UDK 543:341.217:669.15
Izvirni znanstveni članek

ISSN 1580-2949
MATER. TEHNOL. 35(6)343(2001)

INTERNATIONAL COOPERATION OF THE INSTITUTE OF METALS AND TECHNOLOGY - LABORATORY FOR ANALYTICAL CHEMISTRY

MEDNARODNO SODELOVANJE INŠTITUTA ZA KOVINSKE MATERIALE IN TEHNOLOGIJE - LABORATORIJA ZA ANALIZNO KEMIJO

Tatjana Drglin

Inštitut za kovinske materiale in tehnologije, Lepi pot 11, 1000 Ljubljana, Slovenija
tatjana.drglin@imt.si

Prejem rokopisa - received: 2001-11-26; sprejem za objavo - accepted for publication: 2001-12-13

The successful cooperation of a laboratory for analytical chemistry in an inter-laboratory comparison is very important in the process of accreditation. A proficiency testing programme was coordinated by The Japan Accreditation Board for Conformity Assessment (JAB). A total of 67 laboratories from 31 countries participated in the program; 40 members were from APLAC (Asia Pacific Laboratory Accreditation Cooperation) and 27 were from EA (European Cooperation for Accreditation).

The laboratory's ability to competently perform the analysis of C, Si, Mn, P, S, Cu, Ni, Cr, V, Mo, Al in low-alloy steel is presented.

Key words: inter-laboratory comparison, low-alloy steel, chemical analysis, C, Si, Mn, P, S, Cu, Ni, Cr, V, Mo, Al

Predstavljeno je uspešno sodelovanje Laboratorija za analitsko kemijo v medlaboratorijski primerjavi, ki jo je organiziralo Japonsko združenje za akreditacijo (JAB) in je ključnega pomena pri postopku akreditiranja laboratorija. V medlaboratorijski primerjavi je sodelovalo 67 laboratorijev iz 31 držav; 40 sodelujočih laboratorijev je bilo iz APLAC-a (Asia Pacific Laboratory Accreditation Cooperation) in 27 laboratorijev iz EA (European Cooperation for Accreditation). Rezultati dajejo jasen vpogled v usposobljenost laboratorija za analizo C, Si, Mn, P, S, Cu, Ni, Cr, V, Mo in Al v malo legiranih jeklih.

Ključne besede: medlaboratorijska primerjava, malo legirano jeklo, kemijska analiza C, Si, Mn, P, S, Cu, Ni, Cr, V, Mo, Al

1 INTRODUCTION

Participating laboratories were supplied with two low-alloy steel samples (chromium molybdenum steels for structural use). The samples were solid, about 30 mm in diameter and about 30 mm thick, and marked C-9 and C-10. Prior to the distribution of the samples, 5 samples were tested using spark-discharge optical emission spectrometry for the homogeneity of all 11 elements.

Participants were asked to analyse the carbon, silicon, manganese, chromium, molybdenum (reported to 0,001 mass %) and phosphorus, sulfur, copper, nickel, vanadium, aluminum (reported to 0,0001 mass %). The thermal method (1) and wet chemical anlysis (2-9) were chosen to determine the concentration of some elements to four decimal places. Each laboratory was required to report the selected analytical method and a typical reference material to be used for validation (of a calibration graph) for each element.

2 EXPERIMENTAL

2.1 Methods

Samples were tested by wet chemical standard methods and the thermal (combustion) method. For the determination of P, V and Mo we used modified and validated methods. Selected methods are summarized in **Table 1.**

Table 1: Applied standard/validated methods
Tabela 1: Uporabljene standardne/validirane metode

Element	Analytical method	Standard	Usefulness (%)
C	FIR	ISO 15350	0,005-4,3
Si	GR	ISO 439	0,10-5,0
Mn	FAAS	ISO 10700	0,002-2,0
P*	MAS	ISO 10714	0,001-1,0
S	FIR	ISO 15350	0,0005-0,33
Cu	FAAS	ISO 4943	0,004-0,5
Ni	FAAS	ISO 4940	0,002-0,5
Cr	FAAS	ISO 10138	0,002-2,0
V**	FAAS	ISO 9647	0,005-1,0
Mo***	FAAS		
Al	FAAS	ISO 9658	0,005-0,20

Abbreviations for the methods:
FAAS - flame atomic absorption spectrometry
FIR - infrared absorption method after combustion
GR - gravimetric method
MAS - spectrophotometric method (molecular absorption spectrometry)
* The method for the determination of P is applicable only for samples containing less than 0,1% chromium. A modified method was used.

** The method is not advisable for V contents below 0,005%. Samples were analysed by FAAS and MAS.
*** The method for the determination of Mo was in-laboratory validated.

2.2 Instrumentation

Flame atomic absorption spectrometric analyses were carried out in a Perkin Elmer 2380 Atomic Absorption Spectrometer. Cu, Cr, Mo, Ni, Mn, Al and V hollow cathode lamps were used.

Carbon and sulfur were determined with an ELTRA CS 800 analyser.

Spectrophotometric measurments were performed with an OPTON PM6.

Table 2: Used certified reference materials
Tabela 2: Uporabljeni standardni referenčni materiali

Element	CRM
C	BAS 460/1, IRSID 185-1
Si	BAS 087-1
Mn	BAS 087-1
P	BAS 087-1, BAS 096-1, BAS 195-1
S	BAS 460-1, IRSID 185-1
Cu	BAS 195-1, BAS 096-1
Ni	BAS 096-1, BAS 088-1, NIST 170A
Cr	BAS 195-1, BAM 178-1
V	BAS 096-1
Mo	BAS 195-1, BAM 178-1
Al	BAM 178-1, BAS 096-1, NIST 170A

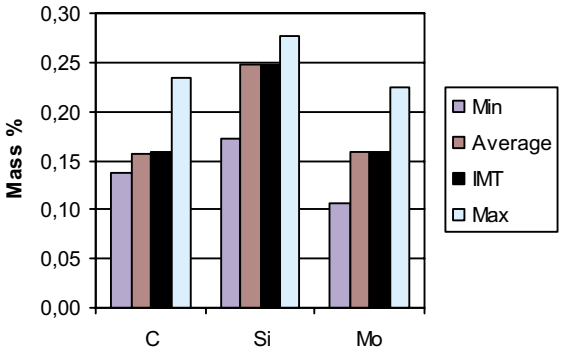

Figure 1: Mass % of C, Si and Mo in sample C9
Slika 1: Masni % C, Si in Mo v vzorcu C9

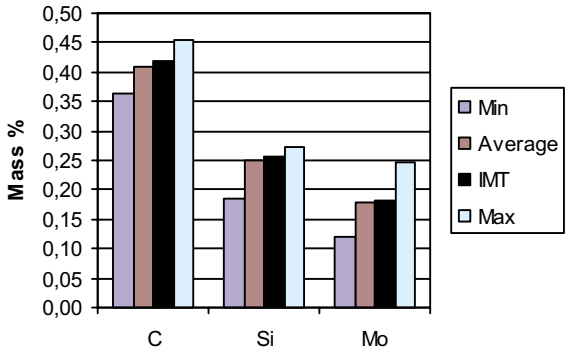

Figure 4: Mass % of C, Si and Mo in sample C10
Slika 4: Masni % C, Si in Mo v vzorcu C10

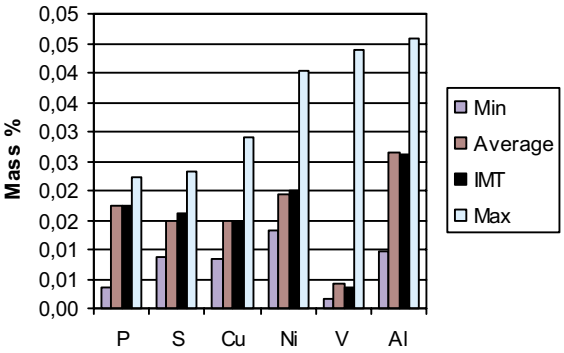

Figure 2: Mass % of P, S, Cu, Ni, V and Al in sample C9
Slika 2: Masni % P, S, Cu, Ni, V in Al v vzorcu C9

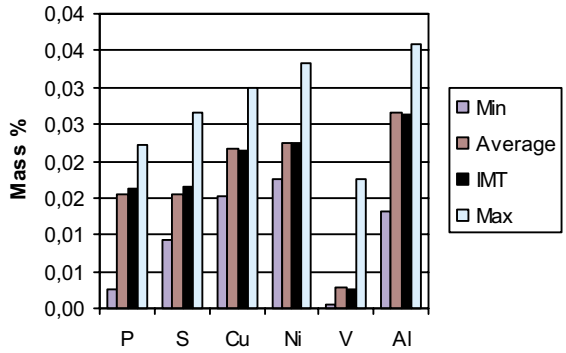

Figure 5: Mass % of P, S, Cu, Ni, V and Al in sample C10
Slika 5: Masni % P, S, Cu, Ni, V in Al v vzorcu C10

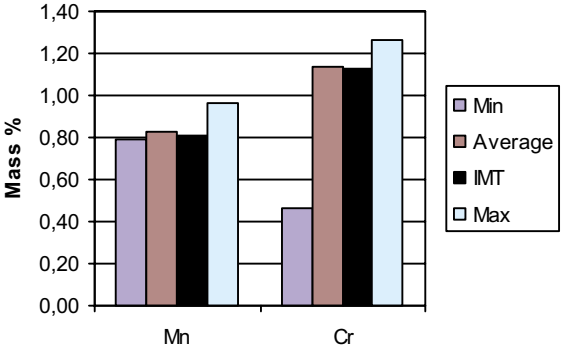

Figure 3: Mass % of Mn and Cr in sample C9
Slika 3: Masni % Mn in Cr v vzorcu C9

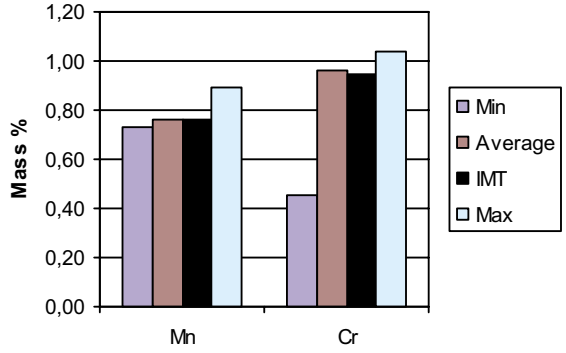

Figure 6: Mass % of Mn and Cr in sample C10
Slika 6: Masni % Mn in Cr v vzorcu C10

2.3 Calibration

In the field of the chemical analysis of metals, primary standards are not used as the source of traceability, instead, certified reference materials (CRMs) and/or RMs are used for calibration and/or its validation. Participating laboratories used approximately 50% of CRM/RMs from either BAS (Bureau of Analysed Samples) or NIST (National Institute of Standards and Technology). More than 10 CRMs/RMs brands made up the other half in each element. The CRMs used in our laboratory are shown in **Table 2**.

3 RESULTS AND DISCUSSION

In order to achieve the programme's aim of assessing laboratories' testing preformance, z-scores were used. The z-score is a measure of how far the result is from the consensus value - a normalized value which gives a "score" to each result relative to the other results in the group. A z-score close to zero would indicate that the result agrees well with those from other laboratories while an outlier would be any result which has an absolute z-score value greather than three. Six kinds of z-scores were calculated. Nearly 10% to 20% of laboratories were outliers with /z-score/ > 3. Moreover, nearly 15% to 25% of laboratories were outliers with a point out of the 5% probability level ellipse in a Youden plot (10), after discarding laboratories with /z-score/ > 3. The average was also calculated after discarding outliers with /z-score/ > 3. The results of the inter-laboratory comparison are shown in **Figure 1 to 6**.

4 CONCLUSIONS

72 laboratories were registered in the presented inter-laboratory comparison. 5 laboratories resigned from the cooperation and 14 laboratories participated only partially.

From the APLAC TO26 Low-Alloy Proficiency Testing Programme-Final report (11) we can see that our laboratory is one of the 20 laboratories with all /z-score/ < 3 and all results in a 5% probability level ellipse in the Youdens plots.

5 REFERENCES

[1] Steel and iron-Determination of total carbon and sulfur content-Infrared absorption method after combustion in an induction furnace (routine method); ISO 15350:2000(E)

[2] Steel and iron-Determination of total silicon content-Gravimetric method; ISO 439:1994(E)

[3] Steel and iron-Determination of manganese content-Flame atomic absorption spectrometric method; ISO 10700:1994(E)

[4] Steel and iron-Determination of phosphorus content-Phospho-vanadomolybdate spectrophotometric method; ISO 10714:1992(E)

[5] Steel and cast iron-Determination of copper content- Flame atomic absorption spectrometric method; ISO 4943:1985(E)

[6] Steel and cast iron-Determination of nickel content- Flame atomic absorption spectrometric method; ISO 4940:1985(E)

[7] Steel and iron-Determination of chromium content- Flame atomic absorption spectrometric method; ISO 10138:1991(E)

[8] Steel and iron-Determination of vanadium content- Flame atomic absorption spectrometric method; ISO 9647:1989(E)

[9] Steel-Determination of aluminium content- Flame atomic absorption spectrometric method; ISO 9658:1990(E)

[10] ISO/TC 69/SC 6 N 427; ISO/DIS 13528 (2000-10-23) "Statistical methods for use in proficiency testing by interlaboratory comparisons"

[11] APLAC TO26 Low-Alloy Proficiency Testing Programme-Final report (2001-10-22)