COMPARATIVE STUDY BETWEEN HOT EXTRACTION METHODS AND MERCURY METHOD – A NATIONAL ROUND ROBIN TEST

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ABSTRACT

A round robin test is presented comprising comparative measurements using hot extraction at different degassing temperatures as well as the mercury method. A major focus of the investigation was verification of the maximum degassing temperature for analysing the diffusible hydrogen in weld metals with bcc-lattice structure. The analyses were executed using a basic stick electrode with high weld metal cracking, a high-alloyed supermartensitic filler wire with different hydrogen contents in the shielding gas and a high-strength solid wire. The results show that degassing temperatures of 150 °C and 400 °C do not lead to an increase in the measured contents of diffusible hydrogen as compared to measurements at room temperature. The measuring techniques and procedures specified in ISO/DIS 3690:2009 for determining the diffusible hydrogen content in weld metals with bcc-lattice structure yield approximately the same results. This is to say that the mercury method and the hot extraction methods with thermal conductivity detector (TCD) can be regarded as equivalent reference methods.

IIW-Thesaurus keywords: *Hydrogen; Mercury; Measurement.*

1 INTRODUCTION

Hydrogen may cause considerable damage in metallic structural materials. Most notably hydrogen embrittlement manifests itself by a significant decrease in ductility through to the formation of cold cracks involving serious damage. At sufficiently high residual stresses, cracking may occur even without additional external loading. Under unfavourable conditions (e.g. high-strength steels, high restraint effect), a hydrogen content of a few ppm is enough to cause embrittlement. This implies that for cold crack-resistant welding of higher-strength materials with bcc-lattice structure, for instance, it is most important to specify exact limit values for diffusible hydrogen, since the toughness of such steels is substantially impaired already at low hydrogen concentrations.

The determination of diffusible hydrogen in weld metal has been standardized at an international level in ISO/DIS 3690:2009 [1]. This standard specifies requirements concerning the sampling procedure and the analysis method for determining the diffusible hydrogen in weld metal with bcc-lattice structure. Capture and measurement of the diffusible hydrogen following the mercury method has so far been recognized as a so-called reference method.

Against the background of the great health and environmental hazards arising from mercury, however, its

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use has been restricted in many countries for a long time. (See also the common European strategy for mercury [KOM(2005)20, SEC(2005)101)].

Consequently, alternative test methods need to be introduced with at least the same or better linearity and measuring accuracy compared to the mercury method. It is above all essential to assure, based on comparable terms of sales of the material and filler material producers, the transferability of data for the diffusible hydrogen content measured by the mercury method to the results from alternative analysis methods, e.g. thermal conductivity detector (TCD), gas chromatography (GC) etc. and vice versa.

A multitude of investigations are reported in literature dealing with the determination of hydrogen contents in metallic welded joints. Some significant examples of comparative studies between the mercury method and alternative test techniques, e.g. carrier gas hot extraction or so-called certified reference materials (CRM), are described in [2-8].

For example, the study presented by Elvander *et al.* [2] shows that the results from carrier gas hot extraction are, in regard to linearity and repeatability, only consistent with those from certified reference materials, if identical calibration routines were adopted concerning hydrogen volumes, detector systems and carrier gas. Jenkins *et al.* [3] discovered in their investigations, for example, that depending on the degassing temperature the results of carrier gas hot extraction may appreciably exceed the values of vacuum hot extraction. This was attributed to the residual moisture of the carrier gas. Moreover, a significant influence of specimen preparation (surface condition) on the analytical result was observed. It was furthermore emphasized that the hydrogen analysis should be adapted to the type of filler material microstructure (microstructure-dependent hydrogen diffusion behaviour, release of trapped hydrogen). Hart *et al.* [4] demonstrated that up to a maximum degassing temperature of 400 °C hot gas extraction is suitable for determining the diffusible hydrogen content. Higher degassing temperatures are only applicable for measurement of the total hydrogen content in the weld metal.

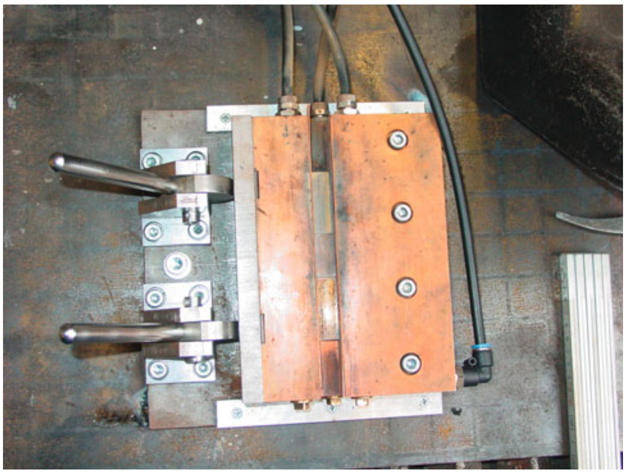


Figure 1 – Fixture design with water cooling for consistent welding conditions, top view

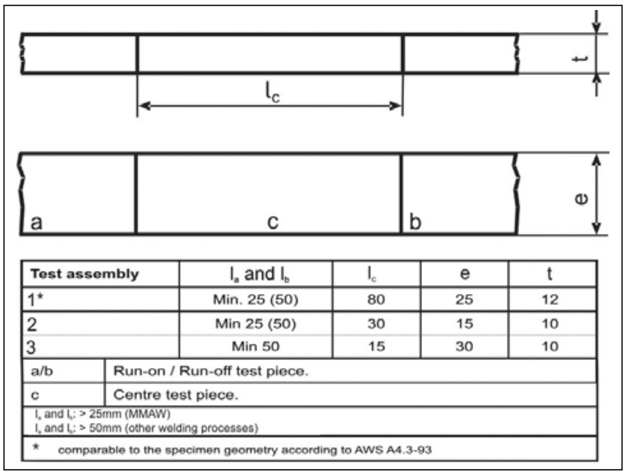
With a view to provide good applicability and high benefit of ISO/DIS 3690 [1] to industry, a national round robin test was conducted in Germany. Comparative measurements were carried out using hot extraction at different degassing temperatures as well as the mercury method. Within the scope of this round robin test, analyses were performed for determining the weld metal diffusible hydrogen content using a basic stick electrode with high weld metal cracking resistance (expected diffusible hydrogen content of around $H_{D,ref}$ = 3 ml/100 g) and a high-strength solid wire with a hydrogen content of around $H_{D,ref}$ = 1 ml/100 g. In addition, a high-alloyed supermartensitic filler material was selected with different hydrogen contents in the shielding gas (0 % and 5 % H_2-addition to the shielding gas). This investigation mainly focused on identifying the maximum degassing temperature for the analysis of diffusible hydrogen in weld metals with bcc-lattice structure. It is presumed for these materials that at maximum degassing temperatures of up to 400 °C the measurements detect only diffusible hydrogen.

2 ROUND ROBIN TEST PROCEDURES ACCORDING TO ISO 5725-2 [9]

2.1 Welding processes and filler materials for weld metal production

Unlike hitherto performed round robin tests for which welding filler materials were usually delivered to the participating laboratories, the round robin test described here was carried out using weld metal specimens which were prepared by only one laboratory under constant conditions following ISO/DIS 3690 [1] and supplied to the participating laboratories.

The specimens were fixed during welding in a water-cooled welding unit, see Figure 1. The specimen fixture was provided via two eccentric levers. In this fixture, test pieces l_c (30 mm) · e (15 mm) · t (10 mm) in size were produced following ISO/DIS 3690 [1], see Figure 2.



Test assembly	l_a and l_b	l_c	e	t
1*	Min. 25 (50)	80	25	12
2	Min 25 (50)	30	15	10
3	Min 50	15	30	10
a/b	Run-on / Run-off test piece.			
c	Centre test piece.			

l_a and l_b: > 25mm (MMAW)
l_a and l_b: > 50mm (other welding processes)

* comparable to the specimen geometry according to AWS A4.3-93

Figure 2 – Specimen geometry following ISO/DIS 3690 [1]

The base material for the test pieces was the higher-strength fine-grained structural steel 1.8928 (DIN EN 10025) (Table 1). The welding filler materials, welding processes and shielding gases, as listed in Table 2, were used. Tables 3 and 4 show the chemical analysis of the applied solid wires.

2.2 Determination of hydrogen content

After welding, the specimens were stored in an insulating receptacle in liquid nitrogen and supplied to the participating laboratories one week after the start of welding. Following the ISO/DIS 3690, Section 4.1.4 [1], the specimens were tested within four weeks after welding. The hydrogen analysis was performed according to the ISO/DIS 3690 [1]. Both the mercury method and the hot extractions with thermal conductivity detector (TCD) were applied (Table 5).

3 RESULTS AND DISCUSSION

3.1 Measured values of individual laboratories and statistical computations

First, the measured results of all participating laboratories were evaluated in a compatibility test in compliance with ISO 5725-2 [9]. The measured values for the individual parameter sets are listed in Table 6 for subsequent statistical evaluation.

Table 1 – Chemical analysis of base material 1.8928 (DIN EN 10025)

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Nb	V
Nominal value in %	≤ 0.18	≤ 0.50	≤ 1.60	≤ 0.02	≤ 0.01	≤ 1.50	≤ 0.60	≤ 1.80	≤ 0.10	≤ 0.10
Measured value in %	0.15	0.30	1.29	0.012	0.001	0.05	0.10	0.04	0.03	0.001

Table 2 – List of welding filler materials and shielding gases

Parameter set	Welding filler material	Designation	Welding process, shielding gas	Micro-structure	Hydrogen content $H_{D,ref}$
1	basic electrode	DIN EN ISO 2560-A: E42 4 B 32 H5 (Ø 4 mm)	MMA	ferritic	≈ 5 ml/100 g
2	high-alloyed solid wire	DIN EN 12072-GZ 1363 L (Ø 1.2 mm)	MAG, EN 439-M12	super-martensitic	≈ 1-2 ml/100 g
3	high-alloyed solid wire	DIN EN 12072-GZ 1363 L (Ø 1.2 mm)	MAG, EN 439-R1 +5 % H2	super-martensitic	≈ 6-7 ml/100 g
4	high-strength solid wire	DIN EN 12534-G Mn4 Ni2.5CrMo (Ø 1.2 mm)	MAG, EN 439-M21	ferritic	≈1-2 ml/100 g

Table 3 – Chemical analysis of supermartensitic solid wire (parameter set 2 + 3)

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Nb	V
Producer	0.010	0.50	0.59	0.014	0.002	12.0	2.73	6.41	0.011	0.03

Table 4 – Chemical analysis of high-strength solid wire (parameter set 4)

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Nb	V
Producer	0.11	0.75	1.90	0.007	0.014	0.46	0.53	2.24	none	0.004

Table 5 – Overview of applied analysis techniques

Method	System/Designation	Temperature in °C
Mercury	Y-tube	room temperature
	U-tube	room temperature
Hot extraction	(TCD) Yanako	150
	(TCD) H-mat 221	400
	(TCD) Carrier gas hot extraction	400

Table 6 – Measured results of laboratories

		Mercury method			Hot extraction		
Temperature		**RT**	**RT**	**RT**	**150 °C**	**400 °C**	**400 °C**
Laboratory		***1***	***2***	***3***	***4***	***5***	***6***
Parameter set	1	4.80	none	4.17	none	4.80	4.43
		5.00	5.95	none	5.12	3.78	4.05
		4.50	5.48	4.21	4.60	3.56	4.04
		5.40	5.51	4.33	5.39	3.11	3.62
		5.20	none	none	5.53	3.60	4.08
	2	2.70	none	none	4.14	2.99	2.80
		3.20	4.22	none	4.63	3.40	2.73
		2.40	4.08	none	4.16	4.81	2.73
		2.20	4.94	none	3.63	2.87	3.10
		2.20	none	none	3.52	2.36	2.68
	3	9.20	none	9.09	9.81	9.21	8.81
		8.60	10.51	9.54	9.63	11.70	none
		8.70	11.87	9.32	10.85	10.37	7.28
		9.70	10.36	none	9.88	8.08	8.20
		8.20	none	9.87	9.44	7.45	7.65
	4	2.60	none	none	2.32	2.22	2.32
		2.10	2.95	2.53	2.18	2.43	1.56
		2.60	2.79	2.06	1.92	none	1.74
		2.40	2.57	1.89	2.01	1.87	1.98
		2.50	none	1.73	1.98	1.90	1.65

Table 7 contains the average values and the standard deviations of the laboratories.

The values for the total average value m_j, the repetition variance s_{rj} and the comparison variance s_{Rj} for the individual parameter sets are given in Table 8. The highest measured hydrogen content was registered with parameter set 3, because welding was performed using a hydrogen containing gas mixture. The lowest measured hydrogen content was achieved in MAG-welding using the high-strength solid wire electrode (parameter set 4). The total average value for manual metal arc welding using the basic electrode is 4.55 ml/100 g. This corresponds with investigations of [4].

Table 7 – Summary of average values and standard deviations of laboratories

		Measuring technique					
		Hydrogen content in ml/100g (mercury method)			Hydrogen content in ml/100g (hot extraction)		
Temperature		**RT**	**RT**	**RT**	**150 °C**	**400 °C**	**400 °C**
Laboratory		***1***	***2***	***3***	***4***	***5***	***6***
Parameter set	1	Ø4.98±0.31	Ø5.64±0.21	Ø4.23±0.06	Ø4.95±0.36	Ø3.77±0.56	Ø4.04±0.25
	2	Ø2.54±0.37	Ø4.41±0.37	none	Ø4.01±0.40	Ø3.28±0.83	Ø2.81±0.14
	3	Ø8.88±0.51	Ø10.91±0.67	Ø9.45±0.28	Ø9.92±0.48	Ø9.36±1.53	Ø7.98±0.57
	4	Ø2.44±0.18	Ø2.77±0.15	Ø2.05±0.29	Ø2.02±0.14	Ø2.10±0.23	Ø1.85±0.27

Table 8 – Final values for parameter sets

Parameter set j	p_j	m_j	s_{rj}	s_{Rj}
1 (high HD)	6	4.55	0.36	0.45
2 (low HD)	5	3.33	0.51	0.60
3 (high HD)	6	9.36	0.83	0.89
4 (low HD)	6	2.18	0.23	0.26

p_j - Number of laboratories
m_j - Total average value
s_{rj} - Repetition variance
s_{Rj} - Comparison variance

$$\hat{m}_j = \bar{\bar{y}}_j = \frac{\sum_{i=1}^{p} n_{ij}\bar{\bar{y}}_{ij}}{\sum_{i=1}^{p} n_{ij}} = \text{Total average value} \qquad (1)$$

$$s_{rj}^2 = \frac{\sum_{i=1}^{p} (n_{ij}-1)s_{ij}^2}{\sum_{i=1}^{p} (n_{ij}-1)} = \text{Repetition variance} \qquad (2)$$

$$s_{Lj}^2 = \frac{s_{dj}^2 - s_{rj}^2}{\bar{\bar{n}}_j} = \text{Variance between laboratories} \quad (3)$$

$$s_{Rj}^2 = s_{rj}^2 + s_{Lj}^2 = \text{Comparison variance} \quad (4)$$

where

n_{ij} is the number of test results in the cell for laboratory *i* at level *j* (ISO 5725-2) [9]

y_{ij} is any one of the test results (ISO 5725-2) [9]

3.2 Comparison between mercury method and hot extraction by regression analysis

The linear regression technique was used to ascertain the functional relationships y = f(x) between the hydrogen contents measured by the mercury method (reference method) and hot extraction (alternative method) in the form of reference-equivalence-functions y = mx+n. The coefficients m and n of the linear regression function were determined following the method of least squares.

As can be seen from Figure 3, the hydrogen contents determined by linear regression between hot extraction and mercury method yield a rise m for the regression straight line of 0.94 with an offset n = -0.3662.

This evaluation demonstrates that particularly from a hydrogen content of about H_D = 3 ml/100 g up, the hydrogen contents measured by hot extraction are slightly lower compared to those obtained from the mercury method. At lower hydrogen contents (< 3 ml/100 g), however, this procedure-specific difference does not occur.

3.3 Influence of degassing temperature

Figures 4 and 5 represent the average values and standard deviations of the individual laboratories for parameter sets with relatively high and low hydrogen contents, respectively.

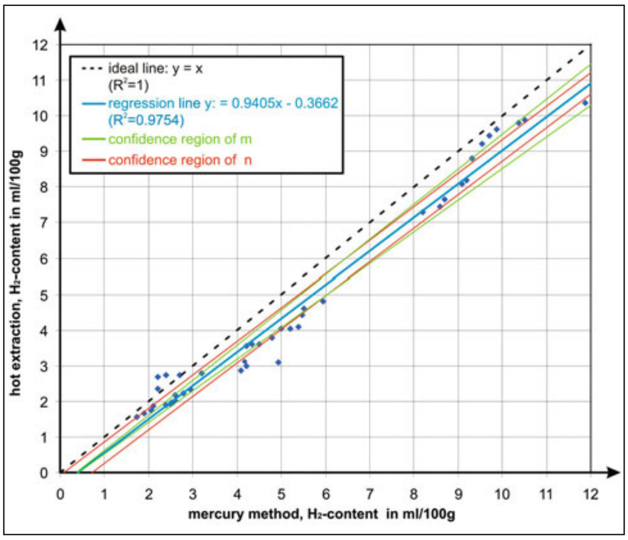


Figure 3 – Comparison of hydrogen contents measured by hot extraction and mercury method

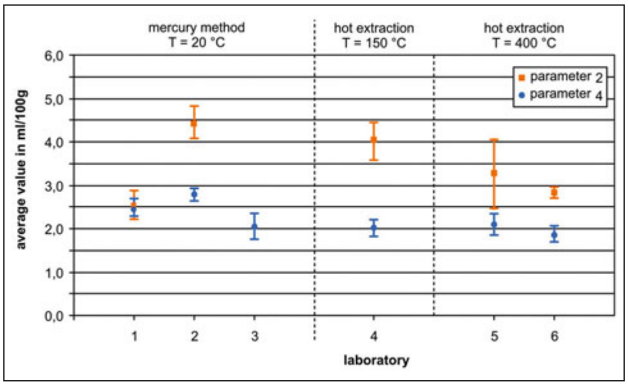


Figure 4 – Average values of parameter sets 2 and 4 with relatively low H_2-contents depending on degassing temperature

It turns out that with both parameter sets, i.e. with relatively low and relatively high hydrogen contents, hot extraction at a degassing temperature of 150 °C as well as of 400 °C does not yield higher diffusible hydrogen contents than the mercury method at a degassing temperature of room temperature.

The determined standard deviations are in comparable order of magnitude to the already available results of [2], [4], [7] and [8]. Comparisons between mercury method and hot extraction at 400 °C made in the investigations of [3] and [8] revealed that the standard deviations of the mercury method are higher than those of hot extraction. In the round robin test reported here, there was no such a tendency.

In Figures 6 and 7, the absolute and relative standard deviations, respectively, are shown versus the average value. Both graphs illustrate that even though the absolute standard deviations (Figure 6), as expected, display a minor rise with increasing hydrogen content, the relative standard deviations are independent of the hydrogen content. Any change in the standard deviation depending on the measuring technique cannot be proven.

3.4 Determination of the laboratory-specific error in the total average value of the individual parameter sets

The absolute as well as the relative laboratory-specific errors in the total average value of the individual para-

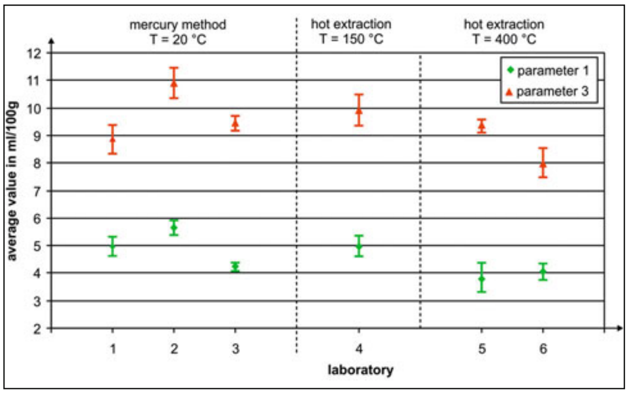


Figure 5 – Average values of parameter sets with high H_D contents depending on degassing temperature

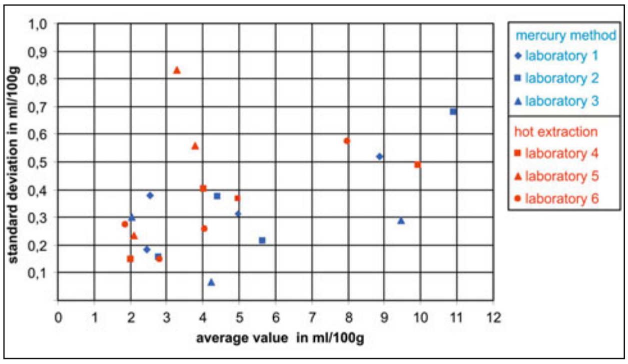


Figure 6 – Absolute standard deviation versus average value of H_D content

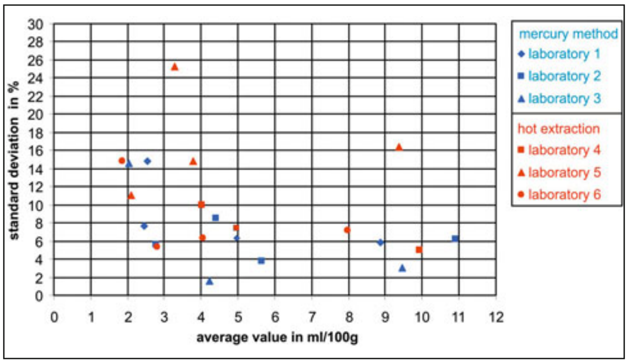


Figure 7 – Relative standard deviation versus average value of H_D content

meter sets were additionally determined according to Equations (5) and (6) in order to ultimately assess the influence of the hydrogen analysis procedure standardized in ISO/DIS 3690 [1].

Absolute laboratory-specific error: $\bar{y}_{ij} - \hat{m}_j$ (5)

Relative laboratory-specific error: $f = \pm\left(\frac{\bar{y}_{ij} - m_j}{m_j}\right) \cdot 100\%$ (6)

Figures 8 and 9 represent the absolute and relative laboratory-specific errors of the individual parameter sets.

It can be concluded that a maximum relative laboratory-specific measuring error of more than 30 % may occur in this round robin test using the procedure currently specified in ISO/DIS 3690 [1] for diffusible hydrogen measurement. However, the correspondent absolute laboratory-specific errors are relatively low at a hydrogen content of around H_D = ± 1 ml/100 g. (see Figure 8). Any definite dependence on the analysis procedure cannot, however, be discovered.

4 CONCLUSIONS

With a view to providing good applicability and high benefit of ISO/DIS 3690 [1] to industry, a national round robin test was conducted in Germany. Comparative measurements were carried out using hot extraction at different degassing temperatures as well as the mercury method. This investigation was mainly focused on verifying the maximum degassing temperature for the analysis of diffusible hydrogen in materials with bcc-lattice structure. The investigations can be summarized as follows:

– In this round robin test, the weld metal specimens were prepared by only one laboratory under constant welding conditions according to ISO/DIS 3690 [1]. This enabled deliberate evaluation of the hydrogen analysis procedure as standardized in ISO/DIS 3690 [1] and of the adopted hydrogen analysis methods.

– It can be deduced that particularly for diffusible hydrogen contents exceeding H_D = 3 ml/100 g, the hydrogen contents measured by hot extraction are slightly lower than those obtained from the mercury method. At lower diffusible hydrogen contents (H_D < 3 ml/100 g), however, this procedure-specific difference does not occur.

– Degassing temperatures of 150 °C and 400 °C do not lead to an increase in the measured contents of diffusible hydrogen compared to measurements at 20 °C (room temperature).

– The magnitudes of the determined standard deviations are independent of the analytical procedure and of the degassing temperatures predefined for his study. Their order is comparable to the already available results presented in [2], [4], [7] and [8]. As expected, the absolute standard deviations rise slightly with increasing hydrogen content, whereas the relative standard deviations are independent of the hydrogen content.

– In order to evaluate the procedure specified in the revised ISO/DIS 3690 [1] for measuring the diffusible hydrogen content, the absolute and relative laboratory-specific errors in the total average value of the individual parameter sets were considered. The maximum relative laboratory-specific measuring error was > 30 %. However, the correspondent absolute laboratory-

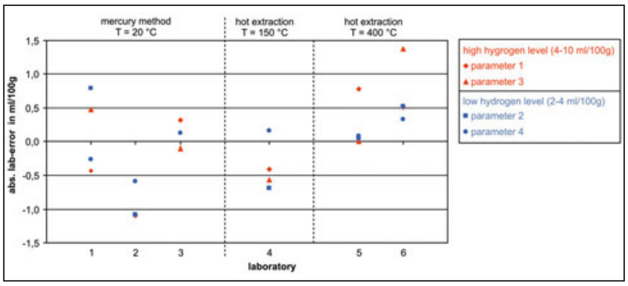


Figure 8 – Absolute laboratory-specific error in total average

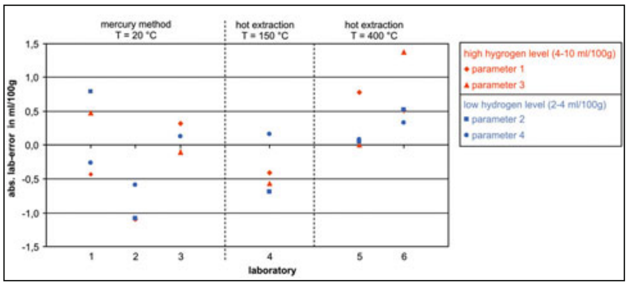


Figure 9 – Relative laboratory-specific error in total average

specific errors are relatively low at a diffusible hydrogen content of around HD = ±1 ml/100 g. Any definite dependence on the analysis procedure could not be determined.

– This round robin test demonstrates that the measuring methods and procedures contained in ISO/DIS 3690 [1] for determining the diffusible hydrogen content in weld metals with bcc-lattice structure yield approximately equal results. The mercury method and the hot extraction methods with thermal conductivity detector (TCD) can be regarded as equivalent reference methods. It is however undoubtedly necessary to take account of the high health hazards involved in the handling of mercury.

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