General Materials Report

GM 1 and GM 2

Hydrogen in Steel Standards

Produced and Certified by The Welding Institute

Cambridge, England

These standards are being distributed by NBS within the U.S.A. as General Materials, GM 1 and GM 2.

GM-1 is a set of 15 cylinders, 5 each of H1, H2, and H3, containing nominally 0.05, 0.10, and 0.20 ml hydrogen, respectively.

GM-2 is a set of 15 cylinders, 5 each of H4, H5, and H6, containing nominally 0.20, 0.60, and 1.10 ml hydrogen, respectively.

The certified hydrogen content for H1 through H6 and batch numbers are given on the attached certificate of The Welding Institute. Both the type and batch number have been etched on each individual specimen so that the user can determine the certified hydrogen content for each individual specimen.

Testing Study

A testing study of these hydrogen in steel standards was conducted for NBS by C. C. Carson and C. B. Worcester, Materials and Processes Laboratory, Large Steam Turbine-Generator Division, General Electric Company, Schenectady, N. Y.

A statistical sampling for all six types was made and hydrogen was determined in all these samples by the hot-extraction technique. The hot-extraction technique and the apparatus used are described in "Determination of Hydrogen in Steel" Chester C. Carson, Anal. Chem. 32, 936, July 1960.

Initially a temperature of about 650 °C was used as indicated on the attached certificate. This temperature yielded significantly lower hydrogen values than those certified. At the recommendation of Mr. Carson (see above reference) the temperature was raised to about 975 °C. The entire statistical sampling test was then conducted at this higher temperature. In general, the results obtained were in close agreement with the certified values.

(over)

For the H1, H2, and H3 types, certified to two decimal places at nominally 0.05, 0.10, and 0.20 ml hydrogen, all samples yielded the certified value within ± 0.01 ml of hydrogen. For the H4, H5, and H6 samples, also certified to two decimal places at nominally 0.20, 0.60, and 1.10 ml hydrogen, all samples except one yielded the certified value within ± 0.02 ml of hydrogen. For an as yet unexplained reason, one sample of H5 gave a higher, more discrepant value.

The within type precision was calculated on the basis of 6 samples per type. The relative standard deviation ranged from 0.5 to 5.3% with the higher values generally associated with the lower hydrogen contents. When averaged for all types H1 through H6 (36 samples) a relative standard deviation of 2.7 percent was obtained.

In this country the procedure generally used for the determination of hydrogen following the hot-extraction technique is to separate the evolved gases then analyze for the hydrogen only. In England and elsewhere, the procedure often has been to analyze without separation. This, may account, in part, for the low values obtained at General Electric with the low temperature.

Another point of interest: The Welding Institute certificate states that the standards may be used successfully at temperatures as high as 1000 °C as long as it is recognized that evolution times are increased when the $\alpha \rightarrow \gamma$ transition point is passed. The testing at G.E. indicated the opposite to be true; that is, the time for complete evolution of hydrogen at about 975 °C was less than the complete evolution of hydrogen at about 650 °C.

It is concluded that these hydrogen in steel standards produced by the Welding Institute should serve well in the calibration and checking of hydrogen analysis equipment,--whether such equipment involves evolution of the gas at 650 or 975 °C, and whether the equipment is the type that determines gas content directly or the type that separates and then analyzes.

Washington, D.C. 20234
June 14, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

THE WELDING INSTITUTE

Abington Hall Cambridge
England

Certificate of Preparation of Hydrogen Analysis Standard

These standards have been carefully prepared in the laboratories of The Welding Institute and are supplied for the calibration and checking of hydrogen analysis equipment. The actual hydrogen content of each standard is certified to two decimal places.

NO. OF STANDARDS	TYPE	BATCH NO.	HYDROGEN CONTENTS (ml. N.T.P.)	DATE OF MANUFACTURE
30	H1	26	0.05	23. 1. 70
30	"	27	0.05	23. 1. 70
30	"	28	0.05	23. 1. 70
30	"	29	0.05	23. 1. 70
30	"	30	0.05	23. 1. 70
29	"	31	0.05	23. 1. 70
30	"	32	0.05	23. 1. 70
29	"	33	0.05	23. 1. 70
30	"	34	0.05	2. 2. 70
30	"	35	0.05	2. 2. 70
30	"	36	0.05	2. 2. 70
30	"	37	0.05	2. 2. 70
29	"	38	0.05	2. 2. 70
30	"	39	0.05	2. 2. 70
29	"	40	0.05	2. 2. 70
29	"	41	0.05	2. 2. 70
25	"	42	0.05	6. 2. 70
500				

Originally designed and developed at The Welding Institute (formerly the British Welding Research Association) these standards are now being prepared in, and distributed from the Institute's laboratories. Production is under the direct supervision of staff responsible for the original research.

DESCRIPTION

The standards consist of mild or low-alloy cylinders with accurately machined blind holes. A spherical stainless steel ball is welded on to each cylinder in an atmosphere of dry hydrogen at known temperature and pressure. The exact volume of molecular hydrogen thus enclosed is given by the physical volume of the cavity and the temperature and pressure of hydrogen at the instant of sealing. The standard is indefinitely stable (several years) at room temperature but a quantitative recovery of hydrogen is obtained when it is analysed at 600-700°C. The production and testing of these standards has been fully reported in the literature. (F. R. Coe, N. Jenkins and D. H. Parker, Anal. Chem., 1967, 39, 982-993).

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NO. OF STANDARDS	TYPE	BATCH NO.	HYDROGEN CONTENTS (ml. N.T.P.)	DATE OF MANUFACTURE
29	H2	31	0.09	24. 11. 69
29	"	32	0.09	24. 11. 69
29	"	33	0.09	24. 11. 69
29	"	34	0.09	28. 11. 69
29	"	35	0.09	28. 11. 69
30	"	36	0.09	28. 11. 69
29	"	37	0.09	28. 11. 69
29	"	38	0.09	28. 11. 69
29	"	39	0.09	28. 11. 69
29	"	40	0.09	28. 11. 69
29	"	41	0.09	15. 12. 69
30	"	42	0.09	19. 12. 69
30	"	43	0.09	15. 12. 69
30	"	44	0.09	15. 12. 69
30	"	45	0.09	15. 12. 69
30	"	46	0.09	15. 12. 69
30	"	48	0.09	15. 12. 69
500				

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NO. OF STANDARDS	TYPE	BATCH NO.	HYDROGEN CONTENTS (ml. N.T.P.)	DATE OF MANUFACTURE
30	H3	18	0.19	4. 11. 69
30	"	19	0.19	7. 11. 69
30	"	20	0.18	7. 11. 69
30	"	21	0.18	7. 11. 69
30	"	22	0.18	7. 11. 69
29	"	23	0.18	7. 11. 69
30	"	24	0.18	7. 11. 69
30	"	25	0.18	7. 11. 69
30	"	26	0.19	10. 11. 69
30	"	27	0.19	10. 11. 69
30	"	28	0.19	10. 11. 69
30	"	29	0.18	10. 11. 69
30	"	30	0.18	10. 11. 69
30	"	31	0.18	10. 11. 69
29	"	32	0.19	14. 11. 69
30	"	33	0.19	14. 11. 69
22	"	34	0.18	14. 11. 69

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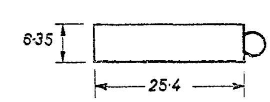
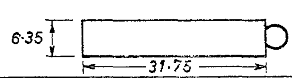
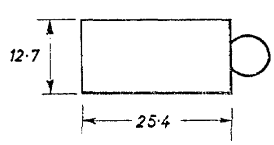
METHOD OF USE

These standards are intended to be used for the calibration of hydrogen analysis equipment and for the regular checking of procedures in the same way that reference samples are used for the metallic elements in routine chemical analysis. Six standards are available providing three levels of hydrogen at each of two specimen sizes. Details are given below. Before filling and welding, cylinders and lids are vacuum degassed to remove residual hydrogen and thereafter are handled only with forceps or gloved hands. <u>As issued the standards are READY FOR USE and require no surface preparation.</u> If the standards have been handled they should be rinsed with acetone and dried in a hot air blast before use. Standards should be stored in a dry container with desiccant to avoid corrosion in damp and acidic laboratory atmospheres. If rusting occurs during prolonged storage it should be gently removed with a wire brush and the standard degreased and dried before use. (It must be remembered that mechanical surface treatment introduces traces of hydrogen into the surface of the steel).

The standard is introduced into the analytical apparatus in the same way as a routine hydrogen specimen with the exception that, in contrast to steel, much more time is available since the standard is not losing hydrogen at room temperature. The standard is analysed and instrument response related to the certified hydrogen content. Several standards should be used at the three hydrogen levels to produce a reliable calibration curve that takes into account variations in instrument response.

The standards have been designed to simulate as closely as possible the behaviour of solid steel specimens. The time for complete evolution of hydrogen at 600-700°C is 10-15 minutes for the small sizes and 40-60 minutes for the large sizes thus resembling the testing times for solid specimens. There is an initial delay of about 2 and 6 minutes respectively for the two sizes, after the commencement of the analysis before any hydrogen emerges from a standard. This is the only feature which distinguishes standards from routine specimens in normal analysis and occurs because of the time taken to raise the temperature of the standard so that the molecular hydrogen is mobilised and a diffusion gradient through the specimen established.

Testing temperatures other than 600-700°C may be used if required in special work. Little or no hydrogen can be recovered from a standard, even with prolonged heating, at temperatures below 300°C. Standards may be used successfully at temperatures as high as 1000°C as long as it is recognised that evolution times are increased when the $\alpha \rightarrow \gamma$ transition point is passed.

TYPE NO.	DIMENSIONS, (mm)	APPROX. OVERALL LENGTH, (mm)	APPROX. WEIGHT, (g)	APPROX. * HYDROGEN CONTENT, (ml. N.T.P.)	PRICE
H1		27	6	0·05	
H2		27	6	0·10	
H3		35	6·6	0·20	
H4		29	24	0·20	
H5		30	22	0·60	
H6		32	20	1·10	

* *Precise hydrogen contents of the standards supplied, corrected for temperature and pressure at the time of filling, are quoted to two decimal places on page 1 of the certificate.*

TYPICAL APPLICATIONS

In addition to their use for calibration and checking of equipment detailed above, standards can, and have been used in various research investigations. Specimen surface treatments and apparatus blanks have been investigated and analytical and sampling errors isolated in normal analysis. Diffusion rate measurements can be made since the wall thickness of a standard can be altered by room temperature machining without disturbing the enclosed hydrogen volume. Likewise a standard may be machined into the form of tensile test specimen or used in studies of hydrogen pickup during corrosion. Institute staff will be glad to advise on the suitability of standards for these and other new applications.

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30	H4	27	0.19	26. 9. 69
30	"	28	0.19	26. 9. 69
30	"	29	0.19	26. 9. 69
30	"	30	0.19	29. 9. 69
30	"	31	0.19	29. 9. 69
30	"	32	0.19	29. 9. 69
30	"	33	0.19	29. 9. 69
29	"	34	0.19	29. 9. 69
29	"	35	0.19	29. 9. 69
29	"	36	0.19	29. 9. 69
30	"	37	0.19	29. 9. 69
30	"	38	0.19	3. 10. 69
29	"	39	0.19	3. 10. 69
29	"	40	0.19	3. 10. 69
30	"	41	0.19	3. 10. 69
29	"	42	0.19	3. 10. 69
26	"	43	0.19	3. 10. 69
500				

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DESCRIPTION

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29	H5	50	0.57	21. 7. 69
30	"	51	0.57	21. 7. 69
29	"	52	0.57	22. 7. 69
29	"	53	0.57	22. 7. 69
30	"	54	0.57	22. 7. 69
30	"	55	0.57	22. 7. 69
29	"	56	0.57	22. 7. 69
30	"	57	0.57	22. 7. 69
28	"	58	0.57	25. 7. 69
29	"	59	0.56	25. 7. 69
28	"	60	0.57	25. 7. 69
29	"	61	0.57	25. 7. 69
29	"	62	0.57	25. 7. 69
30	"	63	0.56	5. 8. 69
27	"	64	0.56	5. 8. 69
28	"	65	0.56	6. 8. 69
29	"	66	0.57	6. 8. 69
7	"	67	0.57	6. 8. 69

500

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29	H6	51	0.99	18. 6. 69
29	"	53	1.01	19. 6. 69
29	"	54	1.00	19. 6. 69
28	"	58	1.01	20. 6. 69
30	"	59	1.05	20. 6. 69
29	"	60	1.02	20. 6. 69
29	"	61	1.03	20. 6. 69
30	"	62	1.06	11. 7. 69
8	"	65	1.05	11. 7. 69
27	"	67	1.04	14. 7. 69
29	"	68	1.04	14. 7. 69
27	"	69	1.05	14. 7. 69
30	"	70	1.02	11. 8. 69
29	"	71	1.03	11. 8. 69
30	"	72	1.04	11. 8. 69
29	"	73	1.03	11. 8. 69
28	"	74	1.01	11. 8. 69
30	"	75	1.03	11. 8. 69
500				

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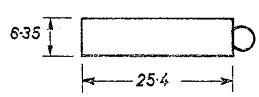
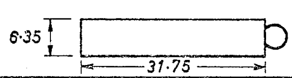
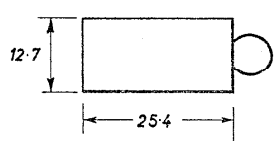
H1		27	6	0·05	
H2		27	6	0·10	
H3		35	6·6	0·20	
H4		29	24	0·20	
H5		30	22	0·60	
H6		32	20	1·10	

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