Analyses on copper samples from Micans

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Contents

1. Introduction

This Memo presents the results of work performed at Uppsala University relating to samples studied at Microbial Analytics Sweden AB, Micans. Three tasks have been performed:

1. Characterisation of the canister copper studied in Micans experiments. The results of fusion analyses to determine hydrogen content are presented in section 2a. The results of gas emission analyses when heating the canister copper samples are presented in section 2b. XPS analyses of two copper surfaces are presented in section 2c; one untreated sample and one where the surface has been treated with the method adopted at Micans, using SiC-polishing and sulfamic acid leaching (Bengtsson et al. 2013).
2. Preparation of samples of several copper qualities for subsequent study of hydrogen evolution when the samples are submerged in pure, oxygen free water at Micans. These samples were prepared with the surface treatment method based on electropolishing used at Uppsala University (Boman et al. 2014). During the sample preparation, hydrogen emission to vacuum when heating the samples to 400 °C was monitored. The list of samples prepared for Micans and the results of the hydrogen emission monitoring is presented in section 2d. The results of the subsequent experiments at Micans are presented in Johansson et al. (2015).
3. Analyses of water composition after the exposure of the copper to pure, oxygen free water in test tubes at Micans. ICP-MS analyses of water from four test tubes with copper, and one containing only water, are presented in section 2e.

2. Summary of results

2 a. Gas fusion analysis of the hydrogen content in canister copper

The results from the analysis of the hydrogen content in canister copper samples performed at Degerfors Laboratorium AB are summarized in Table 2.1. The equipment was a Leco ONH-836. The test certificates are presented in the Appendix. Also presented in the Appendix are two figures showing the hydrogen release as a function of time during the heating prior to melting. From these figures, a measure of the mobile hydrogen content is determined as hydrogen released below 900 °C (ASTM E1019). In these figures, the red curve indicates the temperature increases as a function of time (the left y-axis is the signal, the right y-axis is the heating power corresponding to temperature and x-axis time is in seconds) and the area before melting the sample is interpreted as a measure of the hydrogen at the surface layer. As can be seen in both figures there are three peaks. The first peak is a measure of the instrument background. The second peak is a measure of the mobile hydrogen (amount of hydrogen under 900 °C. The third peak is hydrogen evolved above 900 °C up to the melting point. The result is shown in Table 2.1, batch 2 mobile H.

Table 2.1 Hydrogen content in copper samples from two different batches

Sample	H/ppm	Description
batch 1*	1.0	Polished at Degerfors
batch 2**(from lid TX183)	1.6	Unpolished, untreated
batch 2 mobile H	0.26	Unpolished, untreated
batch 2 after heating at 500°C 4 h	<0.2	Unpolished, heat treated to 500 °C

**Samples from batch 1 had the size 10 x 1 x 0.2 cm (exact sample size used by Degerfors Laboratorium is not known).*

***Samples from batch 2 had been cut into 0.5 x 0.5 x 0.2 cm sizes.*

2 b. Gas desorption analysis of canister copper

The following analyses were performed on canister copper samples from a TX183 batch (batch 2 in Table 2.1), which were cut into pieces of 1 x 1 cm^2 with thicknesses of 0.2 cm each with a weight of 3.7 g. The different steps illustrate the effects of the heat treatments on some of the samples studied in Johansson et al. (2015) and in SKBdoc 1470267 as a function of temperature, mass or surface scratching. In this study a temperature of 600°C was used as a maximum temperature and the heating rate was 1°C/min in order to ensure that the sample temperature was as close as possible to the furnace temperature. The tube was evacuated for at least 12 hours down to 4 x 10^{-8} Torr before starting the measurement.

The figures show the partial pressures from H_2 (red), H_2O(blue), CO or N_2 (light blue), O_2 (green) and CO_2 (orange). The linear parts in grey show the temperature, with its scale to the right. Results obtained with a copper foil sample from Goodfellow (untreated) are shown in Figure 2.9 for comparison.

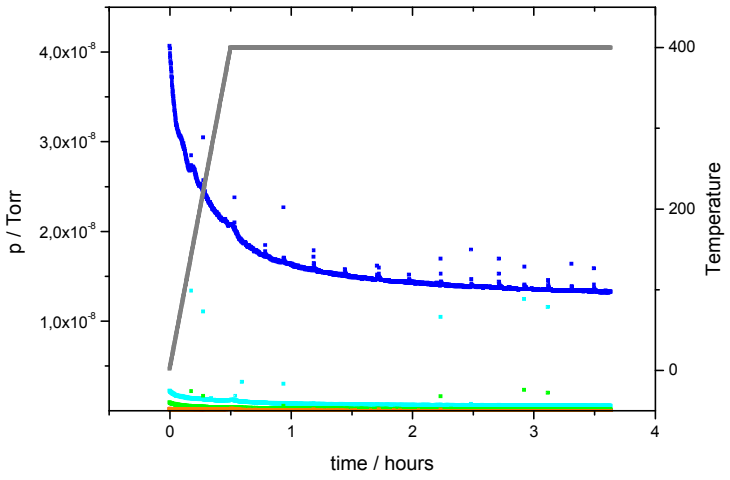

Figure 2.1 Background of the empty tube

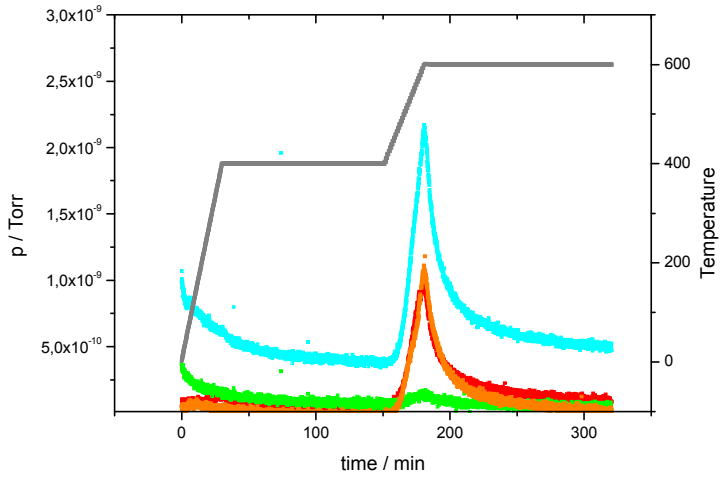

Figure 2.2 The tube is vented in air and reheated to 400°C and 600°C showing gas desorption as a larger part of the tube is heated.

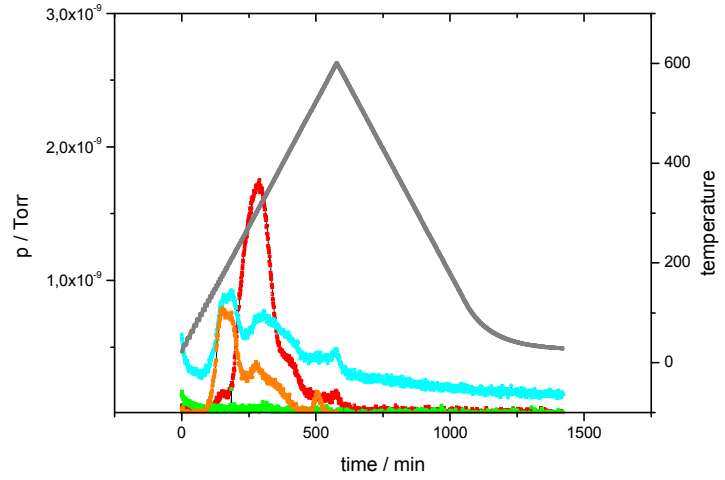

Figure 2.3 Two copper pieces (3.7 g) are placed in the tube inside a glovebox and heated to 600°C, showing a complete desorption under 500°C.

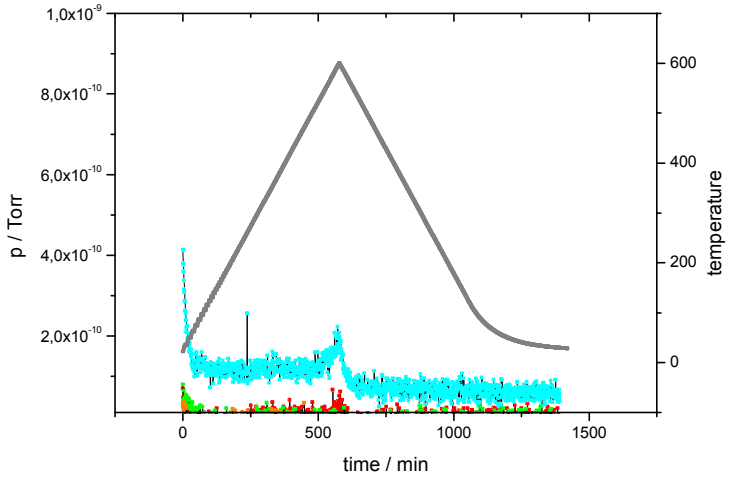

Figure 2.4 No further desorption is observed after a second reheating

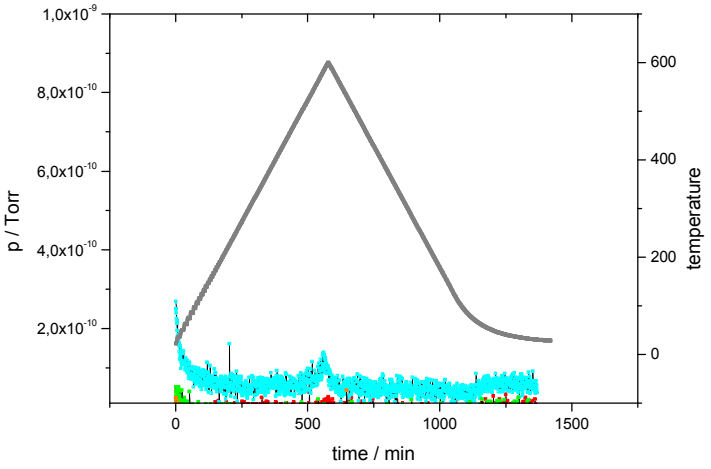

Figure 2.5 The sample is reduced in a H_2 atmosphere at 300°C and then heated in vacuum.

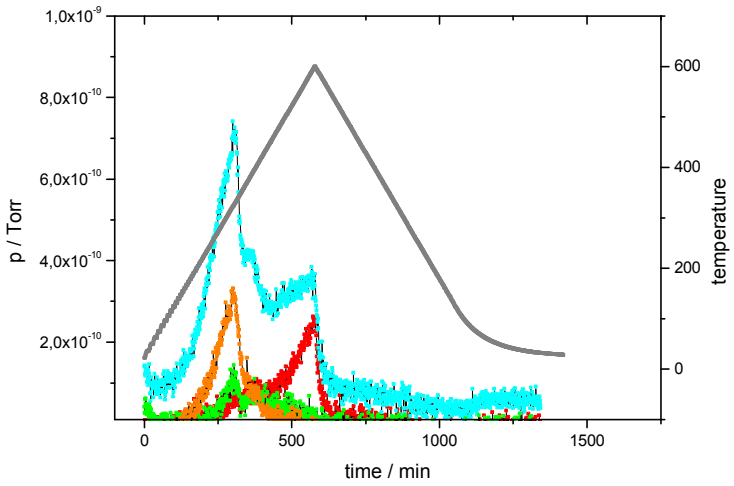

Figure 2.6 The copper is scratched with SiC paper (grit 320) inside a glovebox and reheated. Resin remains from the SiC paper on the surface decompose at about 300°C.

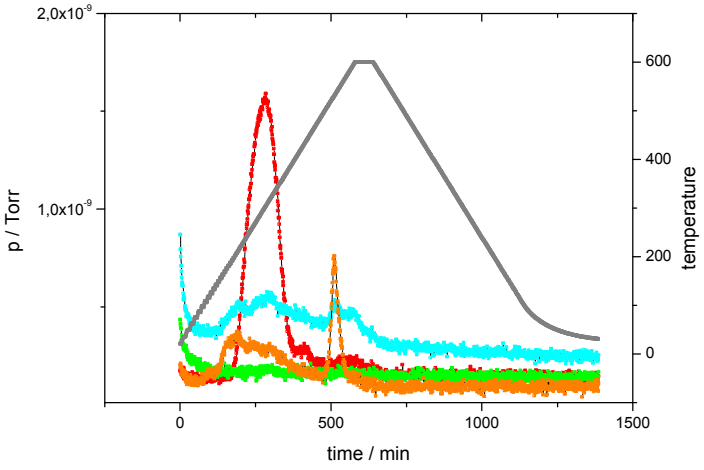

Figure 2.7 Two new copper pieces are scratched in air and heated to 600°C. In this case CO_2 desorption is observed around 500°C

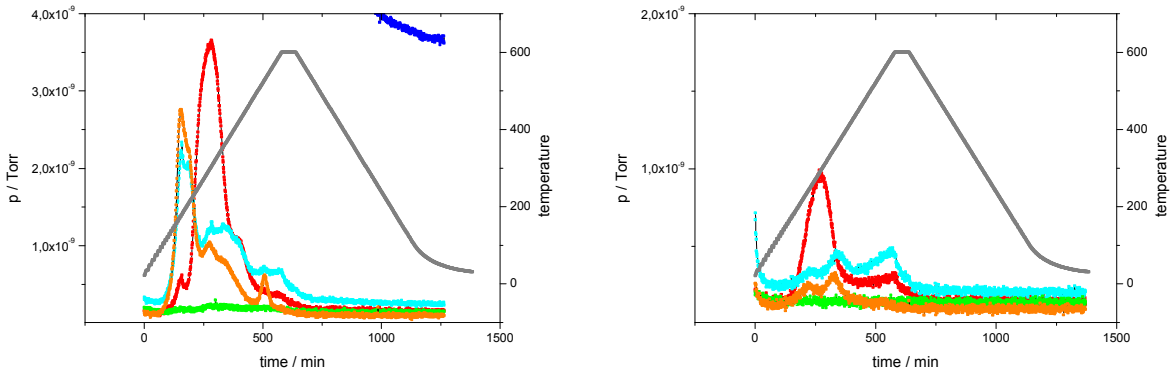

Figure 2.8 The partial pressure of hydrogen is related to the amount of copper as shown when four pieces (left) or one piece (right) are heated.

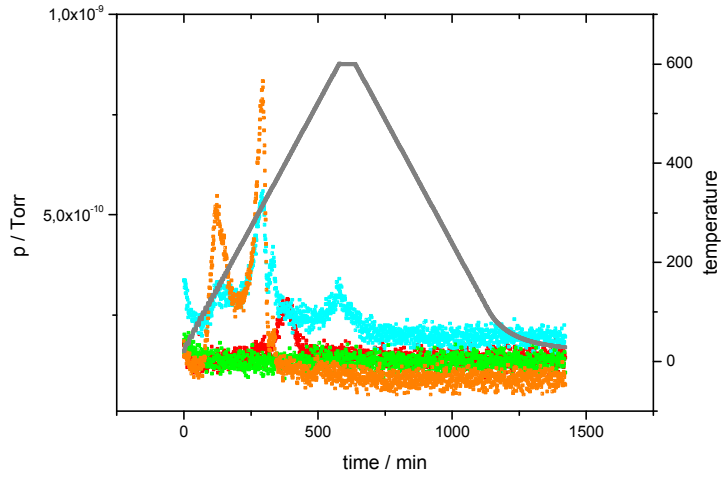

Figure 2.9 Desorption analysis from 99.95% OFHC copper (from Goodfellow, 1 g) is shown as a comparison.

The hydrogen peak in Fig 2.6 may have its origin from the equipment (see Fig 2.2) or from the SiC grinding paper.

Generally, the highest hydrogen partial pressure is observed at 400 °C (from Fig 2.3). Scratching with SiC grinding paper introduces impurities that cannot be defined by this method.

2 c. XPS analyses of surfaces of canister copper samples used in Micans' experiments

Two samples from Micans (XPS Kontroll 2014-03-06; XPS_3 2014-03-06) cut into 1 x 1 cm pieces were analysed (in May 2014) using XPS and handled in an inert atmosphere during the transfer to the analysis chamber. The Reference sample (XPS Kontroll) was unpolished and Sample 3 (XPS_3) was prepared at Micans using their surface treatment method with polishing and sulfamic acid. Neither of the samples had been exposed to pure water prior to the XPS analyses. The elemental analysis of the surfaces is presented in Table 2.2. Figure 2.10 shows the overview spectra, while Figure 2.11 gives the high resolution spectra. The samples were not sputtered. The oxygen content at the surface is high in both samples and the Cu *2p* peaks are similar, however a low intensity peak at higher binding energy show the presence of CuO in the reference sample. The Cu *LMM* spectrum of the reference sample, shows a broad feature around 570 eV, the structure of which indicates mixed Cu oxidation states of Cu(0) and Cu(I). After the surface treatment the Cu *LMM* spectrum is similar to the one observed for pure Cu metal.

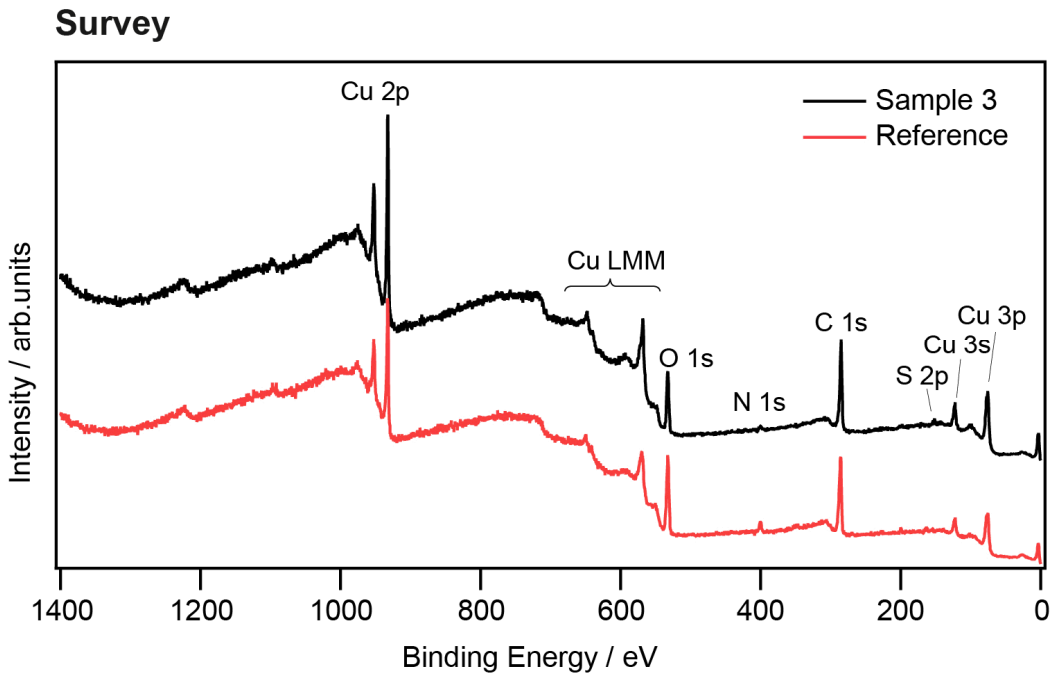

Fig 2.10. Overview spectrum of the unsputtered surfaces of the reference sample and sample 3 from Micans (surface treated using polishing and sulfamic acid).

Table 2.2 at% concentrations from XPS

Atom	Reference	Surface treated
Cu	12.2	17.2
O	23.6	19.6
N	4.6	1.6
C	57.8	60.6
S	1.8	1.0

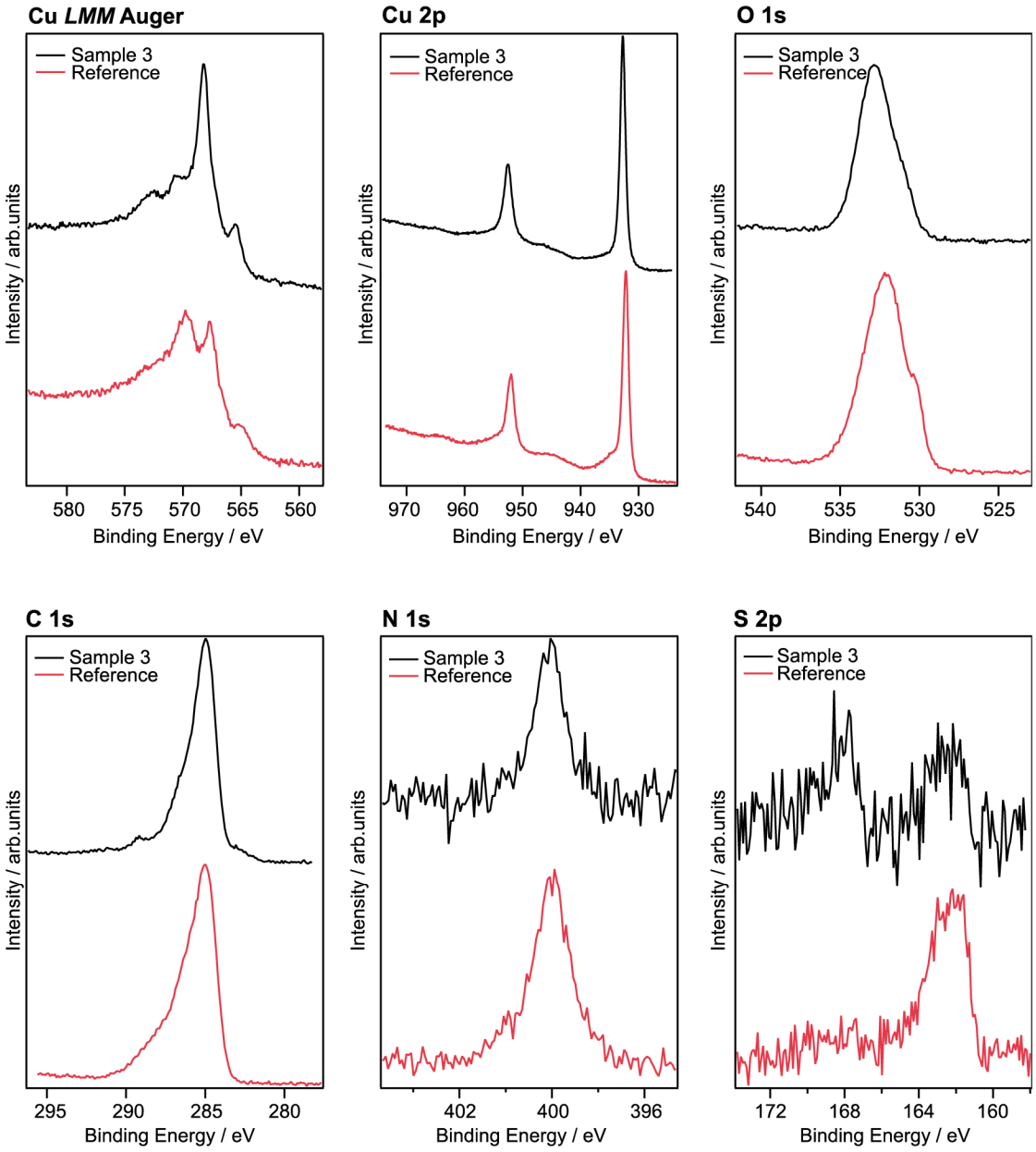

Figure 2.11. High resolution spectra from the elements in Table 2.2

2 d. Hydrogen desorption analysis of copper samples prepared for Micans

The main purpose of these analyses was to confirm the complete degassing of the bulk of copper samples that were prepared for subsequent use in Micans´ experiments. The heat treatments at 400°C in ultra high vacuum show that the desorption of hydrogen is complete in all samples after annealing for 3 hours. A slower heating rate (1°C /min) than the one used in these analyses (13 °C/min) show that hydrogen desorption starts at 200°C. This means that there is delay between the sample temperature and the furnace temperature of approximately 30 minutes. Also, when comparing the partial pressures, the differences in volume between the samples should be taken into account.

Table 2.3 give a summary of the samples that have been studied in order to observe the differences in hydrogen desorption between canister copper and Cu foils of different purities and the effect of surface treatment.

Canister copper samples

The plots shown in Figs. 2.12 - 2.15 show that there is a clear influence of the surface treatment on the hydrogen desorption from the bulk with two processes being observed as shown in Fig. 2.15. The amount of hydrogen in the Micans' treated samples is higher than the Uppsala treatment method (Figure 2.15). The fast desorption of hydrogen in the Micans' treated samples indicate that a large amount of hydrogen is dissolved close to the surface.

Table 2.3 Summary of samples, purity and sizes

Sample	Source[5]	Surface treatment	Purity of Cu foil	Sample thickness[3]	Number of pieces
A:1, A:2	Canister	Micans[1]		2 mm	2 each
B:1, B:2	Canister	UU[2]		2 mm	2 each
J	Canister	UU		2 mm	4
M	Canister			2 mm	4
C, K[4]	Foil, AA	UU	99.9999%	0.25 mm	4 each
F	Foil, AA		99.9999%	0.25 mm	4
G	Foil, G	UU	99.95%	0.1 mm	4
H	Foil, G		99.95%	0.1 mm	4

[1] See Johansson et al. (2015)

[2] Electropolishing in H_3PO_4 solution and heating in H_2 atmosphere at 300°C for 1h

[3] The area of each piece was 10x1 cm but the thickness varied

[4] The samples were scratched with SiC, but after the degassing.

[5] AA: Alfa Aesar, G: Goodfellow

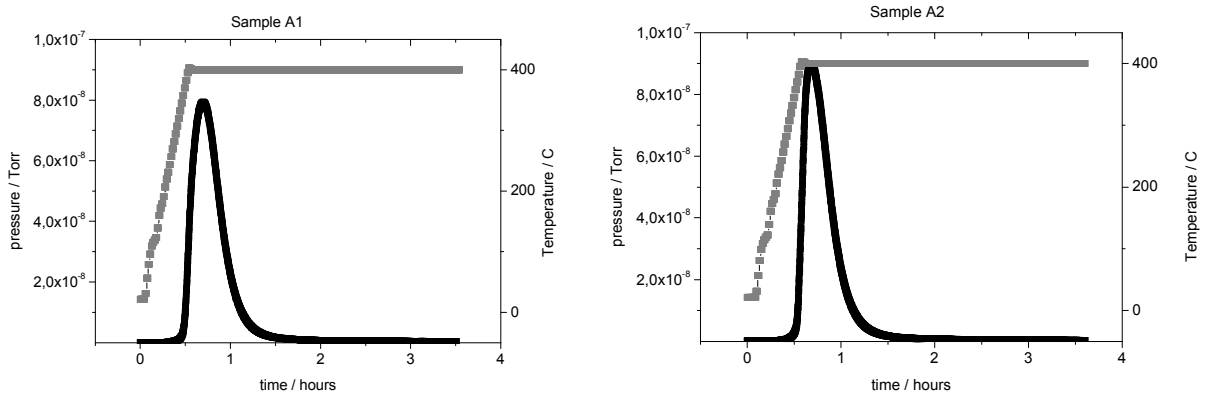

Figure 2.12 Canister copper surface treated using Micans' method.

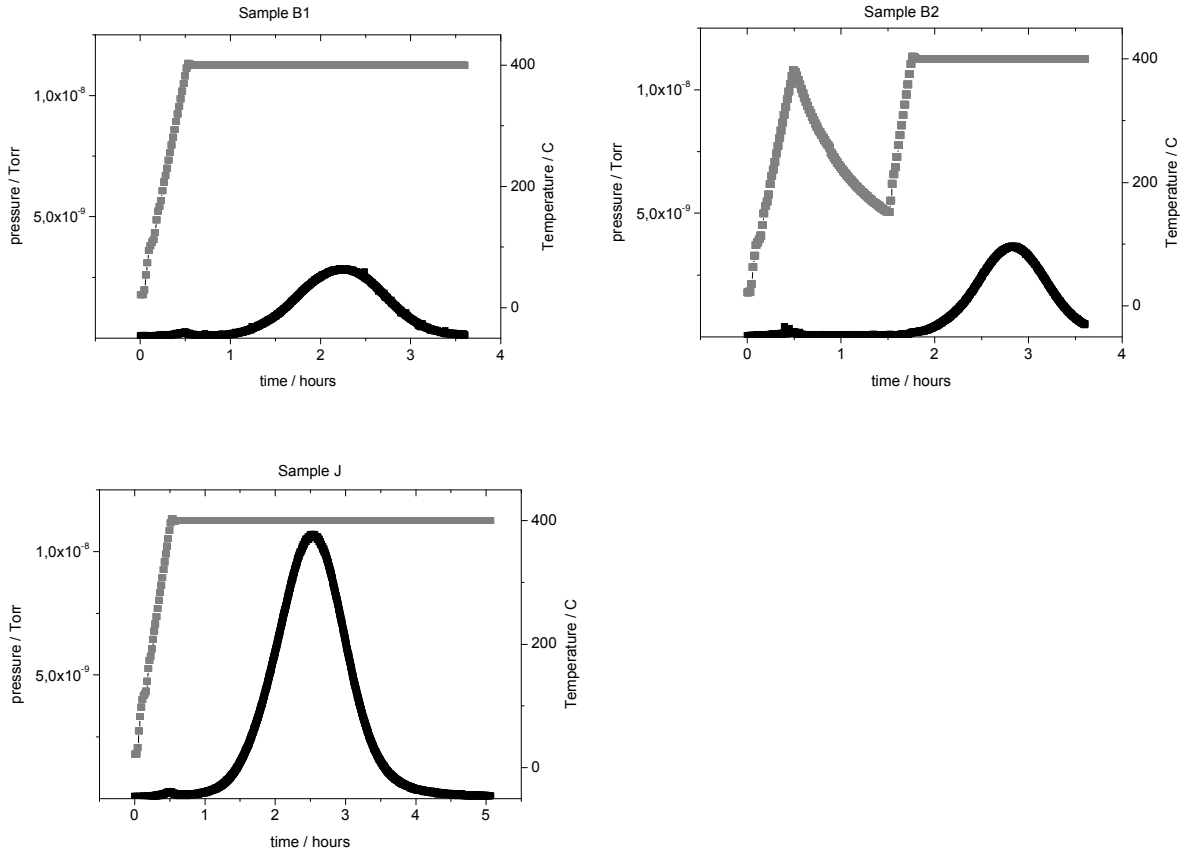

Figure 2.13 Canister copper surface pretreated by electropolishing and annealing at 300°C in H_2 for one hour. The furnace malfunctioned during the heating of sample B:2. Note also that Sample J is twice the volume of samples B:1 and B:2.

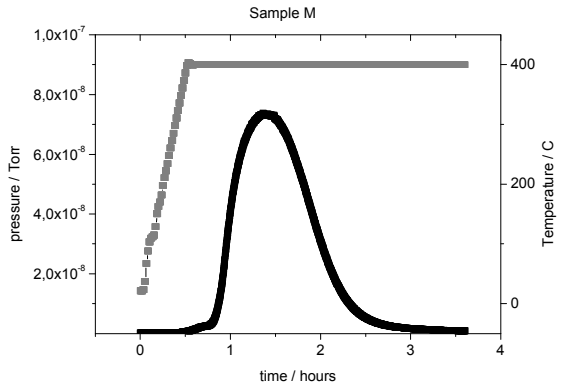

Figure 2.14. Untreated canister copper.

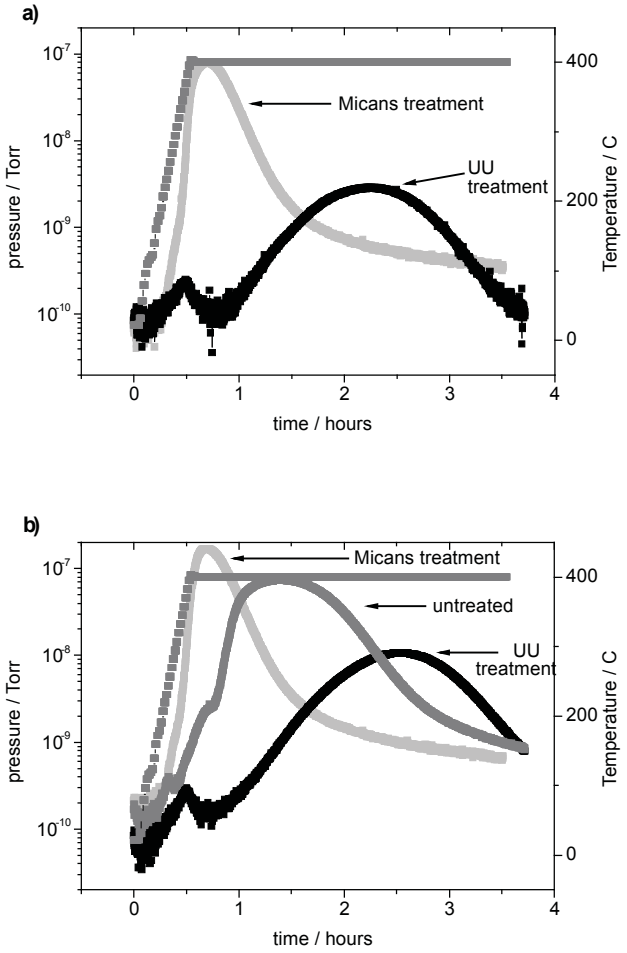

Figure 2.15. a) Samples A:1 (grey) and B:1 (black) and **b)** Samples A:1+A:2: (light grey), M (grey) and J (black). The pressure axis is on a logarithmic scale.

Copper foil samples

Two processes are observable, first a desorption from the surface, which gives the highest partial pressure and then desorption from the bulk which is a more prolonged process. These are clearly seen in Fig. 2.16. The lowest partial pressures are observed in Cu foil of 99.9999% purity after UU's surface treatment. Generally, the UU's surface treatment reduces the hydrogen content in the copper samples considerably.

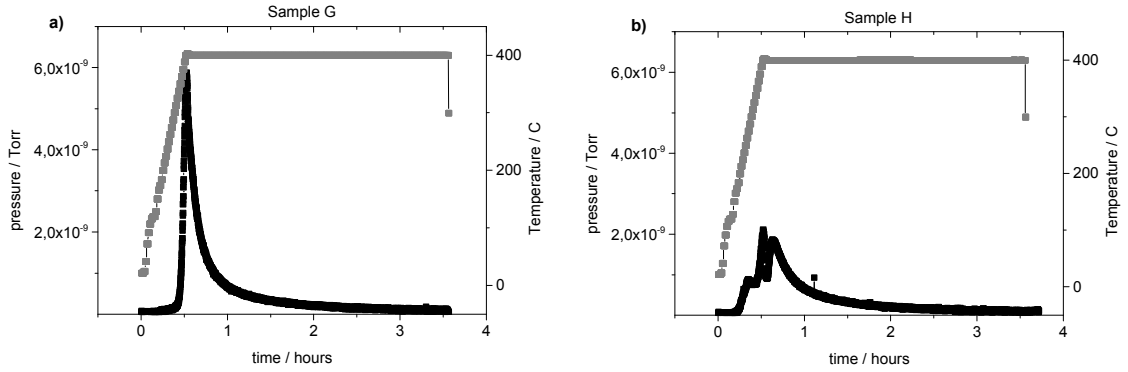

Figure 2.16. Cu foil of 99.95% purity **a)** sample G (UU's surface treatment) and **b)** sample H (untreated)

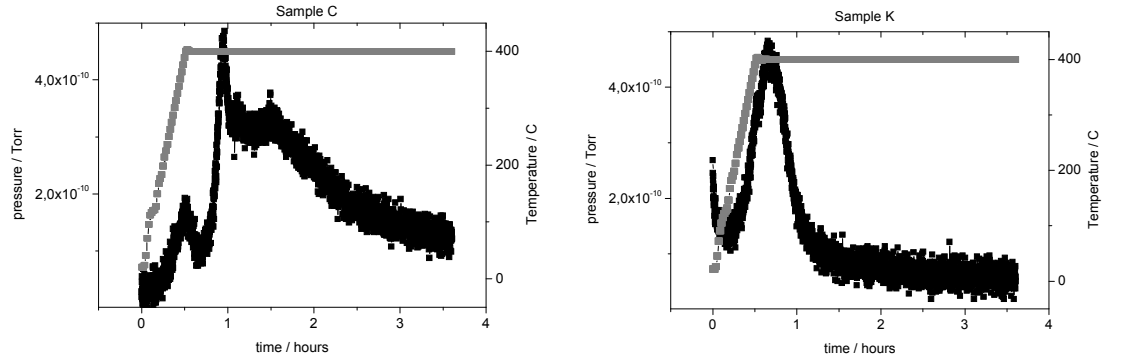

Figure 2.17 Cu foil of 99.9999% purity surface treated using UU's method.

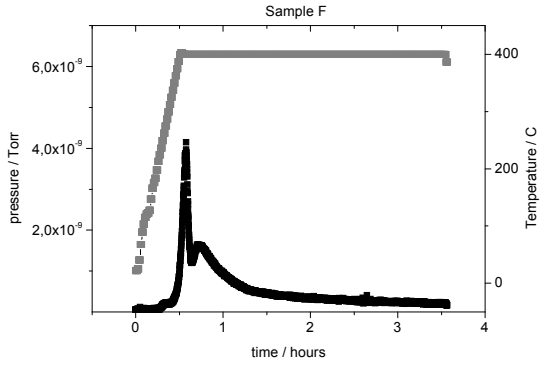

Figure 2.18 Cu foil of 99.9999% purity untreated.

2 e. ICP-MS analysis of water used in Micans' experiments

Five water samples were analyzed using ICP-MS and the results are presented in the table below. For details on the sample identification code, see Johansson et al. (2015). The tube containing copper in the UK1:1 sample (treated using the Uppsala method) was opened in air before the measurement. This may have influenced the amount of copper in the water. Note also that this is the only water sample that was transported from Micans to Uppsala with the copper rods still in the test tube. C:2 is a water sample that has been in contact with SiC scratched copper (Cu 99.9999%).

Observe that the reference water in table 2.4 has the highest silicon concentration. This may indicate problems with the water and/or the glassware used in the experiments.

Table 2.4 Concentration of analysed elements from ICP-MS measurements

Sample	**NN1_6** canister copper in water, room temp., ca 6 months	**N9:3** canister copper 70°C, then room temp, in total ca 10 months	**N3:1** - reference water in glass test tube (no copper) ca 2 years	**C:2-sample water** in tube with SiC scratched copper (99.9999 % Alfa Aesar), ca 9 months	**UK1:1** copper sample (99.9999 % Alfa Aesar) in water, ca 13 months
Sample prep.	Mar. 2013 (V12)	Nov. 2012	2012-10-25	2014-02-21	2013-10-07
ICP-MS	2013-09-17	2013-09-17	2014-11-13	2014-11-13	2014-11-13
Element	Concentration (ppb)	Concentration (ppb)	Concentration (ppb)	Concentration (ppb)	Concentration (ppb)
Li	1.38	1.94	7.44	7.93	9.54
B	45.22	1240.69	2995.95	3677.51	4508.03
Na	190.81	2464.28	6094.31	7277.33	7843.89
Mg	9.85	25.19	61.22	78.61	22.60
Al	2.25	0.40	19.00	205.63	1726.43
Si	362.79	11087.34	24065.84	15310.25	23078.42
P	5.48	9.21	3.99	5.11	17.28
Cl	209.38	389.48	4346.15	4144.86	3913.65
K	522.70	4245.74	6022.94	6449.26	7854.49
Ca	1135.65	1307.61	6480.42	3824.58	3698.42
Sc	0.22	4.46	3.67	2.64	3.67
Ti	1.25	4.40	2.21	1.65	4.31
V	0.04	0.22	0.41	0.16	0.18
Cr	5.45	8.28	3.35	0.87	1.43
Mn	1.40	0.25	6.57	5.27	3.33

Fe	16.99	0.45	15.30	67.15	37.31
Co	0.08	0.13	0.40	0.67	0.09
Ni	0.37	0.02	8.37	1.95	3.86
Cu	168.11	442.41	0.21	23.50	3340.18
Zn	47.39	35.02	2568.35	973.02	2900.25
Ga	0.00	0.02	0.05	6.78	1.31
Ge	0.01	0.01	0.03	0.62	0.05
As	0.01	0.05	0.03	0.03	2.30
Se	1.99	1.70	0.45	0.26	0.37
Br	7.34	352.20	57.05	15.23	15.02
Rb	0.08	0.39	4.41	4.71	6.23
Sr	1.63	0.24	10.22	5.95	5.87
Y	0.00	0.00	0.00	1.04	0.38
Zr	0.00	0.00	0.05	0.23	6.77
Mo	0.04	0.80	1.34	2.54	3.33
Rh	0.01	0.00	0.00	0.00	0.11
Pd	0.00	0.00	0.08	0.03	0.24
Cd	0.00	0.00	0.00	1.00	0.09
Sn	0.01	0.01	0.01	0.06	0.46
Sb	0.00	0.03	0.03	1.39	27.98
I	0.89	0.89	0.83	0.71	0.64
Cs	0.00	0.01	0.03	0.06	0.07
Ba	1.74	0.08	24.88	55.12	17.18
La	0.00	0.00	0.00	0.10	0.13
Ce	0.00	0.00	0.01	0.01	0.20
Nd	0.00	0.00	0.00	0.05	0.12
Gd	0.00	0.00	0.00	0.36	0.05
Yb	0.00	0.00	0.00	0.25	0.01
Hf	0.00	0.00	0.00	0.01	0.20
W	0.00	0.02	0.01	0.09	0.12
Au	0.00	0.00	0.05	0.00	0.04
Pb	0.00	0.00	0.01	0.05	8.02
Bi	0.00	0.00	0.00	0.00	0.89

3. References

Bengtsson A, Chukharkina A, Eriksson L, Hallbeck B, Hallbeck L, Johansson J, Johansson L, Pedersen K, 2013. Development of a method for the study of H_2 gas emission in sealed compartments containing canister copper immersed in O_2-free water. SKB TR-13-13, Svensk Kärnbränslehantering AB.

Boman M, Ottosson M, Berger R, Andersson Y, Hahlin M, Björefors F, Gustafsson T, 2013. Corrosion of copper in ultrapure water. SKB R-14-07, Svensk Kärnbränslehantering AB.

Johansson J, Blom A, Chukharkina A, Pedersen K, 2015. Study of H_2 gas emission in sealed compartments containing copper immersed in O_2-free water. SKB TR-15-03, Svensk Kärnbränslehantering AB.

Unpublished documents

SKBdoc 1470267 ver 1.0. Copper in ultrapure water. Svensk Kärnbränslehantering AB.

Appendix

D-LAB
DEGERFORS LABORATORIUM AB

Provningsresultat / Test Results:

Ordernr / Orderno: DL-29311

Beställare / Client	Referens / Reference
Uppsala Universitet	**Mats Boman**

Adress / Address: Box 538, 751 21 UPPSALA

Er beställning / Your order No	Ankomstdag / Sample Registration Date	Utskriftsdatum / Date of issue	DL ID
	2013-11-13	2013-11-15	508151

Provbeteckning / Sample identity: 2. SKB as received

Noteringar / Notes:

Resultat/Results

H	1.0 ppm

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IBAN: SE8480000815629833744494
BIC/SWIFT: SWEDSESS

D-LAB
DEGERFORS LABORATORIUM AB

Provningsresultat / Test Results:

Ordernr / Ordernr: DL-32817

Beställare / Client	Referens / Reference
Uppsala Universitet	**Pedro Berastegui**
Adress / Address: Box 538, 751 21 UPPSALA	

Er beställning / Your order No	Ankomstdag / Sample Registration Date	Utskriftsdatum / Date of issue	DL ID
	2014-10-07	2014-10-08	526963

Provbeteckning / Sample identity: Obehandlat

Noteringar / Notes:

Resultat/Results

H	1.6 ppm

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IBAN: SE8480000815629833744494
BIC/SWIFT: SWEDSESS

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Provningsresultat / Test Results:

Ordernr / Ordernr: DL-32817

Beställare / Client	Referens / Reference
Uppsala Universitet	**Pedro Berastegui**

Adress / Address: Box 538, 751 21 UPPSALA

Er beställning / Your order No	Ankomstdag / Sample Registration Date	Utskriftsdatum / Date of issue	DL ID
	2014-10-07	2014-10-08	526964

Provbeteckning / Sample identity: Värmebehandlad 500grader

Noteringar / Notes:

Resultat/Results

H	< 0.2 ppm

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VAT no.: SE 556609044401

Bankgiro: 5735-6784
Bank: Foreningssparbanken, Degerfors
IBAN: SE8480000815629833744494
BIC/SWIFT: SWEDSESS

D-LAB
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Provningsresultat / Test Results:

Ordernr / Ordernr: DL-32817

Beställare / Client	Referens / Reference
Uppsala Universitet	**Pedro Berastegui**
Adress / Address: Box 538, 751 21 UPPSALA	

Er beställning / Your order No	Ankomstdag / Sample Registration Date	Utskriftsdatum / Date of issue	DL ID
	2014-10-07	2014-10-08	526965

Provbeteckning / Sample identity: obehandlat

Noteringar / Notes:

Resultat/Results

H-Mobilt	0.26 ppm

Note: Not responsible for electronically transferred reports due to changes of data during transmission. Please contact us in doubtful cases.

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