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APPLICATION OF R-CONTROL CHARTS IN INTERNAL QUALITY CONTROL OF ICP-MS ANALYSIS

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Abstract

Sample duplicates represent an important internal quality control (IQC) tool that enables continuous monitoring of analytical method precision during routine laboratory work. In this study, the use of water sample duplicates for monitoring the precision of an ICP-MS method using R-control charts was investigated. For each pair of results, the range (R) was calculated, and the control limits were established based on a reference data set. The results indicate that R-control charts enable straightforward monitoring of agreement between duplicate results and timely detection of deviations, demonstrating that sample duplicates are a useful tool for the IQC of an ICP-MS method.

***Keywords**: ICP-MS; internal quality control; R-control charts*

1. INTRODUCTION

Testing laboratories operating in accordance with the requirements of ISO/IEC 17025 are required to implement appropriate procedures for monitoring the validity of test results. Within internal quality control (IQC), in addition to the analysis of certified reference materials (CRMs), blank, spiked and test samples, the analysis of duplicate test samples also plays an important role. Duplicate analysis enables continuous monitoring of the analytical procedure's precision and timely detection of deviations during routine laboratory work.

The Mining and Metallurgy Institute Bor, Republic of Serbia, has been operating under the accreditation system for more than 20 years and implements various IQC procedures through its technical documentation, including duplicate sample analysis.

This study presents the application of duplicate test samples in the internal quality control of an ICP-MS method for water analysis, using R-control charts to monitor the precision of the analytical procedure for manganese (Mn) determination.

2. EXPERIMENTAL

Within the IQC framework, the laboratory performs analyses of control materials, CRMs, blanks, spiked samples, test samples, and duplicate samples. Control and test samples were prepared and analyzed under the same conditions within the same analytical sequence. Together with other control materials, duplicate test samples were analyzed in each analytical batch after every ten test samples to continuously monitor the precision of the analytical procedure [1–3].

Duplicate sample analyses were performed using a NexION 1000 ICP-MS instrument (PerkinElmer, USA), operated using Syngistix software (PerkinElmer, USA). Prior to each analytical sequence, the operating conditions were checked, and the instrument was optimized by aspirating a Tuning Solution containing 1 µg/L of Be, Ce, Fe, In, Li, Mg, Pb, and U (PerkinElmer, USA). Instrument calibration was performed using the MES-21-1 multielement standard solution (AccuStandard, USA), which contained Mn, with a calibration range of 0 - 200 µg/L. Prior to analysis, the samples were diluted twofold with ultrapure water, with rhodium (Rh) added as an internal standard at a concentration of 10 µg/L.

An R-control chart was used to monitor duplicate results, with the range (R_i) for each duplicate pair calculated as the absolute difference between the two results. Control limits were established using the first 60 duplicate results as the reference data set, and only results obtained for samples analyzed within the defined working range of the ICP-MS method were used for their calculation. The center line was defined as the average range ($\bar{R}$). For subgroups of size n = 2, the lower control limit was LCL = 0, while the upper control limit (UCL) was calculated using the appropriate D_4 constant [4]. Results from samples with concentrations exceeding the upper limit of the calibration range were excluded from the calculation of the control limits. Depending on the analyte concentration, such samples were reanalyzed after appropriate additional dilution or by ICP-OES, which is more suitable for the determination of higher analyte concentrations.

3. RESULTS AND DISCUSSION

Based on the reference set of duplicate results, the statistical control limits of the R-control chart for Mn were established. The average range was $\bar{R}$ = 0.86 µg/L, while application of the appropriate constant for subgroups of size (n = 2) resulted in an upper control limit of UCL = 2.82 µg/L. The resulting R-control chart is shown in Figure 1. Most of the range values between duplicates were within the established upper control limit, with the values generally clustered close to the center line. This behavior indicates good agreement between duplicate results and satisfactory precision of the ICP-MS method during routine analysis of water test samples.

The control chart also shows individual range values that considerably exceed the upper control limit. Analysis of these results revealed that the exceedances occurred mainly for samples with elevated Mn concentrations, for which the analyte concentration after the initial twofold dilution exceeded the upper limit of the ICP-MS calibration range. These values were not used to establish the statistical control limits. In such cases, additional dilution and reanalysis were performed, while samples with particularly high

Mn concentrations were analyzed by ICP-OES, which is more suitable for higher concentration levels.

The occurrence of increased ranges for samples outside the appropriate calibration range highlights the importance of selecting a suitable dilution factor for test samples prior to quantitative determination. At the same time, the R-control chart provides a simple visual tool for monitoring agreement between duplicate results and for rapidly identifying analytical batches or individual samples requiring further investigation. Thus, duplicate sample analysis is a useful additional IQC tool for the continuous monitoring of ICP-MS method precision under routine laboratory conditions.

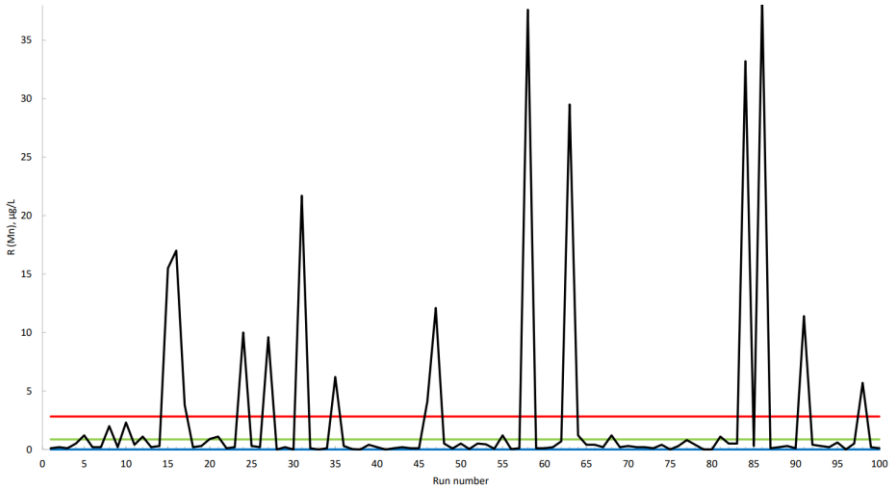


Figure 1. *R-control chart for sample duplicates for the determination of Mn by ICP-MS*

4. CONCLUSION

The application of the R-control chart enabled continuous monitoring of the agreement between duplicate test sample results and assessment of the precision of the ICP-MS method under routine laboratory conditions. Most results were within the established control limits, while exceedances were primarily associated with samples in which Mn concentrations were outside the initial calibration range. The results confirm the importance of selecting an appropriate sample dilution and demonstrate that duplicate analysis, combined with use of R-control charts, represents a simple and effective IQC tool for an ICP-MS method.

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