Effect of Spark Point Location on the Precision of OES Analysis in Quality Control Steel Samples

Abstract

We recently demonstrated that the measurement uncertainty of arc optical emission spectrometry (OES) depends on the milling depth applied to the QC production sample. More specifically, OES analysis in superficial sample layers (milling depth between 0.3 to 0.5 mm) showed a significantly increased measurement uncertainty compared to deeper layers. In an accompanying EMPA study we were able to correlate these findings with morphological data. We observed segregated grains and an uneven element distribution in the superficial sample layer (0.3 mm) whereas the deeper layer (0.9 mm) displayed an evenly distributed micro-segregation pattern. In this study, we investigated the impact of the spark point location on the precision of OES analysis for carbon (C). We found a significantly worse OES precision for spark points located close to the pin of the lollipop sample. This shows that the OES measurement uncertainty not only depends on the milling depth but also the selection of appropriate spark point coordinates on the sample surface.

Key words

• **Steel** • **OES** • **Measurement Uncertainty** • **Precision** • **Spark Points**

Introduction

Spark optical emission spectroscopy (OES) is a frequently used standard method to determine the chemical composition of the steel heat at various stages. The quality control (QC) sample obtained from the liquid steel is the key components in the analytical sequence [1-3]. Due to the large discrepancy between the size of the sample (approx. 100 g) and the steel batch (up to 400 t) even small irregularities in sample composition may seriously reduce the representativeness of the sample. Moreover, once the sample is solidified the spark excitation by the OES instrument usually covers only a small surface area with a low penetration depth. The actually vaporized and analyzed sample material (approx. 1 mg) accounts for only a tiny fraction of the total sample volume. Hence, OES measurement within a non-representative part of the sample leads to false data on chemical composition of the steel batch and increases the total measurement uncertainty.

In previous studies [4, 5] we found a pivotal influence of the milling depth on the

measurement uncertainty with significantly better OES precision within deeper sample layers than within superficial layers. In the present application note, we investigated how the location of the spark point on the sample surface impact the measurement uncertainty. For this purpose, we compared the analytical precision of OES analysis close to the pin with that far from the pin.

Methods

The detailed process of sampling and sample preparation has been described previously [4]. Briefly, we included 300 lollipop-shaped samples that have been taken from the ladle of an electrical steel mill. The study was conducted using an automated robot laboratory. Each sample was milled four times (HS-F 1000, Herzog, Germany) to sequentially achieve a milling depth of 0.3 mm, 0.5 mm, 0.7 mm, and 0.9 mm.

After each milling cycle, we performed a vision analysis of the sample surface using the SparkPoint vision module of the Herzog PrepMaster SCADA system (Figure 1). First, we identified the sample contour using an adaptive limit value method. We then performed a defect detection on the sample surface to determine if any cavities were present around the planned spark point locations. If no significant defects (>0.25 mm) were detected by the software, the coordinates of the six spark points (SP's) were computed and transferred to the robot controller. If major defects were present, the sample was discarded.
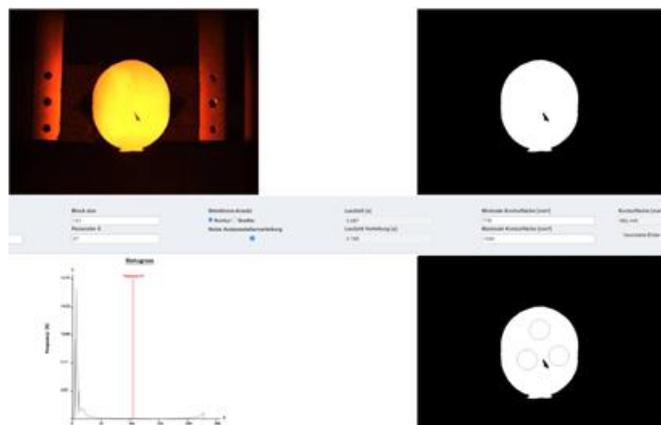
Figure 1: *Screenshot of the SparkPoint module which is part of the PrepMaster Core software.*

The six spark spots were distributed in a circular pattern and the localization of the spark points was identical from sample to sample (Figure 2). Three of the six points were located near to the pin (SP's 1-3), the other three far from the pin (SP's 4-6).
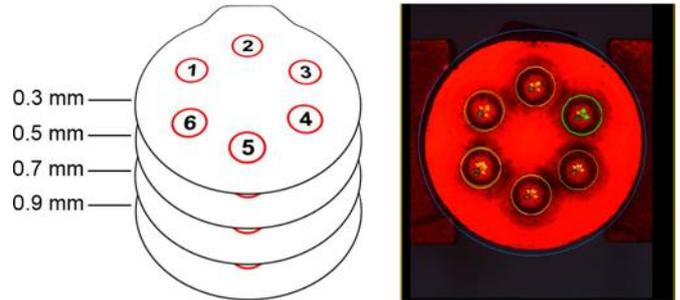
Figure 2: *Location of the six spark points on the surface of the lollipop sample*

After all six OES analyses had been completed, the sample surface was again captured by the SparkPoint software. The burning spots were automatically detected, and the coordinates were stored together with the OES results in the PrepMaster Analytics software for later evaluation.

Using the PrepMaster Analytics software, we calculated the mean percentage mass content for C from the six OES analyses separately for each of the four milling depths (0.3, 0.5, 0.7 and 0.9 mm). Furthermore, in each sample we calculated the relative standard deviation from the mean mass content at each milling depth.

Additionally, we investigated the influence of the spark point location in relation to the sample pin and calculated the mean mass content and its relative standard deviation separately for SP's 1-3 (near to the pin) and SP's 4-6 (far from the pin).

We aimed at assessing the accuracy of the sample preparation using an automated robotic system. Therefore, before insertion into an input rack magazine, the sample height was measured with a caliper at five defined positions to determine the accuracy of material removal by milling. After completion of the four milling cycles, the sample height was measured again. In addition, we compared the actual location of the spark point coordinates with the planned position.

Results

Impact of milling depth and spark point location on measurement uncertainty and mass content

For analysis of C, the mean relative standard deviation (SE) of SP's 1-3 (near to the pin) was 1.89 (0.06) %, 0.89 (0.02) %, 0.71 (0.02) % and 0.77 (0.03) % at a milling depth of 0.3, 0.5, 0.7 and 0.9 mm. For the SP's 4-6 (far from the pin) the relative standard deviation values were 1.07 (0.04) %, 0.77 (0.02) %, 0.64 (0.02) % and 0.61 (0.02) %. The relative standard deviation of the SP's 1-3 and SP's 4-6 was significantly different at a milling depth of 0.3 mm (P<0.001) and 0.5 mm (P< 0.05) (Figure 3).

The mean C mass content (SE) for SP's 1-3 was 0.2049 (0.0021) %, 0.2116 (0.0020) %, 0.2127 (0.0020) % and 0.2116 (0.0021) % at the four different milling depths. SP's 4-6 showed concentrations of 0.2102 (0.0021) %, 0.2124 (0.0020) %, 0.2136 (0.0020) % and 0.2121 (0.0020) %. Statistical evaluation showed no significant differences between values of SP's 1-3 compared to SP's 4-6 (Figure 3).

Accuracy of sample preparation

Based on the height difference before and after milling the mean material removal (SD) was 0.932 (0.045) mm corresponding to a percentage deviation from the target value by 3.6 %. As determined by the vision system, the mean deviation of the actual spark point position from the target position was 0.18 mm in x-direction and 0.13 mm in y-direction. We found slightly larger deviations for the spark points of the left sample side (SP's 1, 2 and 6) with deviations of up to 0.62 mm. A retrospective examination revealed a minor mechanical impairment of the robot hand as the cause.
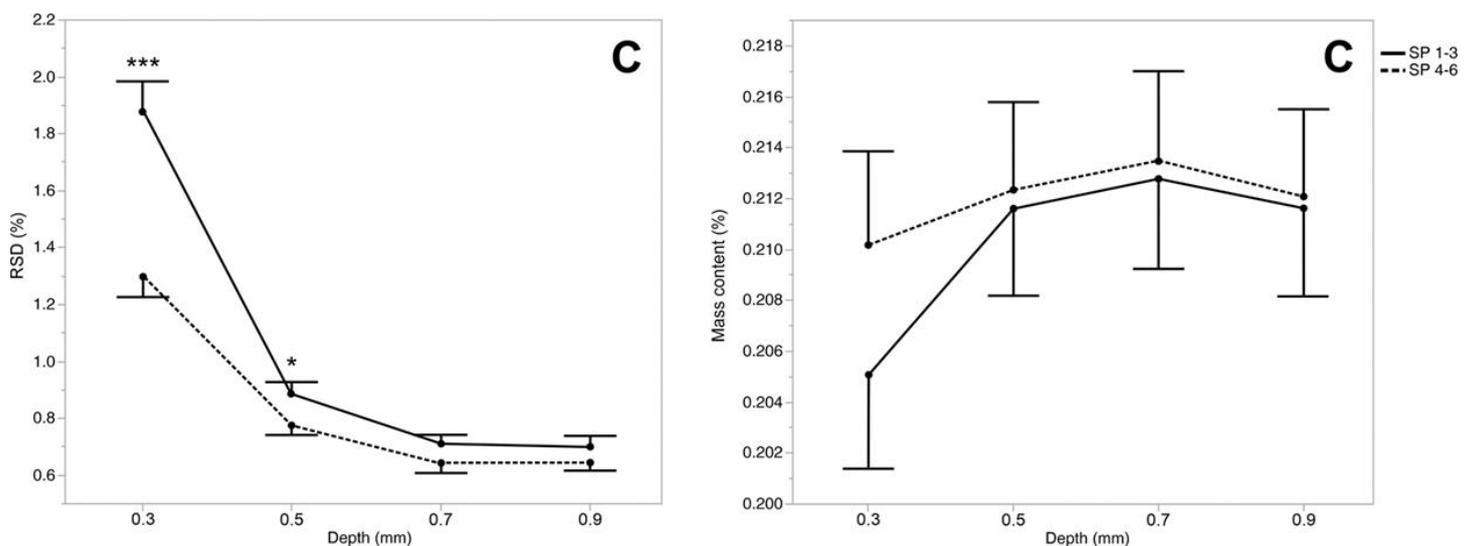
Figure 3: *Left: Display of the relative standard deviation (RSD) for spark points close (SP's 1-3) and far (SP's 4-6) from the pin for the different milling depths. Right: Display showing the mass content for SP's 1-3 and SP's 4-6.*

Discussion

The results of this study demonstrate that OES analysis with spark points close to the sample pin was associated with a significantly higher measurement uncertainty than far from the pin. In addition, this study also confirms previous studies that have shown better repeatability of OES analysis in deeper layers than in superficial layers at a milling depth of 0.3 mm. This trend was clearly evident for both analyses close to the pin and far from the pin. However, the overall repeatability was worse for OES measurement close to the pin. Furthermore, the OES analyses near the pin also showed a lower mass concentration at a milling depth of 0.3 mm than in the deeper layers. This pattern was not detectable in the near-pin analysis.

The cause of these findings is not completely clear but is most likely related to the process of cooling and solidification of the steel melt in the

casting mold. This hypothesis is consistent with the main conclusions of a simulation study computing the flow and solidification pattern of the melt in a lollipop-shaped sample during the sampling process [6].

According to this simulation, the solidification starts immediately after the liquid steel makes contact with the metal mold. The solidification proceeds from the outside to the inside and from the sample pin to the top. The inner sample body is the last region to be solidified. The employed simulation model does not cover all relevant concomitant factors like, e.g., solidification shrinkage and pores formation. Nevertheless, the study reveals that those melt fractions that cool rapidly due to early exposure to the mold exhibit the highest degree of segregation. In good agreement with this we found the worst variability and lowest C concentration in the surface sample layer and the sample portion near to the pin. It should be noted that our study was performed on lollipop samples. A change in the casting mold or method of sampling can already have a significant effect on the solidification pattern of the melt. Therefore, investigations on measurement uncertainty may well show a different distribution pattern than the data presented here.

We assessed the accuracy of material removal in the milling machine and the accuracy in sample positioning by the multi-axis robot. Both parameters showed good accuracy, so that any bias in the data due to inaccurate sample preparation and handling can be ruled out. Concordant with this, the standard deviation values in each data group had only small variances. If other factors like, e.g., reproducibility of sampling or sample preparation would have a confounding impact we would have observed much higher data variability.

All presented data from the vision system and the OES instrument was recorded and evaluated by the PrepMaster Analytics software. The software is designed to process large data volumes from the laboratory and enables the target-oriented extraction of relevant KPIs. Thus, for example, an evaluation of pairwise OES analyses can be carried out without great effort to perform a mapping of the sample surface regarding analytical precision and measurement accuracy. The powerful filter functions of PrepMaster Analytics enable a detailed subgroup evaluation, e.g., for different time periods, sampling locations or concentration ranges.

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