ISSN : 0974-7419 Volume 14 Issue 1

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 14(1) 2014 [05-10]

Validation of method for the analysis of steels and alloys

G.Swarnabala[1]*, N.Saraswati[2], Y.Praveena[2]

[1]C-MET, (Centre for materials for electronics technology - a scientific institution established under the aegis of Department of Electronics and Information Technology (DeitY), Ministry of Communications and Information Technology (MCIT), Govt of India); IDA Phase II, Cherlapally HCL (PO); Hyderabad : 500 051, (INDIA)

[2]Shadan PG Institute, Khairatabad, Hyderabad – 500001, (INDIA)

E-mail : swarnabalaganti@gmail.com

ABSTRACT

Normally for the analysis of stainless steel (SS), low alloy steel (LAS), aluminium alloy (Al A), brass and white metal standard methods are employed wherein gravimetric, titrimetric and Flame Atomic Absorption Spectroscopy (FAAS) are used. These are generally cumbersome, tedious and laborious to use. Present study describes the use of Standard Materials (SM) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The digestion procedure is adopted from the standard methods and then the solution was aspirated to ICP-OES. This was an easy way in which these materials can be analyzed, in comparison with the existing. The method was validated by doing repeatable and reproducible experiments. It was established that the analysis done was valid and acceptable within limits of the analysis of these materials.

To authenticate the above findings, Inter Laboratory Comparison (ILC) for the validation of this test method has been conducted. The present method of analysis can be implemented only if SM, which takes into account the matrix effect, is available, since no primary standards are used in this field of analysis. However, use of ICP-OES was not uncommon or unacceptable. We have compared the method validation and ILC results in which different test methods were employed, to find that the z-scores are lower than 2.0. It may be emphasized that acid dissolution followed by ICP-OES using SM was an authentic way of analysis and was similar to the available methods.

KEYWORDS

Steel;
ICP-OES;
Inter laboratory comparison;
Proficiency testing;
validation.

INTRODUCTION

Analysis of steel and alloys has been a routine affair since hundreds of years, while most of the methods are documented by International Organization for Standardization (ISO), American Society for Testing and Materials (ASTM) and Bureau of Indian Standards (BIS), it is still a test to any existing testing laboratory to authenticate the results. All the analysts have to be trained by quality control personnel. Always the analysis of each is a matter of concern and skill. Hence, every laboratory has to prove its competency for testing these materials. Thus ILC in a particular area around a testing laboratory is advisable, when they are analyzed in large quantities. In this context, we came across a relevant paper[1] in which ILC data was obtained from 67 laboratories of

Full Paper

31 countries for LAS using certified reference materials (CRM) or SM. The results of the same can be seen in the report- APLAC T026 LAPTP[2] in which 20 laboratories have Z- score < 3 with all results in a 5% probability level. In another study[3] only manganese (Mn) was analyzed on FAAS in different SS and Al A CRM's which are in agreement with the certified values.

Primary standards for individual or mixed metals cannot be used for these materials as there are matrix effects involving large amounts of one particular metal to be considered for traceability purpose. So, CRM's and/or SM's are used for calibration and/or its validation. We have used SM's bought from Bureau of Analyzed samples. Analysis of SM was done using the present method of acid digestion followed by aspiration to ICP-OES for all the four categories of steels & alloys. For the sake of comparison, in the case of SS samples alone, classical methods for nickel (Ni) by gravimetric, chromium (Cr), phosphorus (P) & sulfur (S) by titrimetric were performed. The results for the classical methods, method validation for the present method were in agreement with the values given with the supplied certificates for the SM's. The data are presented in results and discussion section.

For the ILC program we have analyzed SS, LAS, Copper alloy (Cu A), and Al A for most of the elements in chemical and a few mechanical properties. Six laboratories have participated in the analysis and the results are presented here. One sample for chemical and two samples for mechanical were distributed from the same lot to all. Methods of analysis for chemical are employed as per the choice of individual laboratory. However, for Universal Tensile Strength (UTS) IS: 1608-2005 and for Vickers Hardness (VH) IS: 1501-2002 were used by all. The required tests for the ILC in both categories given to all laboratories are tabulated in TABLE 1.

TABLE 1 : Parameters analyzed for all categories of steels & alloys.

S.No	Steel/Alloy	Elements Analyzed	
1	Stainless steel (SS)	Chromium (Cr), Manganese (Mn), Molybdenum (Mo), Nickel (Ni), Phosphorus (P), Vanadium (V), Silicon (Si)	Sulphur (S),
2	Low Alloy steel (LAS)	Chromium (Cr), Manganese (Mn), Molybdenum (Mo), Nickel (Ni), Phosphorus (P), Vanadium (V), Silicon (Si)	Aluminium (Al), Copper (Cu)
3	Copper Alloy (Brass, White metal)	Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Zinc (Zn)	Aluminium (Al), Cadmium (Cd), Tin (Sn), Lead (Pb),
4	Aluminium Alloy (Al A)	Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Zinc (Zn)	Magnesium (Mg),
	MECHANICAL PROPERTIES		
1	Universal Tensile Strength (UTS)		
2	Hardness		

EXPERIMENTAL

This section presents data of method validation and ILC for authentication of various steels and alloys.

Method validation

Chemical: Sample preparation

For SS samples, Ni[4], Si as Silica[5] were estimated by gravimetry and Cr, P, S was estimated by titrimetry[6-8]. All elements listed in TABLE 1, except Si & S, present in SS, LAS, Al A, Cu A were estimated by ICP-OES after the digestion using the appropriate standard method for the particular element[9-11].

Mechanical: Sample preparation

For UTS and VH, sample preparation was done as per the standard methods[12,13].

Instrument (ICP-OES)

General operational conditions are: Plasma Gas flow (L/min) - 15, Auxiliary gas flow (L/min) - 1.5, Nebulizer Pressure (kPa) - 200, Viewing Height - 5mm, Pump speed - 15 rpm, Sample uptake Delay - 15s, Replicate Read Time - 1s, Instrument stabilization delay - 15s, Calibration parameter - Linear, Plasma power - 1.2 kW, Torch Type - Fixed, Nebulizer - V-groove, Fast pump rinse - 50 rpm, Rinse time - 10s, Replicates - 5, Line Background correction - Fitted, Concentra-

tion range - 0.05-1.0 %, Error percent - 15%

Inter laboratory comparison (ILC)

Three laboratories have adopted the standard methods mentioned above for the sample preparation for the ILC program. However, the other three laboratories have used different methods of analysis[14-17]. The results of the ILC data are discussed in detail in Results and Discussion section.

RESULTS AND DISCUSSION

Method validation data for steel and alloys

SS, LAS, Al A, Brass and White metal were run on ICP-OES after the sample digestion as described in 1.1. For repeatability data, one sample was run five times. For reproducibility data, three different weights were taken and run five times each. The experiments on elements Si, Cr, Ni, P and S for SS samples were done by gravimetric and titrimetric methods and they were repeated three times for comparison. Ni, Cr and P are repeated on ICP-OES also to compare the values obtained by classical methods. The mean values obtained are given in TABLE 2. The other categories done only with present method are given in TABLES 3-6. However, Si was analyzed gravimetrically for LAS and Al A too. The values are tabulated in TABLES 3-4.

As the values tabulated for method validation are observed to be closer to the true values of the standard, the said analysis is suitable for routine use for all the steel and alloys samples. Thus, it is possible to dissociate the metals of the steel materials in acid forming inorganic soluble salts, which can directly be aspirated to ICP-OES to obtain similar to true value within the acceptable ranges of standard deviation. Only way to establish that this is a right way of analysis is to conduct an ILC and obtain comparable results.

TABLE 2 : Method Validation data for Stainless steel

Elements	True values *(%)	Classical values (%)	Standard Deviation (SD)	ICP-OES mean values (%)	Repeatability mean SD x 10^{-3}	Reproducibility mean SD X 10^{-2}
Mn	1.311 ± 0.013	Nil	Nil	1.31	1.20	0.24
Mo	2.776± 0.021	Nil	Nil	2.77	2.96	1.48
V	0.0346 ± 0.0016	Nil	Nil	0.03	0.21	3.63
Cr	17.84 ± 0.05	17.82	0.020	17.86	5.17	3.77
Ni	10.20± 0.05	10.17	0.006	10.204	3.16	5.92
P	0.0105 ± 0.0005	0.009	0.001	0.01	0.18	0.04
S	0.0069 ± 0.0005	0.0054	0.0004	-	-	-
Si	0.48± 0.007	0.52	0.03	-	-	-

Certified values for the CRM/SM No: 466/2

Inter laboratory comparison (ILC)

The data obtained for the ILC for six laboratories were analyzed by using the following strategy.

Criteria

The results obtained from the participating laboratories are tabulated for statistical analysis. The following criteria have been adopted while assessing and evaluating the z-score.

a) Results not reported are marked 'X'.
b) Mean value, first quartile values, robust z-scores for chemical and z-score for between laboratory and z-score for within laboratory for mechanical are calculated for each parameter.
c) Results that are given with a less than sign, the sign are removed for calculations.

Z-score

The z-score is a normalized value, which gives a score to each result relative to the other members in the group. So a z- score close to zero means that the results agree well with those from other values.

$$Z = (\text{Result} - \text{Median}) / (\text{NIQR})$$

Full Paper

TABLE 3 : Method Validation data for Low Alloy Steel

Elements	True values *(%)	ICP-OES mean values (%)	Repeatability Mean SD x 10^{-3}	Reproducibility mean SD x 10^{-3}
Al	0.046 ± 0.004	0.0464	0.35	0.154
Cr	1.684 ± 0.009	1.6842	3.25	3.94
Cu	0.436 ± 0.007	0.4364	0.13	3.19
Mn	0.419 ± 0.006	0.4192	0.35	1.92
Mo	0.432 ± 0.010	0.4322	0.00066	3.41
Ni	2.07 ± 0.03	2.0758	0.00216	1.44
P	0.074 ± 0.003	0.0742	0.00024	0.24
V	0.44 ± 0.02	0.4413	0.00068	1.66
Si	0.2±1.10	1.97 (classical)	-	-

Certified values for the CRM/SM No: 410/2

TABLE 4 : Method Validation data for Aluminium alloy

Elements	True values* (%)	ICP-OES mean values (%)	Repeatability mean SD x 10^{-3}	Reproducibility mean SD x 10^{-3}
Fe	0.730 ± 0.059	0.7492	2.39	3.11
Mg	0.298 ± 0.02	0.3504	0.26	0.30
Cu	2.180 ± 0.104	2.0524	4.02	5.54
Mn	0.180 ± 0.013	0.1703	0.22	0.33
Ni	0.130 ± 0.011	0.1203	0.26	0.27
Zn	0.470 ± 0.028	0.4808	0.53	2.92
Si	Measured 0.74±0.02	0.890 (classical)	-	-

Certified values for the CRM/SM No: 216/3 (5% Cu and Al alloy)

TABLE 5 : Method Validation data for Brass powder

Elements	True values* (%)	ICP-OES mean values (%)	Repeatability mean SD x 10^{-3}	Reproducibility Mean SD x 10^{-3}
Al	2.22 ± 0.04	2.2208	0.60	3.06
Mn	0.86 ± 0.03	0.8677	1.00	2.34
Ni	0.56 ± 0.02	0.5634	2.20	1.36
Pb	0.35 ± 0.02	0.3504	0.26	0.30
Sn	0.70 ± 0.05	0.70073	0.27	4.83

Certified values for the CRM/SM –brass powder : 325 mesh lot No:H18P19

TheNormalized Inter QuartileRange:

NIQR = 0.7413 x (Q3-Q1)

a. Z scores outside the range ±3 are labeled as outliers.
b. Standardized sum for a pair of test results Si = (Ai + Bi)/•2
c. Standardized difference for a pair of test results Di = (Ai - Bi)/•2 if median A> median B
d. Standardized difference for a pair of test results Di = (Bi - Ai)/•2 if median B>median A
e. Between laboratory Z-score (ZBL) = (Si-med Si)/ NIQR (Si) to show the accuracy or the bias in measurement of the laboratory
f. Within laboratory Z-score (ZWL)= (Di-med Di)/ NIQR (Di) to show the precision or repeatability of the laboratory

TABLE 6 : Method Validation data for White metal

Elements	True values* (%)	ICP-OES mean values (%)	Repeatability Mean SD x 10^{-3}	Reproducibility mean SD x 10^{-3}
Bi	0.11 ± 0.03	0.1097	0.21	0.50 X 10^{-3}
Cd	0.14 ± 0.01	0.1406	0.25	0.29 X 10^{-3}
Cu	4.58 ± 0.08	4.5840	2.66	3.14 X 10^{-3}
Fe	0.024 ± 0.02	0.0243	0.34	0.40 X 10^{-3}
Ni	0.17 ± 0.03	0.1704	0.35	2.06 X 10^{-3}
Pb	3.18 ± 0.06	3.1854	3.89	2.72 X 10^{-2}
Sb	9.45 ± 0.08	9.4541	5.54	1.16 X 10^{-2}
Zn	0.040 ± 0.003	0.0403	0.22	0.27 X 10^{-3}

Certified values for the CRM/SM No: 178/2 (Tin based)

Results

Results are categorized in three parts based on the z-score evaluation

I. Satisfactory:Z<2 for all elements
II. Questionable: 2≤ Z> 3 for all elements
III. Outlier: Z≥ 3 for all elements.

Discussion for results of Z-score of samples:

Chemical:

Z-Score for SS/LAS

all 6 laboratories are <2.0, so results are satisfactory for all the elements.

Z-score for Al alloy

Lab 2 & 5 - Cr is Questionable and for Lab 5- Cu, Ni and Fe are found to be Outliers.

Z-score for Cu alloy

Lab 2 - Zn, Lab - 5 Cu, Ni are questionable and

Lab 5- Sn is found to be outlier.

The results are sent to each individual laboratory for their internal corrections.

Mechanical

Z-score analysis for the tensile strength and hardness for the analyzed sample for all laboratories were found to be satisfactory. Within lab value for Lab 4 is >2 and needs improvement. In Lab 5, the hardness of the sample resulted in non-compliance, which was informed in turn.

All the tables and data for method validation and ILC program are available with authors for ready reference.

CONCLUSION

The ILC in chemical for SS, LAS, Al alloyand Cu alloy are conducted. In the category of mechanical the tensile strength, Vickers hardness is conducted. A total of six laboratories have participated. Most of the results were found to be satisfactory. A few are questionable and a few more are outliers, which were intimated to the individual laboratories separately. Since the results of the z-score of all the chemical testing parameters are found to be in the acceptable limit of <2.0, the method of testing adopted for them using acid digestion followed by ICP-OES using SM is validated. The results of method validation and ILC were compared with the supplied certificate of analysis. They were found to comply.

ACKNOWLEDGEMENT

Authors would like to specially thank Kum B. Divya for her assistance in preparing this manuscript.The author has done the Inter laboratory comparison and method validation in Lucid laboratories pvt ltd, Hyderabad as a part of compliance procedure for NABL accreditation for the laboratory and thank them for allowing to utilize the data.

REFERENCES

[1] TatjanaDrglin, Mater; Technology, **35(6)**, 343-345 **(2001)**.

[2] APLAC T026 Low-alloy proficiency testing programme-Final report (2001-10-22), **(2001)**.

[3] Mohammad Ali Taher; Indian Journal of Chemistry, **43A**, 1249-1252 **(2004)**.

[4] Indian Standard-Methods for Chemical analysis of steels. Part5 determination of nickel by dimethylglyoxime (gravimetric) method (for nickel >0.1percent), IS: 228 (part 5)-1987 (reaffirmed 1997), 3rd Edition, BIS, New Delhi, India, **(1997)**.

[5] Indian Standard-Methods for Chemical analysis of steels. Part 8 determination of silicon by the gravimetric method (for silicon 0.05 to 5.00 percent), IS: 228 (part 8): 1989 (reaffirmed 2004) 3rd Edition, BIS, New Delhi, India, **(2004)**.

[6] Indian Standard-Methods for Chemical analysis of steels. Part6 determination of Chromium by persulphate oxidation method (for chromium >0.1 percent), IS: 228 (part 6)-1987 (reaffirmed 2002), 3rd Edition, BIS, New Delhi, India, **(2002)**.

[7] Indian Standard-Methods for Chemical analysis of steels. Part 3 determination of phosphorus by alkalimetric method, IS: 228 (part 3)-1987 (reaffirmed 2002), 3rd Edition, BIS, New Delhi, India, **(2002)**.

[8] Indian Standard-Methods for Chemical analysis of steels. Part 9 determination of sulphur by evolution method (for sulphur 0.01 to 0.25 percent), IS: 228 (part 9):1989 (reaffirmed 2004), 3rd edition, BIS, New Delhi, India, **(2002)**.

[9] Indian Standard-Methods for Chemical analysis of steels. Parts 1-12 chemical analysis of aluminium and its alloys, IS: 504 (parts 2 to 7): 2002, 3rd Edition, BIS, New Delhi, India, **(2002)**.

[10] Indian Standard-Methods for Chemical analysis of steels. Part 7 determination of molybdenum by alpha-benzoinoxime method in alloy steels (for molybdenum >1 percent and not containing tungsten), IS: 228 (part 7): 1990 (reaffirmed 2006), 3rd Edition, BIS, New Delhi, India, **(2006)**.

[11] Indian Standard-Methods for Chemical analysis of steels. Part 2 determination of manganese in plain-carbon and low alloy steels by arsenite method, IS: 228 (part 2)-1987 (reaffirmed 1997), 3rd Edition, BIS, New Delhi, India, **(1997)**.

[12] Indian Standard Metallic Materials-Tensile testing at ambient temperature, 3rd revision IS 1608:2005, ISO 6892:1998, BIS, New Delhi, India, **(2005)**.

[13] Indian Standard Metallic Materials- Method for Vickers Hardness test for Metallic Materials, 3rd revision, IS 1501:2002, ISO 6507-1:1997, BIS, New

Delhi, India.

[14] ASTM Standard E1086 94, RA 2005 (2008), "Standard Test Method for Optical Emission Vacuum Spectrometric analysis of stainless steel by the point-to- plane excitation technique", ASTM International, West Conshohocken, PA, 2008, DOI 10.1520/E1086-08, www.astm.org, **(2008)**.

[15] ASTM Standard E415 991 RA, 2005 (2008), "Standard Test Method for Atomic Emission Vacuum Spectrometric Analysis of Carbon and Low-Alloy Steel", ASTM International, West Conshohocken, PA, 2008, DOI 10.1520/E0415-08, www.astm.org, **(2008)**.

[16] ASTM Standard E1251, 2004 (2011), "Standard Test Method for Analysis of Aluminium and Aluminium Alloys by Spark Atomic Emission Spectrometry", ASTM International, West Conshohocken, PA,2008, DOI 10.1520/E1251-11, www.astm.org, **(2011)**.

[17] ASTM Standard E34, 1994 RA 2002(2011), "Standard Test Methods for Chemical Analysis of Aluminium and Aluminium-Base Alloys", ASTM International, West Conshohocken, PA,2008, DOI 10.1520/E0034-11E01, www.astm.org, **(2011)**.