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Effect of Milling Depth on the Measurement Uncertainty of OES Analysis in Quality Control Steel Samples

Abstract

Steel samples taken for quality control by using arc optical emission spectrometry (OES) exhibit an inhomogeneous element distribution due to segregation during sample casting. Hence the outcome of the OES measurement might be influenced by the way of sample preparation. In 300 low-alloy samples we investigated the impact of milling depth on the measurement uncertainty of the OES analysis. For determination of C, the extended measurement uncertainty (95% CI) decreased significantly from 1.99 % at a milling depth of 0.3 mm to 0.95 %, 0.78 % and 0.76 % at a milling depth of 0.5, 0.7 and 0.9 mm (P<0.001, student's t-test). Similarly, determination of Cr, Cu, Mn, Mo, Ni and Si revealed a significantly lower measurement uncertainty at deeper milling depths. This study demonstrates the significant impact of sample preparation on the precision of OES analysis.

Key words

• **Steel sample** • **OES** • **Measurement Uncertainty** • **Repeatability** • **Precision**

Introduction

The modern steel-making route is based on the combination of highly complex production processes. Nowadays, most of those processes are closely monitored by means of laboratory analyses. Feedback from the analyzed steel sample is passed on instantaneously to the control center and is used to adjust the production parameters. The demands on laboratories in terms of accuracy and precision of chemical results continue to rise because even tiniest deviations from target values might compromise the desired steel quality. The specification of the measurement uncertainty is

therefore becoming increasingly important for assessing the validity of provided analytical results. Laboratories aim to minimize the measurement uncertainty of used technologies so that clear conclusions can be drawn from the reported results. Furthermore, specification and monitoring of measurement uncertainties are integral parts of the ISO 17025.

Nowadays, spark optical emission spectroscopy (OES) is one of the most frequently used standard methods to determine the chemical composition of the steel heat at various stages. For assessment of the measurement uncertainty of the OES, two major sources must be

considered: Measurement uncertainty for repeatability U_R and the measurement uncertainty for the analytical bias U_B.

In the present study, we focus on the measurement uncertainty for repeatability U_R. It is a well-known phenomenon that each sample taken from a ferrous [1] or non-ferrous [2] melt has per se an inhomogeneous structure. This is due to segregation occurring during the cooling and solidification process of the sample. The inhomogeneous element distribution within the sample has adverse effects on the repeatability of OES measurements. However, the exact quantitative impact of the sample segregation on the OES measurement uncertainty is hitherto unclear.

We therefore determined the precision of consecutive OES analyses at different milling depths by calculation the standard deviation of the mean. Based on these data we computed the measurement uncertainty U_R at different milling depth. All other conditions during sampling and sample preparation were thoroughly controlled to avoid the influence from other potentially compounding factors.

Methods

Sampling and sample preparation

For this study we used 300 QC production samples that have been taken from the ladle of an electrical steel mill. All samples were lollipop-shaped with a diameter of 35 mm and a thickness of 12 mm. For this study, we included only samples with a carbon (C) concentration ≤ 0.3 %.

All samples were prepared and analyzed by using an automated robot laboratory. A multi-axis robot carried the sample from the input magazine to a laboratory milling machine (HS-F 1000, Herzog, Germany). In the first cycle, the infeed of the milling machine was 0.3 mm with a spindle rotation speed of 1000 rpm and a milling head advance of 800 mm/min.

Subsequently, the milled sample surface was examined for cavities and inclusions using the HERZOG Spark Point vision software.

Surface defects with a diameter larger than 0.25 mm were considered as significant. If a significant surface defect was detected the vision system automatically checked whether it would collide with a planned spark point position on the sample surface. In this case, the sample was excluded from further analysis and discharged from the automation. Otherwise, the coordinates of six spark points were calculated by the vision system software and transferred to the robot control unit. The location of the six spark points on the sample surface was identical for each sample and milling depth.

The sample was then positioned by the robot at the spark stand of the optical emission spectrometer (SPECTROMAXx, SPECTRO Analytical Instruments, Germany). The OES analyses were carried out consecutively on each of the six spark point positions. Between two analyses, the robot removed the sample, and the electrode was automatically cleaned by a scraper. All analysis results for each spark point were stored in a data base for later evaluation.

After completing the first six analyses at a milling depth of 0.3 mmm, the sample underwent three further cycles of milling, vision analysis and optical emission spectroscopy. In each of these three cycles, the infeed of the milling machine was 0.2 mm with otherwise unchanged milling parameters. The subsequent procedure of image analysis and OES was identical to the first cycle. In summary, each sample was analyzed six times at a milling depth of 0.3, 0.5, 0.7 and 0.9 mm resulting in a total of 24 analyses per sample.

Repeatability and measurement uncertainty of production samples at each milling depth

In a first step, we calculated the standard deviation s from the six measurements of the concentration of C and the other alloying elements Ni, Mn, Cr, Mo, Cu and Si at each milling depth:

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{(n-1)}} \qquad (1)$$

where n=6, x_i is the ith measurement and $\bar{x}$ is the mean element concentration from the six OES analyses at this milling depth.

The relative standard deviation rs at each milling was calculated according to the following equation:

$$rs = \frac{s}{\bar{x}} \qquad (2)$$

Based on the relative standard deviation we calculated the standard uncertainty u_R of the element concentration according to the equation:

$$u_R = \frac{rs}{\sqrt{n}} \qquad (3)$$

We then multiplied the standard uncertainty u_R by the coverage factor k= 2 to obtain the extended measurement uncertainty U_R at a confidence level of 95 %:

$$U_R = k \cdot u_R \qquad (4)$$

Repeatability and measurement uncertainty of a certified reference sample

At regular intervals (approx. every 400 measurements) we carried out a series of six control measurement of a certified reference material (CRM) sample (SS-CRM no.112, Bureau of Analysed Samples Ltd., UK). In a similar way as for the production samples, we determined the extended measurement uncertainty (confidence interval 95%, k=2) based on equations (1) to (4). At the same time, the ± regular measurement of the CRM sample was used to identify a potential drift of the OES instrument during the test series.

Results

Influence of milling depth on repeatability and measurement uncertainty in production samples

We found a statistically significant influence of the milling depth on the relative standard deviation and the measurement uncertainty. For the analysis of C, the mean relative standard deviation (standard error, SE) was 2.44 (0.04) % at a milling depth of 0.3 mm. At 0.5, 0.7 and 0.9 mm, the relative standard deviation was significantly lower (P<0.001) with values of 1.16 (0.01) %, 0.95 (0.01) % and 0.93 (0.01) % (Figure 1). Figure 2 shows the plot of each individual spark point at its x- and y-coordinates. The color of the point represents the percentage deviation of each individual C analysis from the mean C concentration at the given milling depth. The graphs are arranged by spark point number and milling depth. The spark points at a depth of 0.3 mm reveal a higher portion and wider spread of deviations from the mean C concentration. With increasing milling depth, the number and extent of deviation become lower, and the graphs display an even distribution.
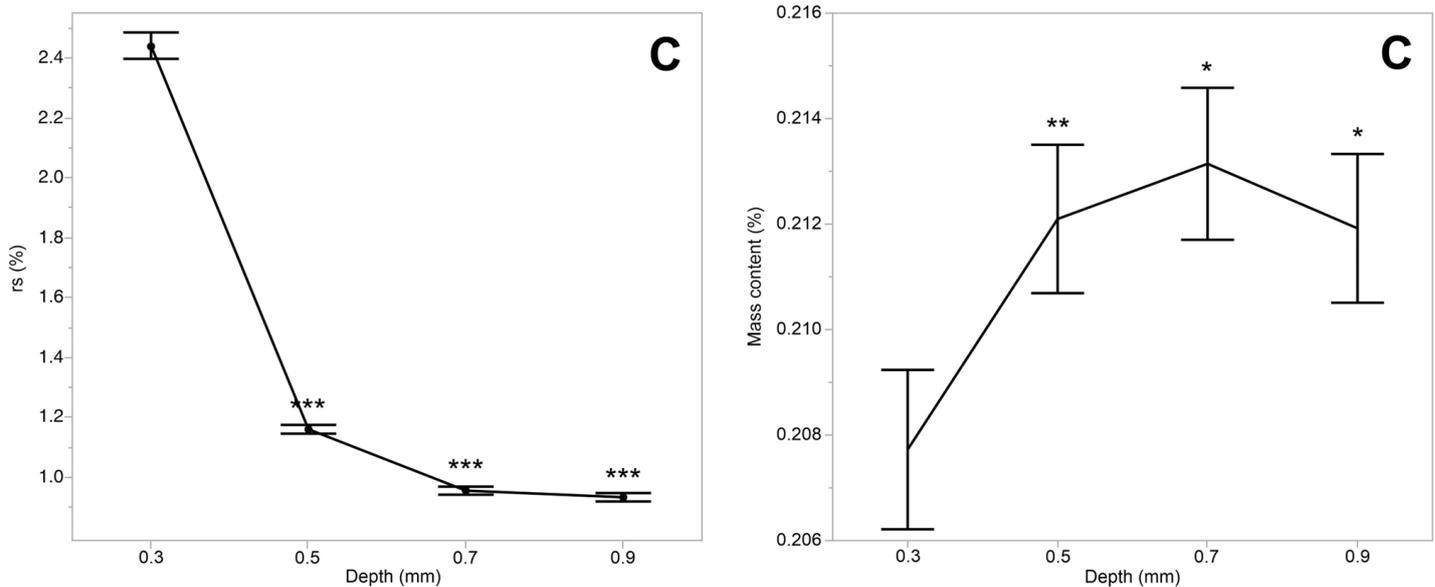
Figure 1: *Left graph: Display of the relative standard deviation (rs ± SE) of the mean mass concentration for C at different milling depths. Right graph: Display of the mean mass concentration (± SE) of C at different milling depths.*
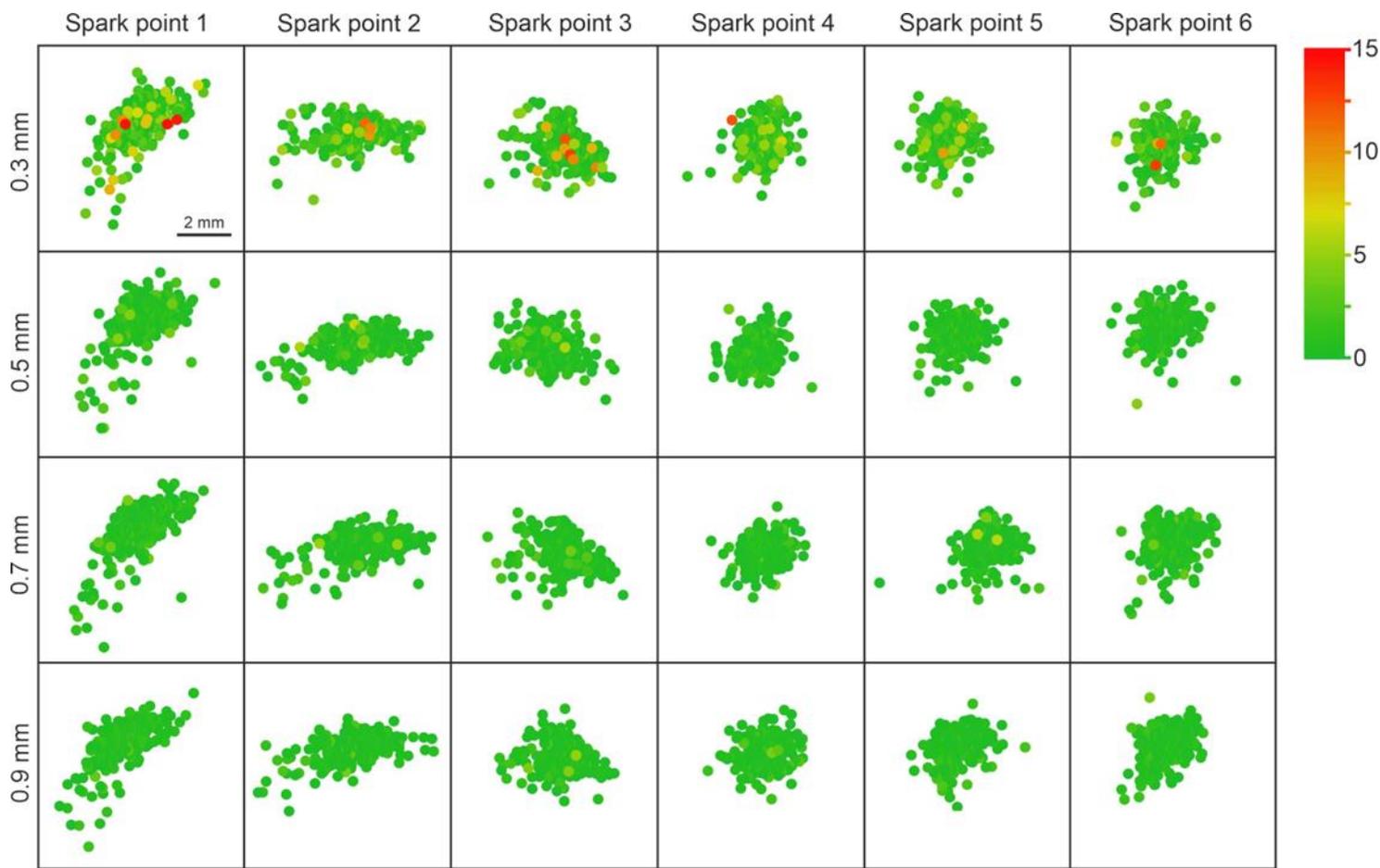
Figure 2: *Scatter plot showing the percentage deviation of the C mass content at each spark point from the mean average C mass content.*

In parallel with the standard deviation, the extended measurement uncertainty U_R for the analysis of C decreased from 1.99 % at 0.3 mm to 0.95 %, 0.78 % and 0.76 % at 0.5 mm, 0.7 mm, and 0.9 mm (Table 1).

For Ni, Mn, Cr, Mo, Cu and Si, the relative standard deviation at a milling depth of 0.3 mm were significantly higher than at 0.5, 0.7 and 0.9 mm. Accordingly, for all elements we found significantly higher U_R values at a milling depth of 0.3 mm compared to 0.5 mm, 0.7 mm, and 0.9 mm (Table 1).

Influence of milling depth on the elemental mass content in production samples

The mean C concentration (SE) at 0.3 mm was 0.2077 (0.0015) %. At 0.5, 0.7 and 0.9 mm the concentration increased to 0.2121 (0.0014) %, 0.2131 (0.0014) % and 0.2119 (0.0014) %. We found a significant mass content differences between 0.3 mm and the other milling depths (P<0.05). For the other alloying elements, we

did not find a significant influence of the milling depth on the percentage mass content.

Repeatability and measurement uncertainty in certified reference sample

The extended measurement uncertainty U_R for the CRM sample revealed following values: C 0.47 %, Si 0.23 %, Mn 0.30 %, Cr 0.30 %, Mo 0.46 %, Ni 0.29 %, Al 0.56 %. During the test series taking place over several days, we could not identify any drift of the OES instrument.

	0.3 mm	0.5 mm	0.7 mm	0.9 mm	CRM
C	1.99	0.95	0.78	0.76	0.47
Cr	0.47	0.38	0.34	0.34	0.30
Cu	0.38	0.27	0.25	0.23	n.a.
Mn	0.36	0.31	0.24	0.26	0.30
Mo	0.55	0.46	0.42	0.43	0.46
Ni	0.45	0.37	0.32	0.33	0.29
Si	0.61	0.47	0.46	0.50	0.23

Table 1: *Extended measurement uncertainty U_R for the alloying elements at each milling depths of the production sample compared to the measurement uncertainty in the CRM sample*

Discussion

In this study, we aimed at specifying the measurement uncertainty for OES analysis as a function of the milling depth. Determination of the measurement uncertainty was based on the calculation of the standard deviation of consecutive analytical results. This method has been used in many previous studies dealing with the precision of OES methods.

Hemmerlin et al [3] compared electrical spark source OES with combustion analysis for determination of the C concentration in steel samples. In the group of samples analyzed by using OES, the mean standard deviation was 2.61 % if samples were prepared by milling. If samples were prepared by grinding, the standard deviation of the OES results was even higher at 6.94 %. In a further study, Luo et al. [4] analyzed steel samples both by spark discharge OES and laser-induced breakdown spectroscopy (LIBS). Based on averaging of six independent measurements of the C concentration, the standard deviation of the OES analysis was between 0.3 and 4.3 % while the values of the LIBS measurement were higher in the range between 3.3 and 8.9 %. For Ni, Mn, Cu, Cr and Si, OES measurements by Luo et al [4] showed a standard deviation between 0.1 and 3.7 % whereas the LIBS analysis revealed higher values in the range between 0.4 and 6.4 %. Another study analyzing these elements by microwave plasma torch OES reported values between 0.5 and 3.5 % [5].

A common finding of this and previous studies is that OES precision varied significantly even within the same sample. Luo et al. pointed out that the variability of these values might be due to the inhomogeneity of analyzed samples but did not detail the underlying cause of sample inhomogeneity [4 [6]]. In the present study, we were able to clearly assign the differences in OES precision to the milling depth. More specifically, the measurement uncertainty of all element concentrations declined with increasing milling depth exhibiting its minimum between 0.7 and 0.9 mm.

Other potentially compounding factors arising from sampling and sample preparation were thoroughly controlled and did not influence the outcome of this study. This is also supported by the fact that the mean values of the standard deviation for each milling depth showed a very small variance with a standard error being mostly below 0.1. This data supports the validity of our results and confirms that the milling depth is the only relevant impact factor for the measurement uncertainty. If other factors like, e.g., reproducibility of sampling would play a role we would have expected a significantly higher variance.

As a comparison to the production samples, we determined the OES measurement uncertainty in a CRM sample. The reference sample is characterized by a high homogeneity of the element distribution. Inhomogeneities due to element segregation are not to be expected and it can be assumed that OES analysis leads to the best possible repeatability with a minimum measurement uncertainty. For Ni, Mn, Cr, Mo and Cu, the measurement uncertainties in the CRM sample corresponded approximately to the values obtained in production samples at a milling depth of 0.7 to 0.9 mm. At a milling depth of 0.7 mm and more, these elements are therefore distributed in a similarly homogeneous manner as in a CRM sample.

For C, the CRM sample showed a measurement uncertainty of 0.47 %, while the measurement uncertainty in the production sample at a milling depth of 0.9 mm was still higher at 0.76 %. A similar phenomenon was observed for Si (0.23 % vs. 0.50 %). It remains to be explored whether a further increase of the milling depth leads to a further reduction of the measurement uncertainty also for those two elements.

This study provided evidence that, at least for C, the milling depth also has an influence on the bias and the associated measurement uncertainty U_B. This can be assumed because of the lower mean concentration value of C at a milling depth of 0.3 mm. However, since no comparison to referenced concentration values

was available, the extent of the bias cannot be determined with certainty. This issue might be subject of future investigations.

In conclusion, the results of this study clearly demonstrate that the measurement uncertainty for repeatability UR can be significantly reduced by an adequate milling depth. Previous investigations showed that wear of the cutting tips may adversely affect the engagement of the milling tips into the sample material and can lead to a significantly reduced milling depth [6]. The condition of the cutting tips can be automatically monitored by using the TCM system of the HERZOG PrepMaster Analytics. In this way, a break-off of the milling plates can be detected at an early stage. Such, it can be prevented that too little sample removal increases the measurement uncertainty of the analytical results.

The results of this study suggest that the differences in UR are due to element segregation within the QC production sample. In the accompanying paper [7], we will present the results of an EPMA investigation of these samples and discuss the influence of the partition coefficient on the element distribution.

References

[1] O. Ericsson: Ph.D. thesis. Skolan för industriell teknik och management, Kungliga Tekniska högskolan (2010).

[2] G. Razaz and T. Carlberg: Materials Science Forum, 794-796 (2014), 83.

[3] M. Hemmerlin, L. Paulard and G. Schotter: Journal of Analytical Atomic Spectrometry, 18 (2003), 282.

[4] L. U. Dan, L. I. Ying, L. I. Xiangyu, Z. H. Zhenyang, W. A. Shigong and Y. Zhang: Plasma Science and Technology, 20 (2018), 075504.

[5] U. Engel, A. Kehden, E. Voges and J. A. Broekaert: Spectrochimica Acta Part B: Atomic Spectroscopy, 54 (1999), 1279.

[6] Herzog Application Note 19/2018

[7] Herzog Application Note 48/2022