The 57th International October Conference on Mining and Metallurgy
05 - 07 October 2026, Bor Lake, Serbia
https://ioc.irmbor.co.rs

DOI: 10.5937/IOC26285D Original Scientific Paper-Chemistry

BLANK SAMPLES AS AN ADDITIONAL TOOL FOR INTERNAL QUALITY CONTROL OF AN ICP-MS METHOD

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Abstract

Blank samples represent an important component of the internal quality control of analytical methods, particularly for assessing contamination and monitoring the limits of detection (LoD) and quantification (LoQ). The aim of this study was to evaluate their application as an additional tool for the continuous monitoring of the stability of an ICP-MS method using Quesenberry Q-statistics. During routine laboratory operation, the CPS values of blank samples for arsenic (As), cadmium (Cd), and nickel (Ni) were monitored. Based on the data obtained, Q-control charts were constructed to identify deviations in the analytical system's performance. The results demonstrate that this approach enables the early detection of changes that may indicate contamination or instrument instability, thereby improving the reliability of analytical results.

***Keywords**: blank samples; ICP-MS; internal quality control; Q-control charts*

1. INTRODUCTION

Modern analytical laboratories employing inductively coupled plasma mass spectrometry (ICP-MS) for trace element determination require continuous and documented internal quality control (IQC) to ensure the accuracy, precision, and reliability of analytical results in compliance with the requirements of the ISO/IEC 17025 standard. Routine IQC procedures include the analysis of certified reference materials (CRMs), duplicate samples, spiked samples, control standards, test samples, and blank samples. The combined use of these quality control tools enables the timely detection of systematic and random errors that may compromise analytical performance.

In ICP-MS analysis, blank samples fulfil several important functions. Besides being routinely used to determine the limits of detection (LoD) and quantification (LoQ), they provide valuable information on potential contamination originating from reagents, laboratory glassware, the sample introduction system, or the instrument itself. An increase in the blank signal is often the earliest indication of changes in instrument performance, particularly in the determination of trace-level elements. Consequently, blank samples are routinely analyzed within analytical sequences, typically representing

at least 5% of the total number of samples, to verify process stability and facilitate the early detection of potential deviations [1,2].

Current IQC guidelines and published studies recommend monitoring blank samples with conventional Shewhart control charts, where process stability is evaluated against predefined control limits [2,3]. Although effective at identifying significant deviations, this approach is less sensitive to gradual process changes, particularly when only a limited number of initial observations are available. To overcome these limitations, Matos et al. [4] proposed applying the Quesenberry Q-statistic for monitoring instrumental blank samples. Unlike conventional control charts, Q-control charts enable sequential process monitoring from the first observation without requiring a large historical reference dataset. This makes them particularly suitable for newly commissioned analytical instruments, following maintenance procedures, or in situations where historical quality control data are limited [5]. However, the application of the Quesenberry Q-statistic to monitor blank samples' CPS values during the routine operation of validated ICP-MS methods has received limited attention.

The aim of this study was to evaluate the applicability of blank samples as an additional tool for the internal quality control of an ICP-MS method using the Quesenberry Q-statistic. The study was based on monitoring the CPS values of blank samples collected during the analysis of water samples over 18 analytical sequences for arsenic (As), cadmium (Cd), and nickel (Ni). Q-control charts were constructed to evaluate analytical system stability, identify potential deviations, and enable the early detection of changes that may indicate system contamination and compromise the reliability of analytical results.

2. EXPERIMENTAL

This study is a continuation of the validation of an ICP-MS method [6]. Following method validation, the performance of the validated ICP-MS method was monitored during routine analysis of water samples at the ICP-MS Laboratory of the Mining and Metallurgy Institute. Daily CPS values of blank samples collected during the first 18 consecutive analytical sequences following method validation were included in the study.

Blank samples were prepared using the same sample preparation procedure as the analyzed water samples, except that no water sample was added. The CPS values of As, Cd and Ni were measured using an ICP-MS NexION 1000 instrument (PerkinElmer, USA) operated with Syngistix software (PerkinElmer, USA). Prior to each analytical sequence, instrument performance was optimized using a Tuning Solution (PerkinElmer, USA). Calibration was performed with a multi-element standard solution (AccuStandard, USA) containing As, Cd, and Ni. Rhenium (Re) and rhodium (Rh) were used as internal standards, and the calibration range covered concentrations from 0 to 200 µg/L.

The statistical evaluation was based on the daily blank samples' CPS values using the Quesenberry Q-statistic. Q-control charts were constructed for each element to enable sequential monitoring of the analytical system's stability and to identify potential deviations. The initial reference dataset consisted of CPS values obtained from blank samples analyzed during method validation, when the instrument performance had been verified under optimal operating conditions. Subsequently, daily CPS values obtained

during routine laboratory operations were incorporated sequentially into the statistical analysis.

3. RESULTS AND DISCUSSION

The results of blank sample CPS values monitoring, processed using the Quesenberry Q-statistic are presented in Figure 1. Q-control charts were constructed for As, Cd, and Ni, with a center line (Q = 0), warning limits (±2), and control limits (±3), enabling sequential monitoring of analytical system stability during routine ICP-MS operation.

For all investigated elements, most Q-values remained within the warning and control limits, indicating stable instrument performance throughout the monitoring period. Single exceedance of the upper control limit was observed for As (Q = 3.13), whereas two exceedances were recorded for both Cd (Q = 3.18 and 3.95) and Ni (Q = 4.11 and 5.20). Following these events, Q-values returned to within the control limits, indicating that the observed deviations were temporary and did not result in permanent deterioration of analytical system stability.

The obtained results demonstrate that the Quesenberry Q-statistic enables effective sequential monitoring of blank samples and facilitates the early detection of deviations that may indicate changes in instrument performance or contamination of the analytical system. Therefore, Q-control charts can be considered a useful complementary tool for the internal quality control of validated ICP-MS methods.

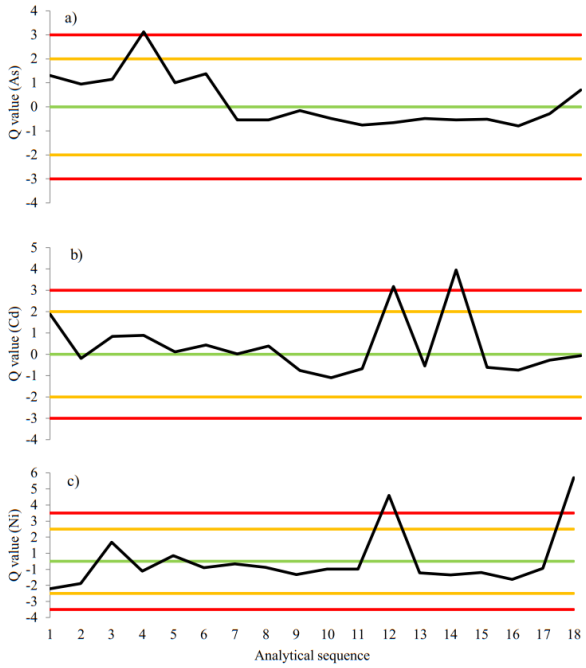


Figure 1. *Q-control charts of blank sample CPS values for: a) As, b) Cd, and c) Ni*

4. CONCLUSION

The results obtained demonstrate that blank samples monitored using the Quesenberry Q-statistic can serve as an effective additional tool for the internal quality control of validated ICP-MS methods. This approach enables continuous assessment of analytical system stability and the early detection of potential deviations, even when only a limited historical dataset is available. Its greatest advantage lies in monitoring newly validated methods, following instrument maintenance, or in laboratories that perform occasional analyses of specific sample matrices, where sufficient historical quality control data cannot be established within a short period.

ACKNOWLEDGEMENTS

This paper was financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, Agreements on the implementation and financing of scientific research work of the National Research Institute in 2026, No. 451-03-33/2026-03/200052 and No. 451-03-34/2026-03/200124.

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