D-Pd system should presumably occur in sites where the D/Pd ratio is particularly high, that is at the CaO-Pd-Sr interface. *Now, considering the much higher loading ratio currently achieved by our electrolytic technique, with respect to those allowed for by the gas loading procedure, it is possible that the Sr→Mo “transmutation” also can occur on our cathode and therefore that Mo be present in the black powders found at the bottom of our electrolytic cell.*

#### 4. ELECTROLYTIC DEUTERIUM LOADING/DELOADING CYCLES

The Pd wire and the components of the electrolyte ( $D_2O$ ;  $C_2H_5OD$ ;  $HgCl_2$ ;  $SrCl_2$ ;  $D_2SO_4$ ;  $Ba(OH)_2$ ) were previously ICP-MS analysed in order to account for their impurities content with particular attention to the presence of Mo. Two experiments have been performed with two different Pd wires, under the following loading conditions: electrolytic current: 10mA; temperature: 26°C; time: 24--96h. Best R/Ro obtained at the end of the loading phases: experiment #1: R/Ro=1.68; experiment #2: R/Ro=1.74.

Deloading phase. Electrolytic current=2mA, for about 2 hours. (temperature: 25°C). When a R/Ro value of 1.1 is reached, the current is raised to 10mA for about 10 minutes. The latter procedure is necessary for a complete deloading of the Pd wire. We observed, after some loading/deloading cycles, that a significant residual stress remains on the Pd wire (i.e. the minimum R/Ro after deloading was higher than the starting one). We noted that the amount of residual stress (0.2-4%) increased more when an higher loading value was achieved during the D loading phase.

Both the experiments reported in this paper consisted in five D loading/deloading cycles and the total time was about 2 weeks. In experiment #1 the black powder, deposited at the bottom of the cell, was collected together with 100cc of solution, evaporated to dryness, solubilized by aqua regia and submitted to ICP-MS analysis. In experiment #2 only the solution was collected, evaporated to dryness and solubilized by aqua regia for ICP-MS analysis.

#### 5. ICP-MS RESULTS

The analyses were performed at the Laboratories of "Centro Sviluppo Materiali" by a high resolution ICP-MS instrument (HP&YOKOGAWA Analytical Systems, model 4500, 1996) calibrated at "low power plasma" in order to reduce possible spectroscopic interference's (polyatomic, oxide, and doubly charged ions), apart isobaric. Calibration factor: 1count= $6 \cdot 10^{10}$ atoms. All the counts, reported in the following tabels, have been corrected for all the "blanks" and the interference effects, if any. Detection limit:  $6 \cdot 10^{11}$ atoms. In the tabels are reported the counts pertinent to the suggested isotopes for ICP-MS analysis and selected for reference and their natural percent abundance in (xx). In some cases and in particular for the main constituents of the black powder we were forced to use isotopes different from ones suggested according to ICP-MS builder, because of instrumental overflow.

*Table 5.1a) – Typical impurities in heavy ethyl-alcohol/water (93:7 by volume), 100ml, after re-distillation.*

Element	Counts
<sup>23</sup> Na(100)	1.2*10 <sup>5</sup>
<sup>47</sup> Ti(7.3)	30
<sup>55</sup> Mn(100)	400
<sup>57</sup> Fe(2.2)	< 10
<sup>63</sup> Cu(69.2)	7.2*10 <sup>3</sup>
<sup>66</sup> Zn(27.9)	760
<sup>88</sup> Sr(82.6)	7.6*10 <sup>3</sup>
<sup>93</sup> Nb(100)	110
<sup>98</sup> Mo(24.1)	26

*Table 5.1b) – Analysis of SrCl<sub>2</sub>. <sup>84</sup>Sr(0.56): 1.4\*10<sup>7</sup> counts.*

Element	Counts
<sup>47</sup> Ti(7.3)	6.2*10 <sup>3</sup>
<sup>57</sup> Fe(2.2)	2.0*10 <sup>3</sup>
<sup>66</sup> Zn(27.9)	< 10
<sup>90</sup> Zr(51.5)	490
<sup>93</sup> Nb(100)	204
<sup>98</sup> Mo(24.1)	32
<sup>137</sup> Ba(11.2)	1.2*10 <sup>4</sup>

*Table 5.1c) – Analysis of HgCl<sub>2</sub>. <sup>202</sup>Hg(29.9): 5.8\*10<sup>6</sup> counts.*

Element	Counts
<sup>47</sup> Ti(7.3)	6310
<sup>57</sup> Fe(2.2)	1.3*10 <sup>3</sup>
<sup>66</sup> Zn(27.9)	400
<sup>88</sup> Sr(82.6)	7.2*10 <sup>3</sup>
<sup>90</sup> Zr(51.5)	380
<sup>93</sup> Nb(100)	10
<sup>98</sup> Mo(24.1)	80

Table 5.1d) – Analysis of the virgin Pd wire.  $^{102}\text{Pd}(1.0)$ :  $7.0 * 10^6$  counts (about 30cm of wire).

Element	Counts
$^{47}\text{Ti}(7.3)$	120
$^{57}\text{Fe}(2.2)$	200
$^{63}\text{Cu}(69.2)$	$2.4 * 10^3$
$^{66}\text{Zn}(27.9)$	<10
$^{90}\text{Zr}(51.5)$	$8.9 * 10^3$
$^{93}\text{Nb}(100)$	< 10
$^{98}\text{Mo}(24.1)$	11

Table 5.1e) – Analysis of the Pt wire (ICP-MS assay performed by the Pt supplier). Impurities in ppm.

Fe	20
Ir	9.1
Na	9.0
Pd	7.3
Cu	5.1
Ca	4.2
Re	3.4
Mg	3.2
Rh	3.2
Al	2.8
Zr	6.9
Ti	1.1
Mn	0.2
Cr	1.3
Au	1.9

Table – 5.2 Main constituents in the Experiment #1, black powder.

Element	Counts
$^{102}\text{Pd}(1.0)$	$2.3 * 10^6$
$^{195}\text{Pt}(33.8)$	$1.5 * 10^6$
$^{84}\text{Sr}(0.56)$	$1.1 * 10^6$
$^{204}\text{Hg}(6.9)$	$7.2 * 10^6$
$^{138}\text{Ba}(71.7)$	$2.3 * 10^5$

Table 5.3 – Other elements (unexpected) in the Experiment #1, black powder.

Element	Counts
<sup>47</sup> Ti(7.3)	1.5*10 <sup>4</sup>
<sup>57</sup> Fe(2.2)	3.0*10 <sup>5</sup>
<sup>63</sup> Cu (69.2)	8.7*10 <sup>3</sup>
<sup>66</sup> Zn(27.9)	2.4*10 <sup>4</sup>
<sup>90</sup> Zr(51.5)	4.6*10 <sup>4</sup>
<sup>93</sup> Nb(100)	5.6*10 <sup>5</sup>
<sup>98</sup> Mo(24.1)	3.4*10 <sup>3</sup>

- \* We inform that Ti, Fe, Zn, Nb, for cross check purposes, were also analysed, because of their relevant amount, by means of another less sensitive analytical technique: ICP-OES analysis (Perkin-Elmer, model OPTIMA3300 XL-DV, 2000). Sensitivity: ≈10ppb (about 1000 times lower than ICP-MS).
- \* We inform that we made other analysis on *Pd wires* before and after electrolysis by SEM-EDAX instrument (at Pirelli Labs). In some “spot areas” of after electrolysis wires, “new” elements like Ti, Fe, Zn were detected.

## 6. COMMENTS ON THE ELEMENTS IN TAB. 5.3

Each of them shows relevant excess counts with respect to the values of “the blank” obtained by summing up the contributions taken from Tab. 5.1a) to Tab. 5.1e), properly “weighed” for the amount used in the experiment, as detailed in § 2 . The anomalous presence of Ti, Cu, Fe, and Zn, has been reported by other researches<sup>1,2)</sup> . The presence of Mo seems to align with the results of Y. Iwamura. At present it is not known to us if Nb, which was found in the black powder at relatively remarkable amount, has been reported in the literature as *foreign elements*. Having assessed the relevant excess amount of the elements shown in paragraph 5.3, we turned to the examination of their isotopic distribution. We found that the isotopic distributions of Ti, Cu, Fe, Zn and Zr were very close to the natural one. Accordingly, it would be concluded, in spite of their relevant amount, that the presence of these elements in the black powder was due to a contamination. *At present, we cannot explain the origin of such a heavy contamination.*

*Table 6.1 – Isotopic distribution of Mo in black powder, Exp.#1 (Mass&Natural abundance/Counts&New abundance).*

Mass number	Natural abundance	Experimental counts	New abundance
92	14.8	2771	16.4
94	9.3	3097	18.4
95	15.9	2044	12.1
96	16.7	2703	16.0
97	9.6	1319	7.8
98	24.1	3461	20.5
100	9.6	1327	8.7

The counts from the mass number 92 to 100 can be attributed to a some Mo contamination in the black powder. However, a significant deviation of the isotopic distribution from the natural one appears at the mass number 94 (natural abundance: 9.3%; found: 18.4%). Such a deviation could be explained by supposing that some foreign <sup>94</sup>Mo was “produced” during the electrolysis. The amount of our foreign Mo (expressed as atoms/cm<sup>2</sup>) is similar to that found by Y. Iwamura, but the mass number is different (94 versus 96). At present no satisfactory explanation of such a discrepancy is available.

## **7. ICP-MS ANALYSIS OF RESIDUE OBTAINED AFTER DISTILLATION OF ELECTROLYTIC SOLUTION**

In the electrolytic solution, after distillation, we have recovered (in consistently lower amounts), the same elements previously found in the *black powder*. No relevant anomalies in the isotopic distribution were detected even for Mo. Isotopic distribution was as following:

**Table 7 – Isotopic distribution of Mo soluble, Exp. #2 (Mass&Natural abundance/Counts&New abundance).**

Mass number	Natural abundance	Experimental counts	New abundance
92	14.8	1600	13.4
94	9.3	1190	10.0
95	15.9	1870	15.7
96	16.7	1940	16.2
97	9.6	1150	9.6
98	24.1	3020	25.3
100	9.6	1138	9.6



## 8. CONCLUSIONS

Several, unexpected, new elements were detected after loading/deloading electrolytic cycles in the above mentioned experimental conditions. Most of these elements have been collected in the insoluble *black powder* that precipitates during the anodic phase of the cycle. Among such foreign elements, Ti, Fe, Zn, Nb were found to be the most abundant components. All of these show an isotopic distribution close to the natural one, so some sort of contamination, at present not yet identified, can not be ruled out. Regarding the presence of Mo, we found that a clear isotopic anomaly occurs at the mass number 94, and not at mass 96 as reported by Y. Iwamura. Further work is necessary: in order to reconfirm our results and to explain the differences with respect to the Y. Iwamura experiments.

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