Report
R-17-15
October 2017

Round-Robin of hydrogen content in copper determined by melt extraction and gas analysis

Michael Granfors

SVENSK KÄRNBRÄNSLEHANTERING AB

SWEDISH NUCLEAR FUEL
AND WASTE MANAGEMENT CO

Box 3091, SE-169 03 Solna
Phone +46 8 459 84 00
skb.se

SVENSK KÄRNBRÄNSLEHANTERING

ISSN 1402-3091
SKB R-17-15
ID 1597013
October 2017

Round-Robin of hydrogen content in copper determined by melt extraction and gas analysis

Michael Granfors, Swerea KIMAB AB

Abstract

Four laboratories, from Finland, Sweden and USA, took part in a Round-Robin test in November – December 2016 concerning determinations of hydrogen in copper samples.

The analytical techniques used were melt extraction followed by either thermal conductivity or IR-absorption.

The results obtained are shown in tables and figures.

Contents

1 Introduction

A Round-Robin test took place in 2016 for the determination of hydrogen in copper. The Round-Robin sample, which were divided and distributed between the participating laboratories, is a Cu-OFP (oxygen-free phosphorous doped) copper material (SKB 2010). The material used in the Round-Robin test is derived from a tube with designation T58 from SKB's Canister Laboratory, Oskarshamn, Sweden.

The Round-Robin test was initiated by SKB (Swedish Nuclear Fuel and Waste Management Co), Stockholm, Sweden. In order to evaluate the effect of hydrogen on properties of the canister material it is important to know the precision with which the hydrogen content of the material can be analysed. Earlier analyses of the hydrogen content of Cu-OFP has indicated large variations in the measured values, which has led to the need to evaluate what variation that can be expected and to understand the cause of variation (SKB 2010, Taxén et al. 2012, Smart et al. 2012, Ottosson et al. 2016, Gordon et al. 2017).

The copper sample was divided into two different sample types for each laboratory. One sample type, named H1, was cut into suitable pieces (W × D × H = 10 × 10 × 20 mm) at Swerea KIMAB to be measured without further preparation by the participating laboratories. The second sample type, named H2, was a larger sample that had to be prepared by the participating laboratories themselves. Instructions where the sample, named H2, should be cut out were given to the participating laboratories. An illustrative figure can be found in the figure below.

The laboratories were given the instructions to make three determinations on each sample types. Some of the laboratories made additional analysis on the spare samples of H1 or sample material H2, which didn't follow the instructions given. The results from these analyses are found in the tables and figures as H1R and H2R, respectively.

In the Round-Robin test four laboratories from Finland, Sweden and USA participated. One laboratory participated by two different techniques, namely melt extraction followed by either thermal conductivity or infrared absorption. All other laboratories used melt extraction followed by thermal conductivity. All the participating laboratories used LECO instruments, except one of the laboratories, which used an ELTRA instrument. The hydrogen content is extracted by fusion of the sample in an inert gas and analysed by a high sensitivity thermal conductivity detector or an infrared absorption detector.

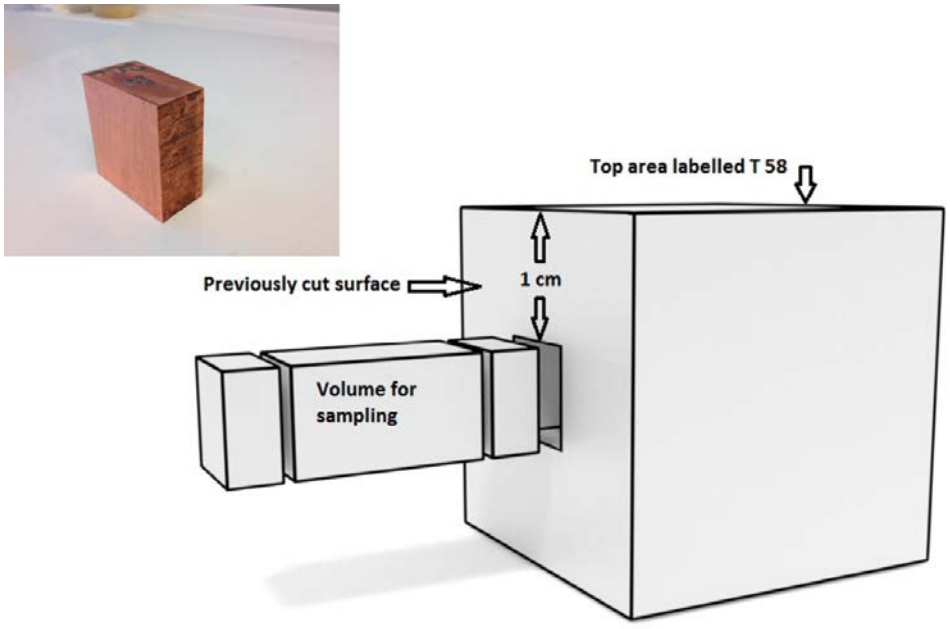

Figure 1-1. *Illustrative figure of where the sample named H2 was cut out.*

All laboratories taken part were coded in order to keep their anonymity. Each laboratory has the same code in all tables and figures. Laboratory 1 and 4 is the same laboratory, but different techniques, thermal conductivity versus infrared absorption.

The laboratories taken part in the Round-Robin test were:

Degerfors Laboratorium, Degerfors, Sweden.

LECO Corporation, Michigan, USA.

Luvata Pori Oy, Pori, Finland.

Swerea KIMAB AB, Kista, Sweden.

Analyses were carried out in a routine basis manner except for the sample named H1, which were analysed by the laboratories without any sample preparation or cleaning. The laboratory coded 2 did wash the samples named H1 prior to analysis. Therefore has their result for sample H1 been reported as H1R instead in the tables and figures.

The results obtained were tabulated, and the values given in the tables are those reported by the laboratories. Figures were drawn for the samples named H1, H2 and H1R, respectively. The solid line in the figures is the mean value and the dotted lines are ± one standard deviation from the mean value.

The Round-Robin test was performed in accordance to ISO/IEC 17043:2010.

2 Results

Table 2-1. Sample H1, hydrogen given in µg/g.

Lab nr	Method	1	2	3	MEAN	σ	Comments:
1	TC	1.370	1.030	1.310	1.24	0.15	Analyzed as Received
4	IR	1.240	1.330	1.230	1.27	0.04	Analyzed as Received
5	TC	2.930	3.280		3.11	0.18	Analyzed as Received
3	TC	4.310	2.400	4.390	3.70	0.92	Analyzed as Received
				MEAN	2.33		
				σ	1.10		

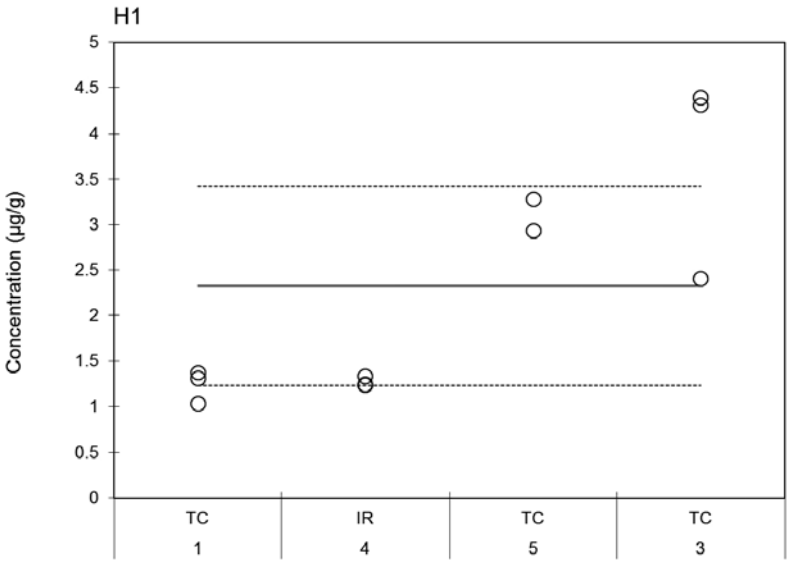

Figure 2-1. *Sample H1, hydrogen given in µg/g.*

Table 2-2 Sample H2, hydrogen given in µg/g.

Lab nr	Method	1	2	3	MEAN	σ	Comments:
2	TC	0.125	0.121	0.131	0.126	0.004	Cut and filed
3	TC	0.310	0.330	0.340	0.327	0.012	Cut, filed and washed
1	TC	0.370	0.380	0.330	0.360	0.022	Cut, abraded sample
4	IR	0.670	0.480	0.410	0.520	0.110	Cut, abraded sample
5	TC	0.480	0.650		0.565	0.085	Cut, filed and washed
				MEAN	0.333		
				σ	0.156		

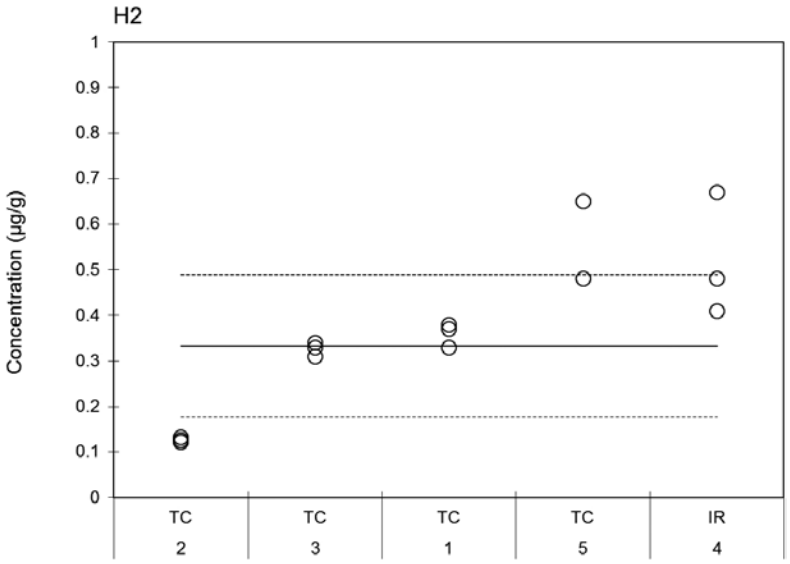

Figure 2-2. *Sample H2, hydrogen given in µg/g.*

Table 2-3. Sample H1R, hydrogen given in µg/g.

Lab nr	Method	1	2	3	MEAN	σ	Comments:
3	TC	0.380			0.380	–	Filed and washed
1	TC	0.340	0.300		0.320	0.02	Filed
2	TC	0.331	0.506	0.419	0.419	0.07	Washed
5	TC	0.800	0.830		0.815	0.02	Washed
				MEAN	0.483		
				σ	0.19		

Table 2-4. Sample H2R, hydrogen given in µg/g.

Lab nr	Method	1	2	MEAN	σ	Comments:
5	TC	0.68	0.70	0.69	0.010	Wet polished + washed

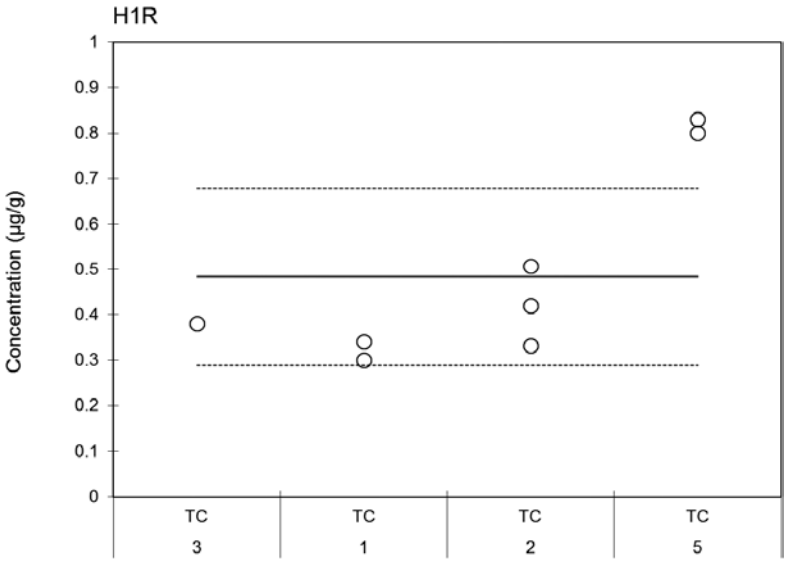

Figure 2-3. *Sample H1R, hydrogen given in µg/g.*

3 Discussion

The samples named H1 were cut and sent to the participating laboratories in small glass bottles. It is obvious from the spread in the results that these samples surfaces have been contaminated by hydrogen either during the preparation at Swerea KIMAB, during the transportation or at the participating laboratories prior to analyses. The mean value for the reported hydrogen content is 2.33 µg/g, which is much higher compared to the sample H2, which has a hydrogen mean value of 0.33 µg/g. Both sampling and sample preparation are important for precise determination of hydrogen in copper. Samples have to be prepared carefully before the analysis to remove the surface contaminations. The sample temperature should not increase because the hydrogen can diffuse out of the sample and a loss of hydrogen can then occur during the sample preparation.

The samples named H2, which have been cut and prepared by the participating laboratories themselves prior to analyzes have much less spread and lower reported hydrogen value than the samples H1. It is obvious that it is important that the samples should be cut out and prepared shortly before the analysis.

The H1R samples are the same samples as H1, but the participating laboratories have abraded, filed or/and washed the sample in a detergent prior to the analysis. The results for these samples are more comparable to the samples named H2, which were cut, abraded, filed or/and washed prior to the analysis. Comparing the mean values for sample H1R and H2 shows that the mean reported hydrogen content for H1R is higher than for sample H2, 0.48 and 0.33 respectively. It should be noted that the means for H1R and H2 are within their respective standard deviations. This shows again the importance of sample cutting shortly prior to the analysis.

4 Conclusions

From this small Round-Robin test it is obvious that the determined hydrogen drastically decreases if the melt extraction of hydrogen is performed shortly after sample preparation. The mean value decrease from 2.3 to 0.3 µg/g for samples prepared long before analysis versus samples prepared shortly prior to the determination. This is a good indication that the main hydrogen content is situated on the surfaces of the samples. The spread between the participating laboratories is about five times for the prior prepared sample as well as the sample prepared by the laboratories themselves. There is a certain spread within some of the laboratories even if they have prepared the samples themselves. This is probably due to the fact of the different procedures in sample preparation as well as that the content of hydrogen is close to the quantification limits of the instruments used in the Round-Robin test.

References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.com/publications.

Gordon A, Sjögren L, Taxén C, Johnasson A J, 2017. Post-test examination of packages 4 and 5 of the MiniCan field experiment. SKB TR-16-12, Svensk Kärnbränslehantering AB.

ISO/IEC 17043:2010. Conformity assessment – General requirements for proficiency testing. Geneva: International Organization for Standardization.

Ottosson M, Boman M, Berastegui P, Andersson Y, Hahlin M, Korvela M, Berger R, 2016. Copper in ultrapure water. SKB TR-16-01, Svensk Kärnbränslehantering AB.

SKB, 2010. Design, production and initial state of the canister. SKB TR-10-14, Svensk Kärnbränslehantering AB.

Smart N, Rance A, Reddy B, Fennell P, Winsley R, 2012. Analysis of SKB MiniCan. Experiment 3. SKB TR-12-09, Svensk Kärnbränslehantering AB.

Taxén C, Lundholm M, Persson D, Jakobsson D, Sedlakova M, Randelius M, Karlsson O, Rydgren P, 2012. Analyser av koppar från prototypkapsel 5 och 6. SKB P-12-22, Svensk Kärnbränslehantering AB. (In Swedish.)

Arkitektkopia AB, Bromma, 2017

SKB is responsible for managing spent nuclear fuel and radioactive waste produced by the Swedish nuclear power plants such that man and the environment are protected in the near and distant future.

skb.se