A COMPARISON OF STATISTICAL APPROACHES TO COMBINE MEASUREMENT RESULTS FROM DIFFERENT METHODS

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INTRODUCTION

According to ISO17034, the characterization of reference materials can be carried out using four different approaches: (i) use of a primary method, (ii) use a single method, for value transfer between closely matched materials (iii) use of one or more methods, performed by a network of competent laboratories, (iv) use of two or more independent methods in one or several laboratories [1]. For the last two options, the measurement results from different analysis methods must often be combined to obtain the certificate value and its uncertainty. However, when the measurement results have inconsistent and/or the uncertainty of each method is very different, it is no recommended the use of ordinary arithmetic mean [2]. In this context, we compared different statistical methods to combine measurement results, for four different measurands.

EXPERIMENTAL

Figure 1 shows the general scheme to obtain and process the analytical results.

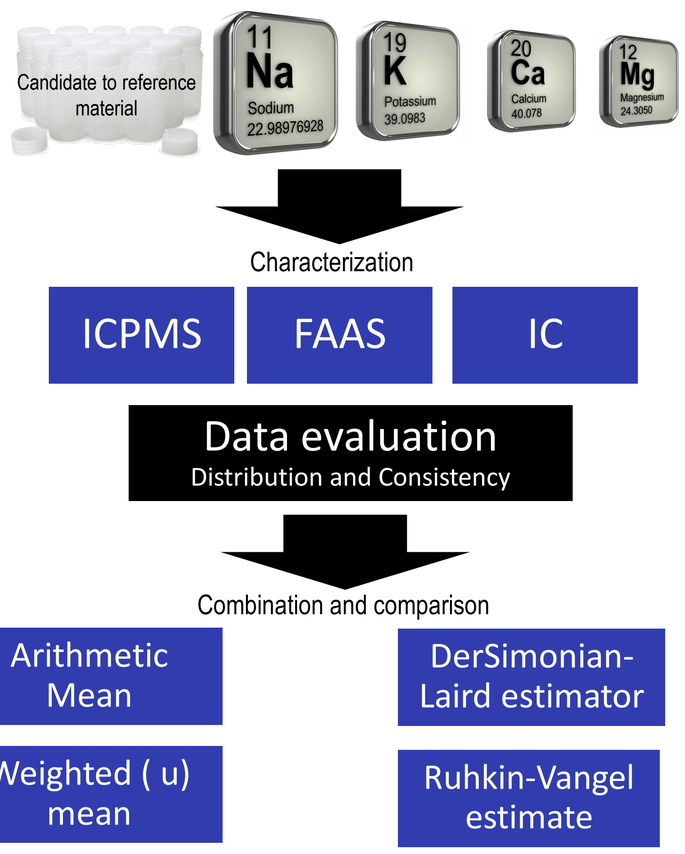


Figure 1. General scheme of this study.

All the measurements were realized using certified reference materials produced by NIST and SMU.

Table 1. Measurement methods and method calibration

ACRONYM	MEASUREMENT METHOD	METHOD CALIBRATION
ICPMS	Inductively coupled plasma mass spectrometry	Bracketing (external calibration) with internal standard normalization
IC	Capillary Ion Chromatog raphy	Bracketing (external calibration) with internal standard normalization
FAAA	Flame atomic absorption spectroscopy	Bracketing (external calibration)

Statistical analyses were performed by using statistical analysis software (R Core Team 2016). The combination measurements results was performed using “metRology” package [3].

RESULTS AND DISCUSSION

Data evaluation: *Normal distribution and consistency check*

The normality of the data was previously analyzed by the Kolmogorov–Smirnov test Shapiro-Wilk. Both tests indicate that the data were normally distributed with a significance level of 0.05. On the other hand, **Table 2** shows the results obtained for each measurement method and the consistency check, which were obtained by Chi-Square test according to CCQM recommendations [1]. Only for magnesium the Chi-Squared test indicated an inconsistency in the results between ICPMS, IC and FAAS. This inconsistency is attributed to the bias between FAAS and the other two techniques.

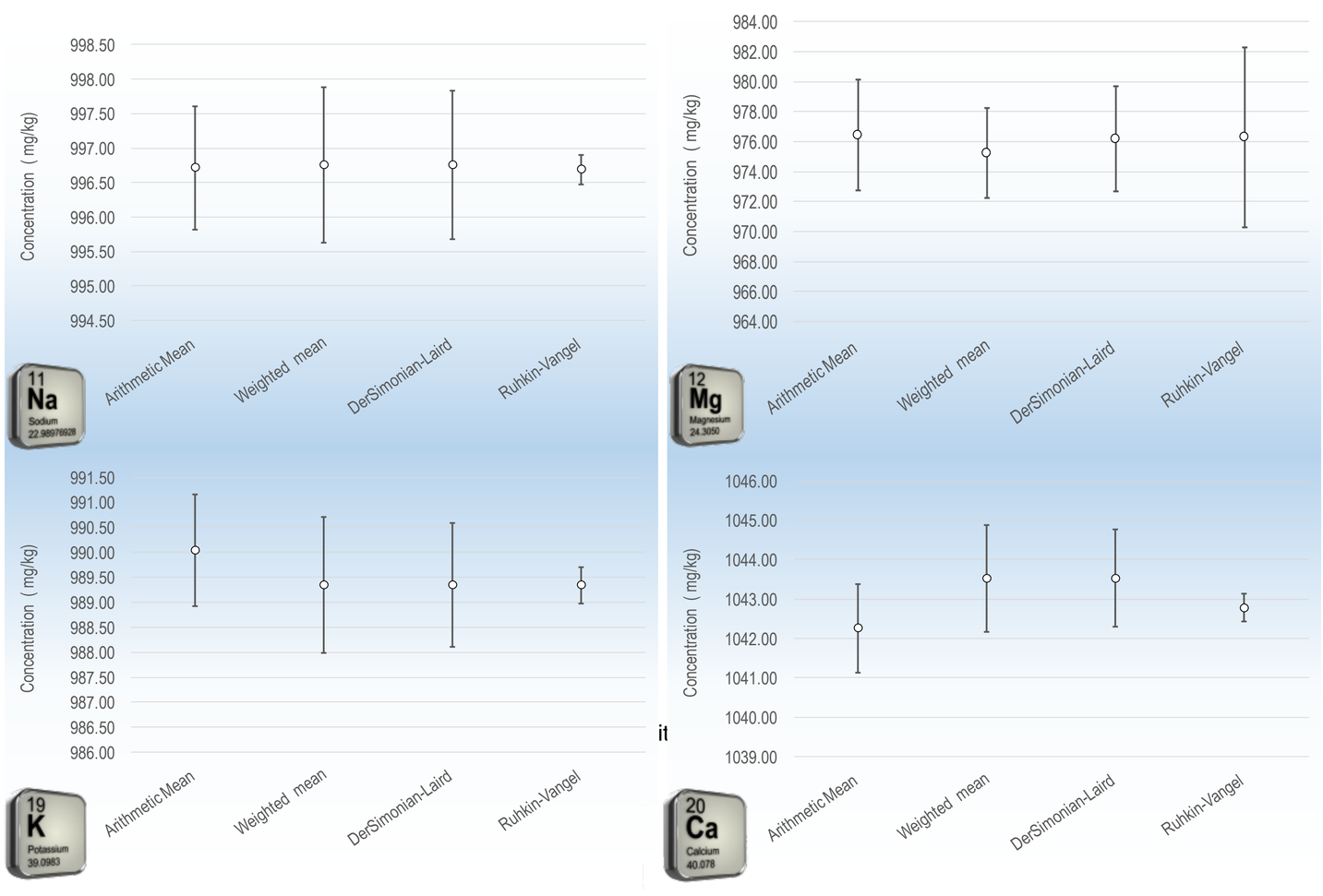
Table 2. Measurement results (mean +/- standard uncertainty) and Chi-Square observed

MEASUREMENT METHOD	Na (mg/kg)	K (mg/kg)	Ca (mg/kg)	Mg (mg/kg)
ICPMS	997.1 +/- 3.6	990.1 +/- 6.4	1039.6 +/- 3.8	978.4 +/- 7.2
IC	996.0 +/- 2.1	991.0 +/- 3.2	1042.9 +/- 3.1	980.1 +/- 2.1
FAAA	997.0 +/- 1.3	989.0 +/- 1.4	1044.2 +/- 1.5	970.9 +/- 1.9
χ^2_{obs}*	*0.17*	*0.35*	*1.35*	*10.71**

* Significant differences $\chi^2_{obs} > \chi^2_{0.05,m-1}$

Combination: *comparison of combining methods*

Figure 2 plots the means and their uncertainties obtained from each combination method (see **Figure 1**). These results show that, in general, the means and uncertainties are similar. However, it was found that only for magnesium the uncertainty obtained by Ruhkin- Vagel method was the largest. And, on the contrary, the uncertainties obtained for sodium, potassium and calcium that have the lowest uncertainties. This situation is attributed to the variation between-method because the weighting factor for Ruhkin- Vagel method is calculated on the basis of this variation [4].



CONCLUSION

In this comparison it was found that the mean estimated by the different methods varied only from 0.007% and 0.123%, while the combined uncertainties presented differences of up to 5-fold, specifically through the application of Rukin-Vangel method in 3 of the 4 elements.

REFERENCES

[1] ISO/CASCO .ISO 17034: General requirements for the competence of reference material producers. 2016.
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[5] DerSimonian, R., & Laird, N. (1986). Meta-analysis in clinical trials. Controlled clinical trials, 7(3), 177-188.