Quality Assurance for the Analysis of Steel by Gas Component Analysis

Alain Salaville, Jérôme Barraqué, JOBIN YVON SAS, Longjumeau, FRANCE

Keywords: quality assurance, steel

1 Overview

Quality assurance of analysis is often demanded by a wide range of users interested in the analysis of raw steel or finished steel products. These users include international public and private organizations, such as the ISO, JIS, ASTM, ASME, LA, and Defense Agencies, manufacturers, such as automobile makers, and individual users.

The most important factor required by any quality assurance is the accuracy of analysis making it possible for all values analyzed to meet authorized standards. The second most important factor is the ease of tracking back to find when, how, by who, and under what conditions or environments the analysis was made.

In order to satisfy these factors, the above tasks must be standardized and prepared in writing as guidelines or references. Their contents must provide steps to make it possible to ensure that the results of analysis will be obtained by taking the provided steps. As an example, quality assurances of analysis are explained below with the carbon detection method (EMIA) and nitrogen detection method (EMGA) provided in Steel Analysis (Analysis of Control of Processes in 24-hour Operation). The example introduced here is typical. Other quality assurance systems may be applied if they are proper and suitable.

2 System configuration

The system configuration is divided into the following 10 items.

1. Manufacturing stage and analysis position:
Standards for the analysis position and timing at manufacturing stage according to the product.

2. Sampling and analysis instructions:
Standards for the elements to be analyzed, the precision of analysis, and the types of samples required.

3. Sampling method:
Standards for how the samples are collected.

4. Sampling arrangement:
Standards for how the samples are handled and stored.

5. Analysis method selection:
Standards for the selection method of analysis based on the expected quantities of analysis elements, required precision of analysis, and required time of analysis.

6. Analysis method
Standards for a whole procedure for analysis.

7. Analyzer operation maintenance:
Standards for the operation, maintenance, and improvement methods of the analyzer to keep it in good operating condition.

8. Analyzer accuracy maintenance:
Standards for the maintenance and improvement methods of the analyzer so that the analyzer can maintain its accuracy of analysis.

9. Analysis criteria:
Standards for criteria of analysis results obtained from unknown samples in accordance with the above standards.

10. Analysis result reporting:
Standards for the means and destinations of correct analysis results to be reported.

Others:
Control of analysis materials, training and authorization of analysis engineers, countermeasures against errors, quality control and records, and more.

JOBIN YVON HORIBA

3 Carbon analysis in steel

3.1 Analysis method selection

Table 1 : Method Selection

		Pig iron	Carbon steel	Alloy steel	Stainless steel
1	Gas capacity method	●	●	●	●
2	High frequency heating and infrared absorption method	●	●	●	●
3	Combustion and infrared absorption method	●	●	●	●
4	Carbon trace quantitative method	●	●	●	

3.2 Analyzer operation maintenance and analyzer accuracy maintenance

1. Creation of Calibration Curve (Once a Year)

a. Standard Sample

Standard sample name	Standard value (%)
JSS 152	0.186
JSS 514	0.098
JSS 512	0.090
JSS 168	0.053
JSS 169	0.047
JSS 155	0.041
JSS 174	0.031
JSS 003	0.0011

Table 2: Standard sample for calibration curve

b. Analysis
Analyze each sample twice in succession to obtain the mean value.

c. Calculation of Calibration Curve
Obtain the relationship between the analysis value and standard value from the linear regression formula.

d. Check
The sensitivity slope (a) must be within 1.5.

2. Performance Check (Once a Year)

a. Standard Sample

Standard sample name	Standard value (%)
WS 205	0.0027
JSS 155	0.041

Table 3: Standard for performance check

b. Analysis
Analyze each sample 10 times in succession and obtain the dispersion as a standard deviation.

c. Criteria
The standard deviation obtained from each sample analyzed 10 times must be within the corresponding value in the Table 3.

Standard sample name	Reference standard Deviation
WS 205	0.0002
JSS 155	0.0010

Table 4: Reference standard deviation

3. Regular Inspection (Once a Month)

Table 5: Inspection item

Inspection item	Key point
Extraction line cleaning	Use a brush or vacuum cleaner
Dust disposal line cleaning	Use a brush or vacuum cleaner
Do not leave any dust. Moving board and pot board	Check that there is no crack or chipping
Combustion tube replacement Interior cleaning	Use a vacuum cleaner
Ground inspection	Check that the ground line is securely connected.

4. Daily Inspection (Once a Day)

Table 6: Standard for daily inscpection

Inspection item	Standard
Dust cleaner cleaning	Within 100 analyses
Cylindrical filter replacement	Within 300 analyses
Magnesium perchlorate replacement on sample side	Within 300 analyses
Ascarite replacement on zero gas side	Within 600 analyses
Operation gas pressure	3.5 kg/cm2
Oxygen pressure	3.0 kg/cm2

5. Analysis Check (Once a Shift)

a. Standard sample

Table 7: Standard for analysis check

Standard sample name	Standard value (%)
WS 205	0.0027
JSS 155	0.041

b. Analysis

Analyze each sample twice in succession to obtain the mean value and dispersion range.

c. Criteria

The mean value must be within the corresponding permissible limitation range in the Table 7.

Table 8: Tolerance

Standard sample name	Tolerance
WS 205	0.0027 ± 0.0002
JSS 155	0.041 ± 0.001

The dispersion range must be within the corresponding dispersion permissible range in the Table 8.

Table 9: Dispersion range

Standard sample name	Tolerance
WS 205	0.0002
JSS 155	0.001

Describe the mean value and range in the X-R control chart and check improper values and errors in periodicity, tendency, and dispersion from the chart.

6. Calibration (Whenever Necessary)

a Standard Sample

Table 10: Standard for calibration

Standard sample name	Standard value (%)
JSS 003	0.0011
JSS 512	0.090

b Analysis

Analyze each sample twice and obtain the me an value to calibrate the calibration curve.

c Check

The sensitivity slope (a) must be within 1.5.

4 Nitrogen analysis in steel

4.1 Analysis method selection

Table 11: Analysis method selection

	Pig iron	Carbon steel	Alloy steel	Stainless steel
1 Ammonia-distilled amidesulfuric acid titration method	●	●	●	●
2 Ammonia-distilled bis extinction method	●	●	●	●
3 Ammonia-distilled indophenol blue extinction method	●	●	●	●
4 Inert gas fusion and thermal conduction method	●	●	●	●

4.2 Analysis method

JIS or 180 standards are often applied to analysis methods. In such cases, a company's standards usually do not specify analysis methods in detail.

1. Ammonia-distilled Amidesulfuric Acid Titration Method

In this method, a sample is decomposed with hydrochloric acid and oxidized with hydrogen peroxide. The residual liquid is processed with sulfuric acid mixed with potassium sulfate and copper sulfate, which generates white smoke. This solution is alkalized with sodium hydroxide. Next, the solution is distilled to extract a liquid to be absorbed by boric acid. Finally, the quantity of ammonium ions is measured by amidesulfuric acid titration.

2. Ammonia-distilled Bis Extinction Method

In this method, a sample is decomposed with hydrochloric acid and filtered to get a solution. The residual liquid is added with sulfuric acid and potassium sulfate, heated, decomposed, and then mixed with the filtered solution. This solution is alkalized with sodium hydroxide. Next the solution is distilled to extract ammonia to be absorbed by water. After citric acid, disodium phosphate, and p-toluenesulfonchloroamido sodium (chloramine T) are added to this liquid, bis-pyrazolone (1-phenyl, 3-methyl, and 5-pyrazolone bis) is further added to generate a color complex. Finally a photometer is applied to measure the optical density of the complex.

3. Ammonia-distilled Indophenol Blue Extinction Method

In this method, a sample is decomposed with hydrochloric acid and filtered to get a solution. The residual liquid is added with sulfuric acid and potassium sulfate, heated, decomposed, and then mixed with the filtered solution. This solution is alkalized with sodium hydroxide. Next, the solution is distilled to extract ammonia to be absorbed by diluted sulfuric acid. This liquid is added with phenol, sodium hypochlorite, and pentacyanonitrosylferrate (III) sodium to generate a blue complex. Finally a photometer is applied to measure the optical density of the complex.

4. Inert Gas Fusion and Thermal Conduction Method

In this method, a sample is put into a graphite pot, melted in inert gas to extract nitrogen to be transferred to a heat conductive cell to measure the change in heat conductivity.

The following analysis items are described.
1) Outline
2) Applicable range and quantity of samples
3) Instruments, materials, and reagents
4) Equipment
5) Quantitative operation
6) Calculation and results

4.3 Analyzer operation maintenance and analyzer accuracy maintenance (inertg gas fusion and thermal conduction method)

1. Creation of Calibration Curve (Once a Year)

a. Standard Sample

Table 12: Standard for calibration curve

Standard sample name	Standard value (%)
JSS 003	0.0014
JSS 050	0.0027
JSS 061	0.0038
JSS 512	0.0069
JSS 515	0.0081
JSS 516	0.0090
JSS 517	0.0104
JSS513	0.0118

b. Analysis
Analyze each sample twice in succession to obtain the mean value.

c. Calculation of Calibration Curve
Obtain the relationship between the analysis value and standard value from the linear regression formula.

d. Check
The sensitivity slope (a) must be within 1.5.

2. Performance Check (Once a Year)

a. Standard Sample

Table 13: Standard for performance check

Standard sample name	Standard value (%)
WS 205N	0.0024
JSS 516	0.0090

b. Analysis
Analyze each sample 10 times in succession and obtain the dispersion as a standard deviation.

c. Criteria
The standard deviation obtained from each sample analyzed 10 times must be within the corresponding value in the Table 13.

Table 14: Reference standard deviation

Standard sample name	Reference Standard (%)
WS 205N	0.0002
JSS 516	0.0003

3. Regular Inspection (Once a Month)

Table 15: Regular inspection

Inspection item	Key point
Cooling water checking	Check that there is no scale or clogging
Vacuum cleaner checking and cleaning	Do not leave any dust
Upper electrode checking and cleaning	Check that there is no crack or chipping
Lower electrode chip replacement	
Interior cleaning	Use a vacuum cleaner
Purifier line copper sulfate replacement	

4. Daily Inspection (Once a Day)

Table 16: Daily inspection

Inspection item	Standard
He gas pressure	3.5 kg/cm2
Air pressure	4.5 kg/cm2
Dust filter replacement	
O-ring cleaning	Removal and greasing
Plunger cleaning	Removal and greasing
Analyzer magnesium perchlorate replacement	Within 500 analyses
Analyzer ascarite replacement	Within 500 analyses
Analyzer copper sulfate replacement	Once each 15-day period

5. Analysis Check (Once a Shift)

a. Standard Sample

Table 17: Analysis check

Standard sample name	Standard value (%)
WS 202N	0.0024
JSS 516	0.0090

b. Analysis
Analyze each sample twice in succession to obtain the mean value and dispersion range.

c. Criteria
The mean value must be within the corresponding permissible limitation range in the Table 15.

Table 18: Criteria

Standard sample name	Standard value ± tolerance
WS 202N	0.0024 ±0.0002
JSS 516	0.0090 ±0.0002

The dispersion range must be within the corresponding tolerance in Table 16.

Table 19: Dispersion range

Standard sample name	Tolerance
WS 202N	0.0003
JSS 516	0.0004

Describe the mean value and range in the X-R control chart and check improper values and errors in periodicity, tendency, and dispersion from the chart.

6. Calibration (Whenever Necessary)

a. Standard Sample

Table 20: Calibration

Standard sample name	Standard value (%)
JSS 003	0.0014
JSS 517	0.0104

b. Analysis
Analyze each sample twice and obtain the mean value to calibrate the calibration curve.

c. Check
The sensitivity slope (a) must be within 1.5.

In the USA:
Jobin Yvon Inc.
3880 Park Avenue
Edison, NJ 08820
Tel: 1-732-494-8660
Fax: 1-732-494-8796
E-mail: info@jobinyvon.com

In France:
Jobin Yvon S.A.S.
16-18, rue du Canal
91165 Longjumeau Cedex
Tel: (33) 1/64 54 13 00
Fax: (33) 1/69 09 90 88

In Japan:
Horiba Ltd.
2 Miyanohigashi, Kisshoin
Minami-ku, Kyoto 601-8510
TEL: (81) 75 313 8121
FAX: (81) 75 321 5725
www.horiba.com

Germany: (49) 89/46 23 17-0
Italy: (39) 2/57 60 56 90
U.K.: (44) 20/82 04 81 42

China: (86) 10/6836 6542
Spain: (34) 91/724 16 57
Other Countries: Contact JY S.A.S.

1-866-JobinYvon
www.jobinyvon.com