The improvement of Quality of Observed Values II
~Detection Limit~

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Abstract

Needless to say, the importance of the quality of observed values shall be emphasized in the field of "TQM", because, the first step of "TQM" should be some data – observed values. Usually, meaning of the quality of observed values should be, a) accuracy (trueness and precision), b) detection limit, c) cost and so on. However, the authors will describe mainly on b), in this paper. The definitions of technical terms related to "Detection Limit" are defined in ISO 11843-1 Capability of detection – Part1:Terms and definitions (1998). The most important terms extracted from the above standard are shown in the following table.

Terms	Symbols	Definition
Critical value of the response variable	y_c	The value of the response variable, Y, the exceeding of which leads, for a given error probability α to the decision that the observed system is not in its basic state.
Critical value of the net state variable	x_c	The value of the net state variable, X, the exceeding of which leads for a given error probability α to the decision that the observed system is not in its basic state.
minimum detectable value of that net state variable	x_d	The true value of the bet state variable, X, in the actual state, which will lead with probability (1-β) to the conclusion, that the system is not in the basic state.

The application of the "Detection Limit" to the actual measurement is discussed in this paper.

1.Introduction

In the 9th Asia Quality Management Symposium (1995, Seoul), the paper about ISO/DIS 11843-1 (Capability of Detection – Part1: Terms and definitions) and ISO/WD 11843-2

(Capability of detection – Part2: Methodology in the linear calibration case) were reported by T. Miyazu and T. Fujimori. After that, ISO/WD 11843-22 (Capability of detection – Part2: Methodology in the linear calibration case) has been prepared by ISO/TC 69/SC 6/WG 5. In addition, four models for estimating the "Detection Limit" have been suggested and discussed in the ISO/TC 69/SC 6/WG 5 meetings during 1996 – 1998.

The authors, therefore, outline on the ISO 11843-1, ISO/CD 11843-2 and ISO/WD 11843-22, respectively. Later on, the differences between the above four models are explained in Chapter 4, using actual data of Ni contents in steel.

2. The outlines of ISO 11843-1 and ISO/CD 11843-2

2.1 The outline of ISO 11843-1

In the ISO 11843-1, terms and definitions of "Capability of Detection" are specified as shown in Fig.1.

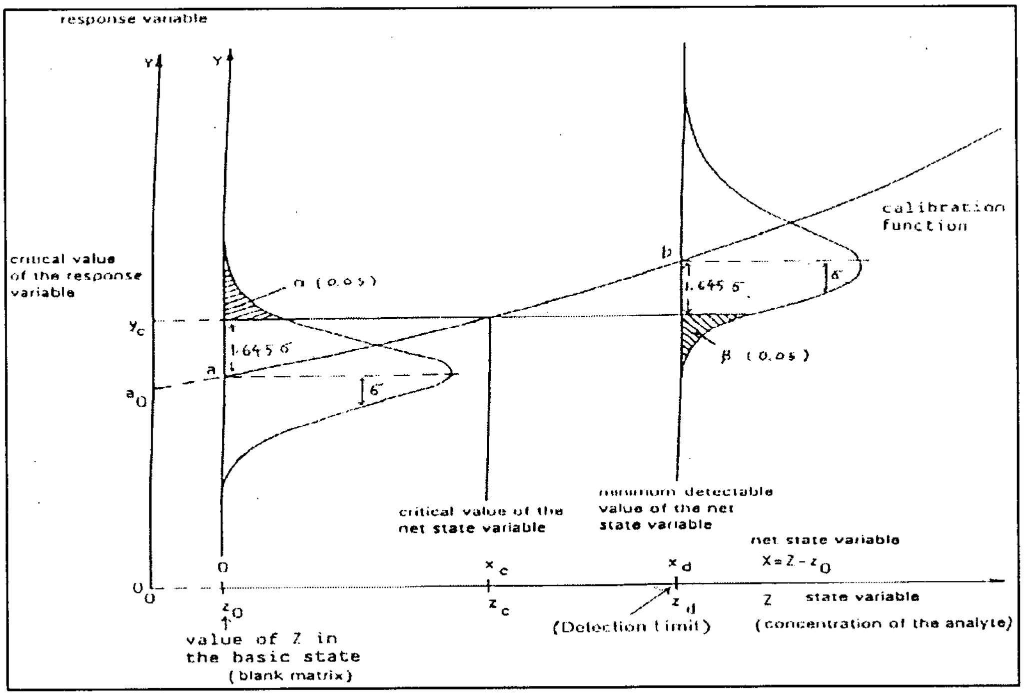


Fig.1: The calibration function, the critical value of the response variable, the critical value of the net state variable and the minimum detectable value of the net state variable

2.2 The outline of ISO/CD 11843-2

In the ISO/CD 11843-2, two models of linear calibration case are shown. One is a methodology that standard deviation is constant (Case1), another is methodology that standard deviation is independent on the net state variables (Case2) as shown in Fig.2 and Fig.3, respectively.

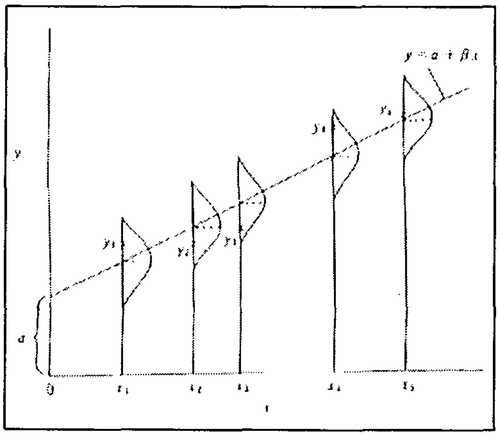


Fig.2: Usual linear model shown in case1

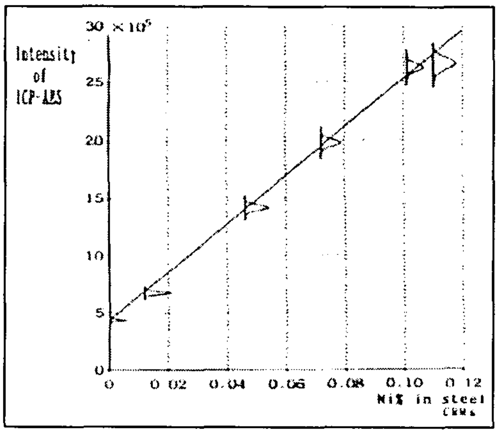


Fig.3: An example of case2
(Relationship between CRM-levels and s.d)

3. The outline of ISO/WD 11843-22

3.1 Experimental design

Firstly, CRM of blank matrix should be prepared. Secondly, many times of measurements should be carried out on the CRM. After that, the average (blank value) and standard deviation can be calculated using this series of data.

3.2 Numbers of replication

This ISO/WD 11843-22 requires at least thirty times of replication on the same blank CRM, to estimate the population standard deviation, as far as precisely. In fact, the example shown in the ISO/WD 11843-22, employs this number – thirty times.

3.3 Assumptions specified

Following the three assumptions are specified in the ISO/WD 11843-22.

- an error of measured value is only random error, not including systematic error.
- both blank and analysis signal are assumed as normal distribution with the same population standard deviation.
- the probability of the first kind error is recommended as 5%.

3.4 Expression figures

Fig.4 is an example for estimating the detection limit by the manner specified in ISO/WD 11843-22. This is simplest model in ISO 11843 series. It seems practical and useful, however, if CRM of blank matrix cannot be prepared, the model of ISO/CD 11843-2 case2 should be used as alternative method. One of such a case is shown in Fig.5

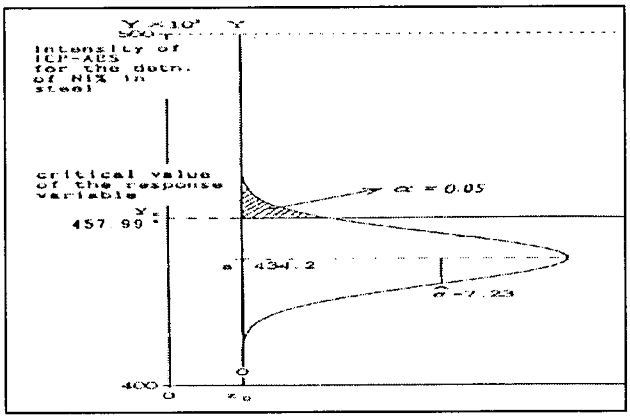


Fig.4: Distribution of the response variable of prepared blank matrix CRM

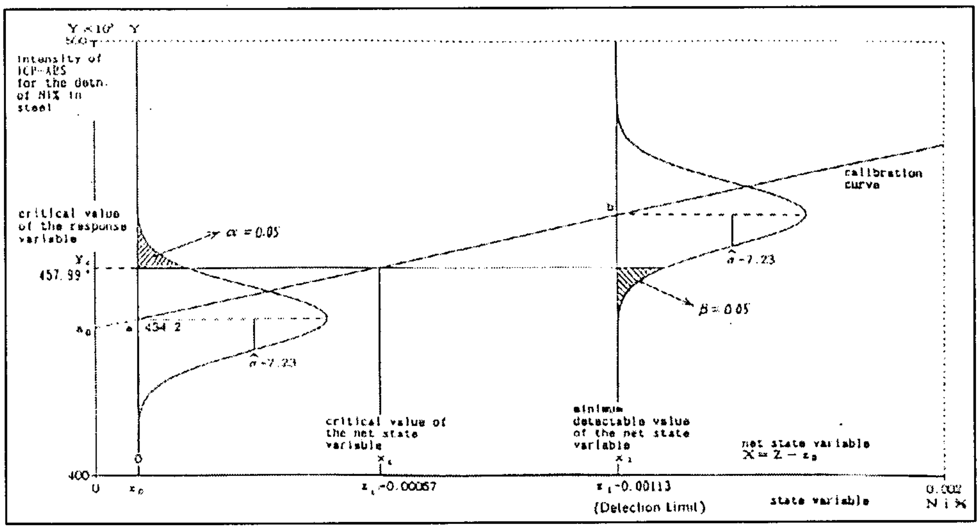


Fig.5: An example of the capability of detection for the detn. of Ni in steel

4. Comparison of four models of "Detection Limit"

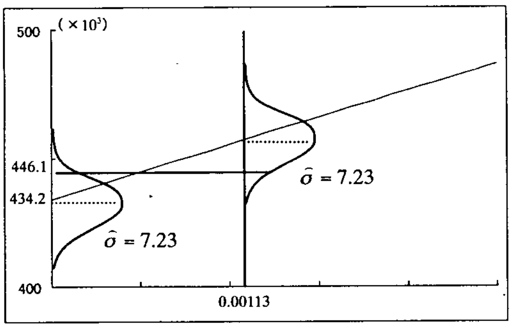
For comparison the four models shown in ISO 11843 series. The authors to estimate the "Detection Limit" in each case, using the data shown in Table1. However, as in evident in Table 1, the standard deviations obtained on six CRMs are significantly different. Therefor, ISO/CD 11843-2, case 1 (Fig.2) cannot be applied, so the estimation of detection limit were carried out on the remaining three case. The results are shown in Table2 and Fig.6 – 11, respectively.

Table 1: Experimental data

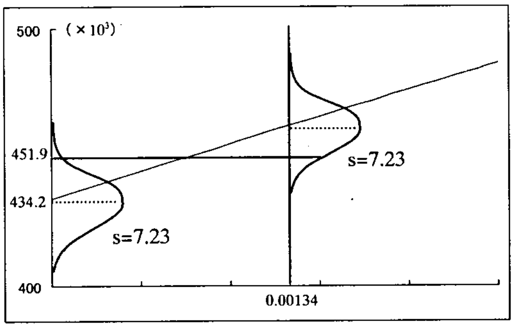
		Fe	168-3	169-5	170-5	171-5	161-5
	Value certified	0.0001	0.012	0.046	0.072	0.101	0.11
1	AM	435391	678560	1424212	2010264	2662913	2713883
	PM	425607	662099	1400643	1972422	2624011	2653619
2	AM	426987	670790	1414311	1969463	2605638	2661274
	PM	421658	657390	1401471	1950683	2597674	2585466
3	AM	433323	678111	1447527	2013999	2623235	2673507
	PM	427723	663799	1402582	1942399	2600978	2605734
4	AM	442082	685911	1450311	2008710	2685086	2718862
	PM	435399	680535	1440654	2018078	2659638	2726078
5	AM	432043	678495	1433599	2002827	2673450	2719090
	PM	412686	647654	1380250	1945247	2571942	2598371
6	AM	426519	666555	1414230	1942558	2623355	2667183
	PM	419239	650291	1379499	1931171	2578707	2596607
Avarage		428221.4	668349.2	1415774.1	1975651.8	2625552.3	2659972.8
Standard deviatior		7233.25	12582.87	23954.87	29501.62	35375.47	52897.62

Table 2: Estimated data

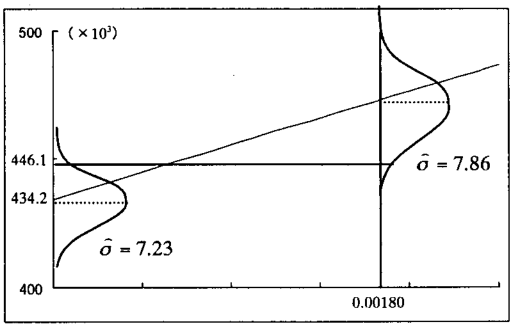
Models	Detection Limit Assumption: normal distribution	Detection Limit Assumption: t – distribution
11843-2 case2-1	0.00113	0.00134
11843-2 case2-2	0.00180	0.00201
11843-22	0.00056	0.00067



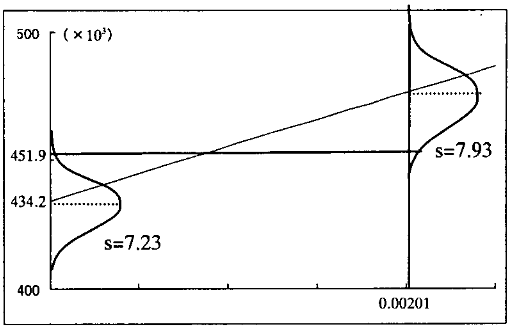
(Fig.6: 11843-2 case2-1 population s.d)



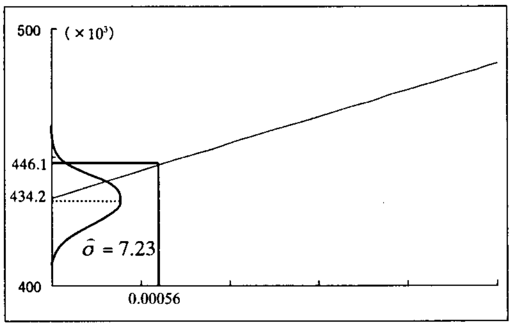
(Fig.7: 11843-2 case2-1 sample s.d)



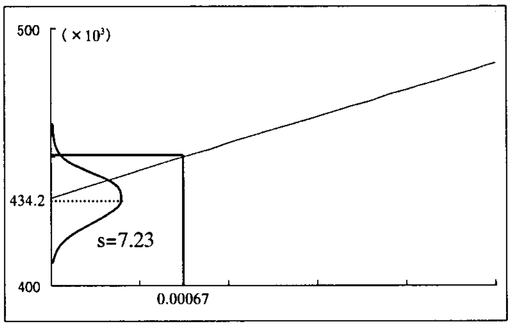
(Fig.8: 11843-2 case2-2 population s.d)



(Fig.9: 11843-2 case2-2 sample s.d)



(Fig.10: 11843-22 population s.d)



(Fig.11: 11843-22 sample s.d)

5. Conclusion

From the above investigation, the following conclusions were obtained.

a) The procedure specified in ISO/WD 11843-22 (Fig.11) should be practical and useful. However, it is based on only one distribution of blank matrix. Therefore it may give an under estimate (Table 2)

b) The procedure specified in ISO/CD 11843-2 case2 needs regression analysis of standard deviation vs. net state variable (e.g. Ni % in steel). It should be not so practical for usual analytical operators.

c) The procedure specified in case 2-1 may be practical for usual operators and gives reasonable figure, so the authors recommend to employ this method, as far as the assumptions are appropriate.

References

1. ISO/TC 69/SC 6/WG 5, "ISO 11843-1 Capability of detection – Part1: Terms and definitions, 1998
2. ISO/TC 69/SC 6/WG 5, "ISO/CD 11843-2 Capability of detection – Part2: Methodology in the linear calibration case, 1998
3. ISO/TC 69/SC 6/WG 5, "ISO/WD 11843-22 Capability of detection – Part22: Methodology for determination of the critical value for the response value when no immediately relevant calibration is made, 1998
4. Toshimi Fujimori, "Statistical Methods for Analytical Engineers, MARUZEN", p.347-p.349, JEMCA, 1995