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PROFICIENCY TESTS AND LABORATORY REFERENCE MATERIALS IN ION CHROMATOGRAPHY

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Abstract – International Schools of Ion Chromatography are well-accepted annual meetings among users of ion chromatography in Slovenia and Croatia. Special attention is also given to some features of metrology e.g. traceability and uncertainty. Within schools, proficiency tests are organized, with the aim of checking the performance of participating laboratories as well as of testing different analytical approaches suitable for certain types of samples. The procedure for preparation of a laboratory reference solution (Cl⁻ and Br⁻) using primary techniques with direct traceability to SI units is also shown

Keywords: ion chromatography, proficiency tests, primary techniques.

1. INTRODUCTION

Enlargement of the common market and distribution of goods across borders have intensified demands for high quality results, comparable between different testing laboratories. Participation in proficiency tests is a frequently adopted approach for improvement of the quality level of the results produced by an analytical laboratory. Another approach is the application of laboratory reference materials (LRM), or certified reference materials (CRM) when higher quality results are required. Together with quality assurance – quality control systems adopted by routine as well as research laboratories, the above mentioned measures improve different features of metrology e.g. traceability and uncertainty, which have been identified as the key parameters of a “high quality” analytical result.

Proficiency testing is becoming an integral feature of laboratory accreditation. This involves regular distribution of test material for analysis to the participating laboratories and subsequent assessment of the resulting data by the organizing body. This testing plays a vital role in the achievement and maintenance of appropriate data quality, in combination with the use of certified reference materials, validated methods and data quality control [1, 2]. Two aims of the proficiency tests can be formulated: (a) to encourage good performance generally, and especially to encourage the use of proper routine quality measures within individual laboratories; to provide feedback to the laboratories and encourage remedial action where shortcomings in

performance are detected; (b) to provide a rational basis for the selection or licensing of laboratories for a specific task (e.g., determination of the compounds in certified reference materials). Within International Schools of Ion Chromatography, four proficiency tests have been organized. Usually, two different samples are distributed among the participants and determination of anions and cations is done exclusively by ion chromatography. As the composition of one sample is more complex, possible difficulties and appropriate solutions are presented and discussed afterwards.

The accuracy and precision of almost every analytical result depend primarily on the uncertainty of the analyte stock solution concentration. There are only a few methods – “Primary Methods of Analysis”, which are directly traceable to SI units. The Consultative Committee on Amount of Substance, International Bureau of Weights and Measures Headquarters, identified the following techniques as potentially primary: gravimetry, coulometry, titrimetry, and isotope dilution mass spectrometry [3]. The concentration of a bromide and chloride laboratory reference solution was determined by several independent primary methods of analysis and the differences between them are presented.

2. PROFICIENCY TESTS

International Schools of Ion Chromatography are well-accepted annual meetings among users of ion chromatography in Slovenia and Croatia. Participants in the schools work mainly in the field of environmental and health related analysis. Since many of them are involved in the process of accreditation, they wish to test their performance. Therefore, in the frame of these meetings four proficiency tests have already been organized. At the beginning, two samples for determination of anions in different concentration ranges were prepared. Later, samples for determination of cations were included in the scheme and the complexity of one sample increased. Participation in the tests is anonymous and the analyses should be done exclusively by ion chromatography. The number of laboratories that decided to take test samples varied from 18 to 23. However, on average 13 (12-14) laboratories submitted their results of analysis to the organisers. Before

distribution, all samples were filtered through 0.2 μm filter and stored in a refrigerator at a temperature of 4 °C.

The organizers evaluated the received data, and reports were sent to participating laboratories. During the following school, the results were discussed. Possible difficulties encountered especially during analysis of more complex samples, and appropriate solutions to these problems were also presented. Data were evaluated according to the deviation from consensus value, which was calculated as an average value of the received data, without taking account of outliers. The criteria for finding outliers was the following:

$$\bar{x} - 2s \geq x \geq \bar{x} + 2s$$

\bar{x} – average of all received data

s – standard deviation of all received data

x – result of particular laboratory

Since most of the proficiency testing schemes evaluate results using z-scores, this presentation was also applied. The z-scores were calculated using the following equation:

$$z = \frac{x - \bar{x}}{s}$$

x - result of particular laboratory

\bar{x} - consensus value

(average value of received data without outliers)

s - standard deviation of received data without outliers

The absolute z-scores allow a direct estimation of the performance of the laboratory by comparison with the following quality limits [2]:

- $|z| < 2$: the performance of the laboratory is considered satisfactory
- $|z| < 3$: the performance of the laboratory is considered questionable
- $|z| > 3$: the performance of the laboratory is considered unsatisfactory.

Graphical representations of determination of Cl⁻ within proficiency test No. AC-04 are presented in Figures 1 and 2.

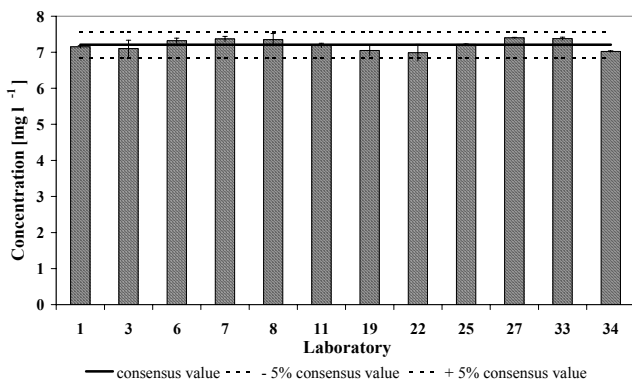


Figure 1: Graphical representation of determination of Cl⁻ in sample A (Proficiency test No. AC-04).

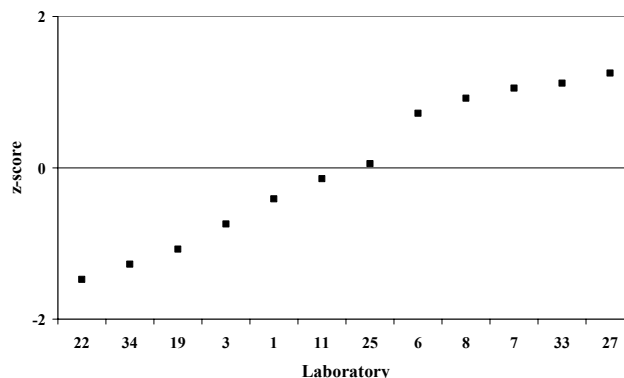


Figure 2: z-score for Cl⁻ in sample A (Proficiency test No. AC-04).

From Figures 1 and 2, we can conclude that the determination of Cl⁻ was carried out satisfactorily; all received results differ from the consensus value by less than 5 % and in addition, the calculated z-scores were below 2. However, a different situation was observed for Ca²⁺ in sample B (Proficiency test No. AC-04) – Figures 3 and 4. The sample consisted of mineral water and containing about 2000 mg l⁻¹ HCO₃⁻. The reason for lower determined values of Ca²⁺ in some laboratories was probably inappropriate storage of samples. In such a case, due to lose of CO₂, the pH value increased and caused precipitation of CaCO₃.

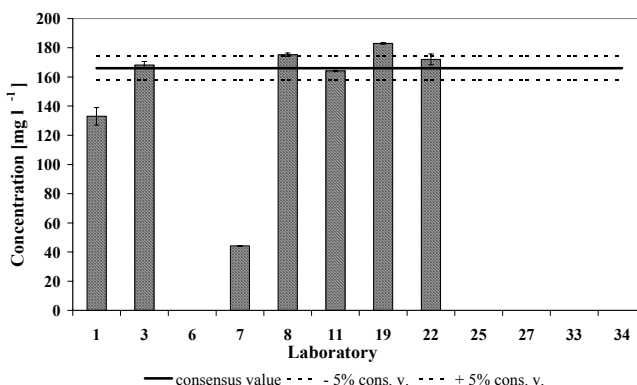


Figure 3: Graphical representation of determination of Ca²⁺ in sample B (Proficiency test No. AC-04).

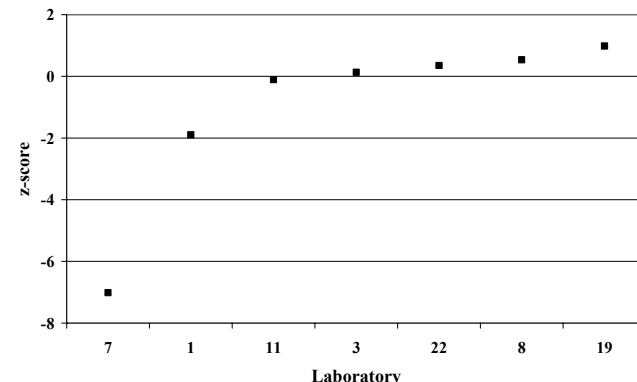


Figure 4: z-score for Ca²⁺ in sample A. (Proficiency test No. AC-04).

According to our experience, referring to the z-score alone is not adequate for proper interpretation of data. The z-scores for the majority of the participating laboratories may be satisfactory not only because their results are close to the consensus value, but also due to high relative standard deviation of reported data (high scattering). Hence, in such cases it is not possible to conclude that determination of a particular analyte is performed satisfactorily.

Comparison of results from all completed proficiency tests within the International School of Ion Chromatography shows that the most problematic anions are NO_2^- and HPO_4^{2-} . However, a considerable increase in quality of the submitted results was observed (Figure 5).

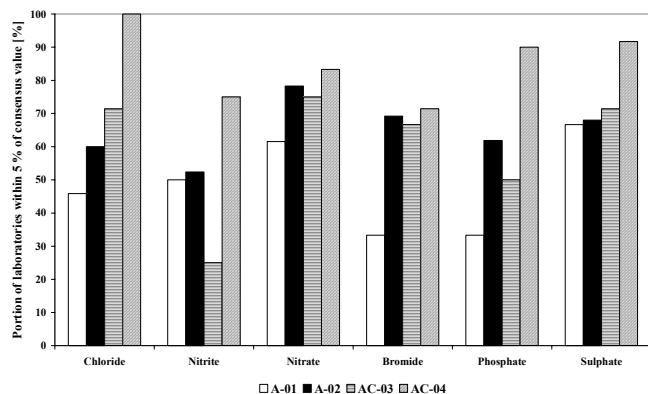


Figure 5: Comparison of results for anions of all accomplished proficiency tests.

According to these results we believe that activities such as proficiency tests are necessary. Only constant satisfactory cooperation in such schemes can give a certain guarantee for accurate results.

3. LABORATORY REFERENCE MATERIAL

As accuracy and precision of analytical results obtained by ion chromatography depend primarily on the uncertainty of the analyte stock solution concentration, the quality of this solution is of crucial importance. Since direct traceability to basic SI units in analytical chemistry can only be achieved with primary techniques, the procedure for preparation of Br^- and Cl^- reference solutions using different and independent primary techniques is shown.

Four independent techniques have been applied to determine the concentration of the 0.10 M KBr stock solution with the smallest possible uncertainty and direct traceability to basic SI units: **A**) gravimetry, **B**) titrimetry with AgNO_3 and two modes of coulometry, e.g. **C**) constant current coulometry (i.e. coulometric titration), and **D**) controlled potential coulometry. The scheme of performed measurements is shown in Figure 6.

All laboratory glass equipment used (pipette as well as measuring flask) was of quality class A. Gravimetric standardisation of the 0.1 M stock solution of KBr was done by precipitation with 0.1 M solution of AgNO_3 , which was previously also standardized gravimetrically (precipitation

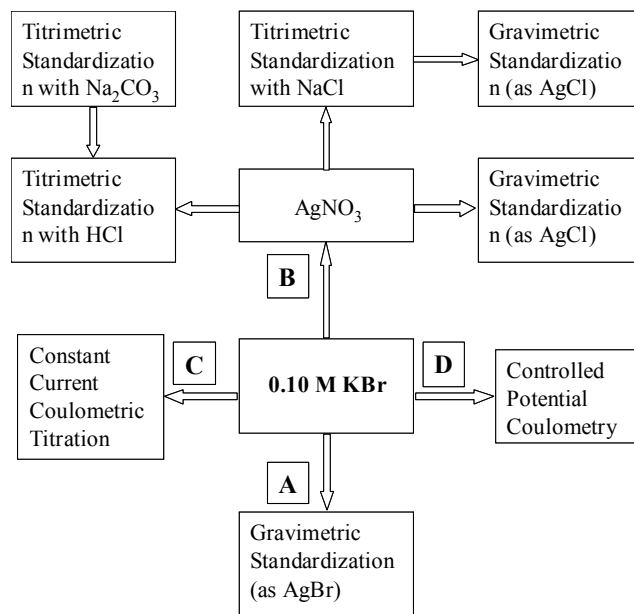


Figure 6: The scheme of applied primary techniques for determination of the 0.10 M KBr laboratory reference solution.

with HCl) and titrimetrically (titration with NaCl and HCl). The same already standardized AgNO_3 solution was later used for titrimetric standardisation of KBr. During constant current coulometric titration, the analyte (Br^-) was titrated by electrochemically generated Ag^+ ion by dissolution of the silver wire. The titration curve was followed potentiometrically using Ag indicator and MSE reference electrodes. The amount of the analyte was proportional to the charge according to Faraday's law. The error in using this technique may appear due to uncertainty in the volume of added analyte, uncertainty in the estimation of the end point of the titration and due to current efficiency lower than 100 %. In constant potential coulometry, the potential of the silver working electrode is controlled by the potentiostat at the value where the reaction proceeds with 100 % current efficiency. During the electrolysis, the charge is measured by the digital integration of the current flowing through the cell. Electrolysis is finished when all bromide present in the cell is deposited on the silver anode. Erroneous results using this method may appear due to side reactions affecting current efficiency, background charge, which is not negligible in comparison with the total accumulated charge and due to uncertainty of the purity of the analyte added. If we compare all these applied techniques (Table 1), we can conclude that gravimetry gives the closest value to its nominal value with the lowest uncertainty. Results obtained by titration with AgNO_3 and controlled potential coulometry are very close to those obtained by gravimetry. Coulometric titration gives significantly higher results (~1.5%) than those obtained by the other three methods.

Table 1: Results of the standardisation of 0.1 M KBr solution by different methods

Method	C(KBr) found (M)	s	RSD %
Titrim. with AgNO ₃	0.1003	0.0003	0.3
Gravimetric as AgBr	0.1001	0.0001	0.1
Coulometric titration	0.1020	0.00042	0.4
CPC	0.1005	0.0005	0.5

4. CONCLUSION

Due to the necessity to have comparable results obtained in different laboratories from different countries, different features of metrology are more and more important. Therefore, within the International Schools of Ion Chromatography, which are well-accepted annual meetings among users of ion chromatography Slovenia and Croatia, we also endeavour to present and discuss these topics. With organisation of proficiency tests we intend to improve the performance of participating laboratories. In addition, because of the importance of quality of laboratory reference materials, we show a method of preparing such material using primary analytical techniques, which are directly traceable to SI units.

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