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DETERMINATION OF THE EVAPORATION FACTOR OF ETHANOL AND ITS CONTRIBUTION TO THE MEASUREMENT UNCERTAINTY IN THE DEVELOPMENT OF A CERTIFIED REFERENCE MATERIAL

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Abstract: This work presents the determination of the evaporation factor of ethanol and the contribution of this source of uncertainty in the process of certifying a reference material composed of solutions of ethanol in water. For this purpose, an experiment involving three technicians was carried out, where each one of them performed measurements during two days. Since the certification process is based on the gravimetric preparation of solutions by two different methodologies: individual and batch, the evaporation experiments involved measurements that complied both methodologies.

Keywords: traceability, uncertainty, alcohol, ethanol.

1. INTRODUCTION

A reliable determination of the measurand and the measurement uncertainty is crucial in the process of certifying a reference material [1]. One of the major sources of uncertainty in the process of developing a certified reference material (CRM) composed of solutions of ethanol in water is the evaporation of ethanol, as this substance is extremely volatile besides being hygroscopic. The ethanol in water CRM is used in Brazil and other countries for the metrological control of breath alcohol analyzers, which are testing devices designed to determine the alcohol present in the expired breath of vehicle drivers [2]. This use provides a legal characteristic to this CRM, emphasizing the urgent need to determine with high reliability all factors that affect the process of determining the ethanol concentration in aqueous solutions.

At Inmetro, the ethanol in water CRM is prepared gravimetrically in five different concentrations, by means of two methodologies. The first is the individual methodology where the CRM is directly prepared into 0,5L bottles. The second is the batch preparation methodology, where the preparation is performed in 5L bottles, subsequently subdivided into 0,5L bottles. In both cases, the certification is performed based on gravimetry whose value is checked by means of gas chromatography with flame ionization detection [3]. Presently, the demand for the CRM is the key reason to choose a methodology. The evaporation factor of ethanol preponderantly affects both methodologies of preparation, as the characterization of the CRM is based on data resulted from weighing the material. Therefore, in order to determine the impact of the evaporation of ethanol in each concentration prepared by each methodology, an experiment involving three technicians was carried out, where each technician performed the same measurements during two days, totalizing six measurements for each concentration in each methodology.

2. PURPOSE

The aim of this work is to determine experimentally how much does the evaporation of ethanol impact the estimation of the concentration and the measurement uncertainty of the certified reference material composed of solutions of ethanol in water prepared by gravimetry in individual and batch methodologies.

3. METHODS

The gravimetric method of preparing the ethanol in water CRM consists of weighing in separate receptacles the target mass of ethanol and the target mass of water according to each one of the five concentrations sought, and blending them subsequently [3]. The experiment for determining the impact of the ethanol evaporation consisted of measurements carried out by three technicians that performed the same measurements during two days, totalizing six measurements for each concentration. Each measurement consisted of weighing the target mass of ethanol for each concentration in a closed receptacle. After determining the initial mass (time (t) = 0), readouts were taken with the receptacle opened for 2 minutes at 4 different points (one point each 30 seconds). With the data obtained, a scatter graph has been drawn for each technician in each concentration. For each case a curve with an equation was obtained, with which was estimated the mass of ethanol that evaporated in a 2 seconds period of time. The statistical analysis of the data, comprehending the comparison between the different technicians in the different days, was performed using the analysis of variance – ANOVA [4].

4. RESULTS

The concentration of ethanol ([ETOH]) in the CRM gravimetrically prepared either by individual or by batch methodology is calculated according to Equation 1:

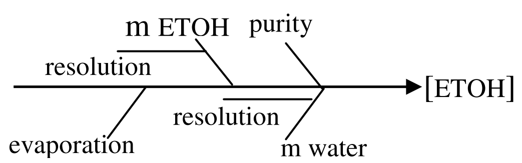
$$[ETOH] = \frac{mETOH}{(mETOH + mágua)} * p * eva \qquad (1)$$

Where:

mETOH = mass of ethanol; mwater = mass of water;
p = purity of ethanol; eva = evaporation factor of ethanol.

The calculation of the measurement uncertainty is based on the Guide for the Expression of Measurement Uncertainty -ISO GUM [5].

The uncertainty inherent to the characterization of ethanol, i.e., to the determination of the concentration of ethanol in each CRM, is calculated on the basis of the uncertainty sources expressed in the cause and effect diagram in Scheme 1.



Scheme 1: Cause and effect diagram for the determination of the measurement uncertainty inherent to the characterization of the concentration of ethanol in water.

Equation 2 shows the mathematical expression, according to the classical method, for the calculation of the combined standard uncertainty inherent to the characterization of ethanol (uc([ETOH])).

$$uc([ETOH]) = \sqrt{(u(mETOH))^2 + (u(mwater))^2 + (u(p))^2 + (u(eva))^2} \qquad (2)$$

Where:

u(mETOH) = uncertainty of the weighed mass of ethanol;
u(mwater) = uncertainty of the weighed mass of water;
u(p) = uncertainty of the purity of ethanol;
u(eva) = uncertainty of the evaporation factor of ethanol;

Table 1 shows the value of the concentration for each CRM and the combined standard uncertainty inherent to the characterization of the material prepared by means of the individual methodology.

Table 1: Certified value and combined standard uncertainty in the five concentrations of the CRM prepared by individual methodology.

MRC	[ETOH] (% *)	uc([ETOH])] (% *)
[1]	0.050822	0.000029
[2]	0.089130	0.000052
[3]	0.12704 0	0.000075
[4]	0.38080	0.00022
[5]	0.49317	0.00029

* % = g ethanol / 100 g of solution

Table 2 shows the value of the concentration for each CRM and the combined standard uncertainty inherent to the characterization of the material prepared by means of the batch methodology.

Table 2: Certified value and combined standard uncertainty in the five concentrations of the CRM prepared by batch methodology.

MRC	[ETOH] (% *)	uc([ETOH])] (% *)
[1]	0.050891	0.000029
[2]	0.081347	0.000047
[3]	0.106784	0.000062
[4]	0.38827	0.00022
[5]	0.45692	0.00026

* % = g ethanol / 100 g of solution

The target mass of ethanol and the target mass of water weighed according to each one of the five concentrations for individual and batch methodologies are present at Table 3 and Table 4, respectively.

Table 3: Target mass to the individual methodology

CRM	Mass of Ethanol (g)	Mass of Water (g)
[1]	0.25483	499.679
[2]	0.40700	499.593
[3]	0.53450	499.466
[4]	1.91542	498.085
[5]	2.48074	497.519

Table 4: Target mass to the batch methodology

CRM	Mass of Ethanol (g)	Mass of Water (g)
[1]	2.49570	4896.853
[2]	3.98860	4894.970
[3]	5.23810	4893.395
[4]	19.04885	4880.951
[5]	22.41461	4877.585

The result obtained by each technician for each one of the five concentrations at the evaporation experiment for the target mass that comply the individual methodology is present at the Figures 1, 2, 3, 4 and 5.

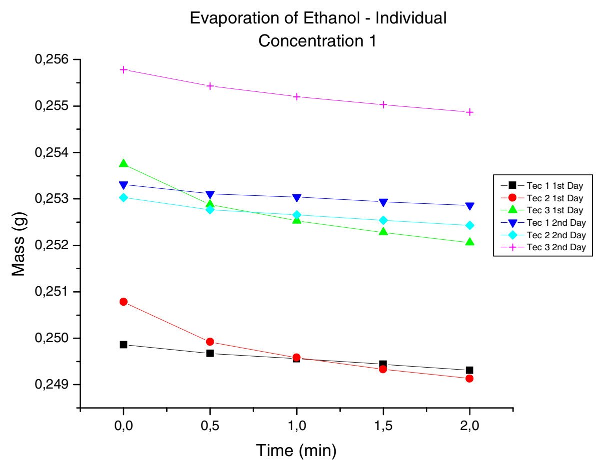


Figure 1: Evaporation experiment for concentration 1 by the individual methodology.

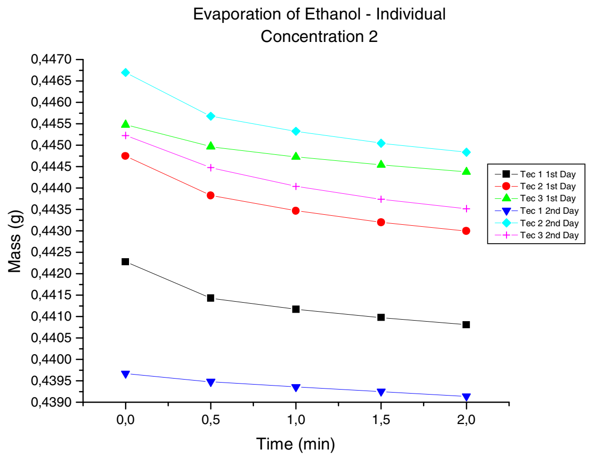


Figure 2: Evaporation experiment for concentration 2 by the individual methodology.

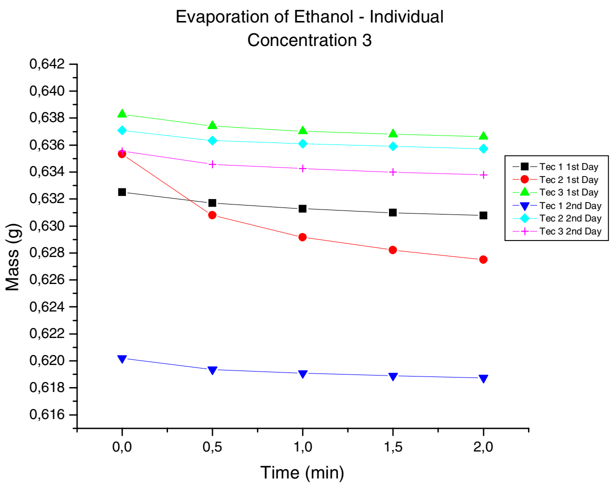


Figure 3: Evaporation experiment for concentration 3 by the individual methodology.

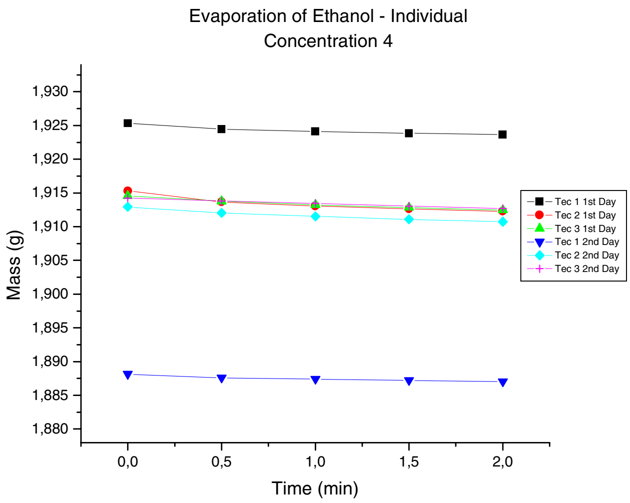


Figure 4: Evaporation experiment for concentration 4 by the individual methodology.

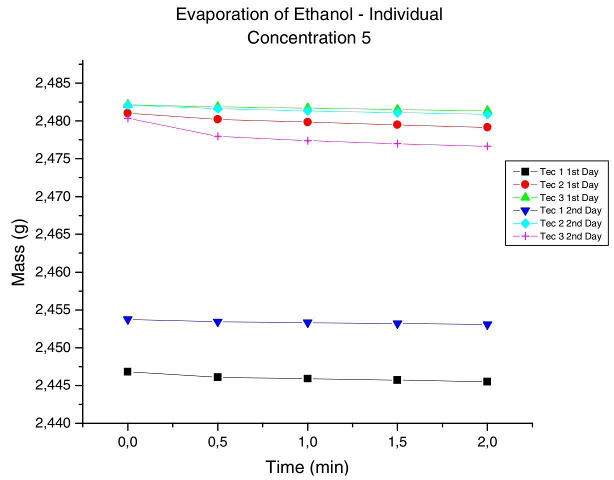


Figure 5: Evaporation experiment for concentration 5 by the individual methodology.

The result obtained by each technician for each one of the five concentrations at the evaporation experiment for the target mass that comply the batch methodology is present at the Figures 6, 7, 8, 9 and 10.

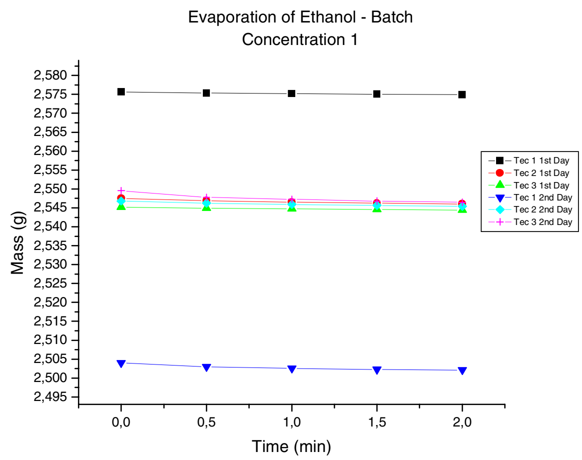


Figure 6: Evaporation experiment for concentration 1 by the batch methodology.

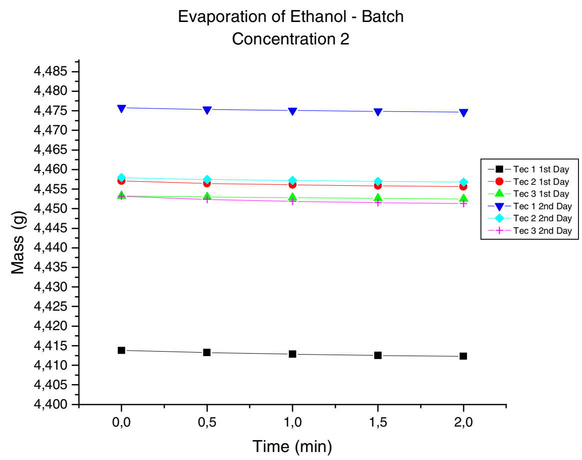


Figure 7: Evaporation experiment for concentration 2 by the batch methodology.

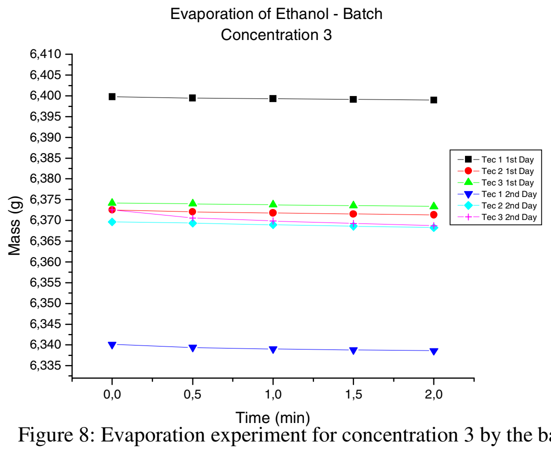


Figure 8: Evaporation experiment for concentration 3 by the batch methodology.

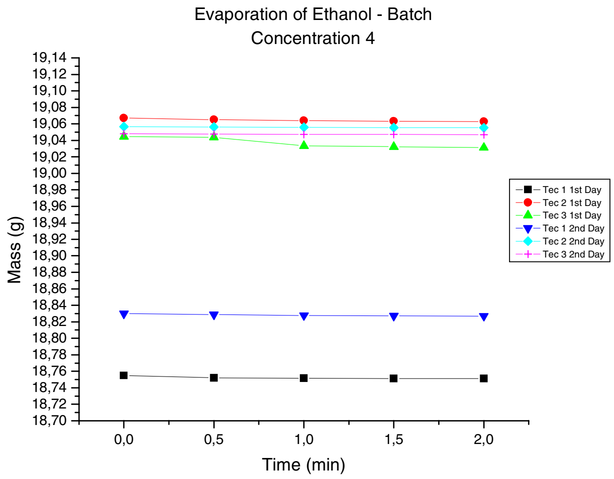


Figure 9: Evaporation experiment for concentration 4 by the batch methodology.

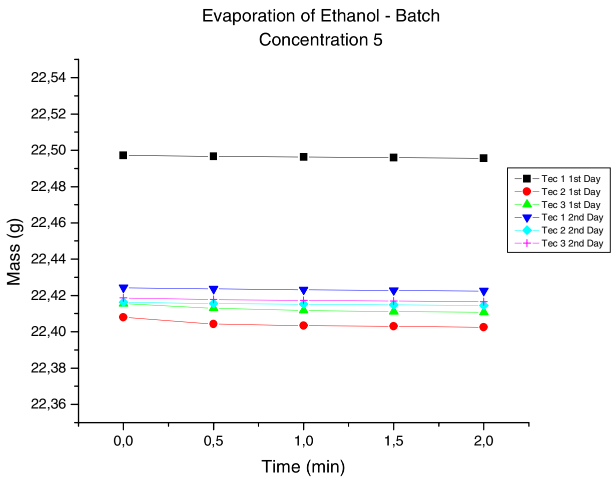


Figure 10: Evaporation experiment for concentration 5 by the batch methodology.

After obtaining each equation related to each technician for all concentrations it was estimated the mass of ethanol evaporated in a 2 seconds period of time. This time is correspondent to the period that the target mass of ethanol is exposed to the environment, before being mixed with the water.

Table 5 shows the percentages of ethanol evaporation for each technician according to the target mass that comply the individual methodology. The values shown for each concentration correspond to the technicians average during the two days.

Table 5: Percentages of ethanol evaporation to the target mass that comply the individual methodology.

CRM	Technician 1 (%evaporation)	Technician 2 (%evaporation)	Technician 3 (%evaporation)	Average (%)
[1]	0.01794	0.03570	0.02090	0.02485
[2]	0.01274	0.02979	0.01042	0.01765
[3]	0.01624	0.05745	0.01824	0.03064
[4]	0.00374	0.00745	0.00469	0.00529
[5]	0.00258	0.00261	0.00548	0.00356

Table 6 shows the values of F calculated by the analysis of variance (ANOVA) among the technicians performing the experiment according to the target mass that comply the individual methodology. The critical value for ANOVA in the five concentrations corresponds to 9,55208.

Table 6: Analysis of homogeneity among technicians.

CRM	ANOVA F calculated
[1]	0.34549
[2]	0.92040
[3]	1.15552
[4]	0.93406
[5]	0.19285

Table 7 shows the evaporation factor of ethanol, the uncertainty associated to this quantity, and its contribution to the combined standard uncertainty of the characterization related to the individual methodology.

Table 7: Evaporation factor of ethanol and associated uncertainty related to the individual methodology.

CRM	Evaporation Factor	Uncertainty associated to evaporation*	Contribution of evaporation uncertainty to the combined standard uncertainty (%)
[1]	0.99975	4.75E-06	16
[2]	0.99982	5.67E-06	11
[3]	0.99969	1.59E-05	21
[4]	0.99995	4.39E-06	2
[5]	0.99996	1.08E-05	4

* Values in % = g ethanol / 100 g of solution

Table 8 shows the percentages of ethanol evaporation for each technician according to the target mass that comply the batch methodology. The values shown for each concentration correspond to the technicians average during the two days.

Table 8: Percentages of ethanol evaporation to the target mass that comply the batch methodology.

CRM	Technician 1 (%evaporation)	Technician 2 (%evaporation)	Technician 3 (%evaporation)	Average (%)
[1]	0.00400	0.00234	0.00482	0.00372
[2]	0.00123	0.00179	0.00127	0.00143
[3]	0.00060	0.00034	0.00219	0.00104
[4]	0.00018	0.00023	0.00255	0.00010
[5]	0.00106	0.00134	0.00110	0.00117

Table 9 shows the values of F calculated by the analysis of variance (ANOVA) among the technicians performing the experiment according to the target mass that comply the batch methodology. The critical value for ANOVA in the five concentrations corresponds to 9,55208.

Table 9: Analysis of homogeneity among technicians.

CRM	ANOVA F calculated
[1]	0.25864
[2]	0.08276
[3]	0.60770
[4]	0.76895
[5]	0.01188

Table 10 shows the evaporation factor of ethanol, the uncertainty associated to this quantity, and its contribution to the combined standard uncertainty of the characterization related to the batch methodology.

Table 10: Evaporation factor of ethanol and associated uncertainty related to the batch methodology.

CRM	Evaporation Factor	Uncertainty associated to evaporation*	Contribution of evaporation uncertainty to the combined standard uncertainty (%)
[1]	0.99969	1.43E-07	2.5
[2]	0.99982	5.61E-07	1.2
[3]	0.99969	9.43E-07	1.5
[4]	0.99995	4.00E-06	0.2
[5]	0.99996	3.98E-06	0.2

* Values in % = g ethanol / 100 g of solution

5. DISCUSSION

The process of preparing an ethanol in water CRM by the gravimetric method, a primary measurement method, provides traceability to the International System of Units (SI) to the measurements performed [6]. The procedure to prepare the ethanol in water CRM performed by Inmetro [3] involve after gravimetric preparation a gas chromatografic analysis using a flame ionization detector (GC-FID) to check the comparability of ethanol concentration achieved by gravimetry and GC analysis. Thus, the chromatography analysis is used to validate the gravimetric preparation. Two statistical criteria are used to check the results: the analysis of variance (ANOVA) and the maximum percent difference acceptable for ethanol concentration that was set as 1%.

At the experiment for the determination of the evaporation factor of ethanol and its impact on the uncertainty of the process, all measurements were performed by the gravimetric method in balances calibrated by the Mass Laboratory of Inmetro. Based on the analysis of variance (ANOVA), one verifies that the measurements performed by the three technicians during the two days to the two ranges of target mass of ethanol that are related to the individual and the batch methodology were considered homogeneous. Tables 6 and 9 show the values of F calculated for each concentration. As the calculated values of F are smaller than the F critical, the data are considered homogeneous, and all data were used in the calculation of the evaporation factor and the associated uncertainty. By analyzing Tables 7 and 10 one observes that the impact of the evaporation in the measurement uncertainty varies for each concentration studied, becoming more significant for the lower concentrations for which the weighed mass of ethanol is too small. So, the evaporation of ethanol has more effective impact over to the individual methodology than to the batch methodology. Regardless of the ethanol concentration studied and the methodology employed, the evaporation factor for the calculation of the concentration may be considered equivalent to 1, according to Tables 7 and 10. The evaporation factor was calculated based on the comparison of the percentages of evaporation obtained after t = 2s, which value was obtained by means of the scatter curve obtained for each technician in each day, in relation to the mass of ethanol in the initial time, t = 0. The value of t=2s is considered as the time during which the ethanol receptacle is kept open during the process of preparation of the CRM.

6. CONCLUSION

The experiment carried out for the determination of the evaporation factor of ethanol and the measurement uncertainty associated to this quantity was considered extremely satisfactory, providing greater reliability to the process of certifying reference material composed of solutions of ethanol in water. According to this experiment the evaporation factor of ethanol, independent of the concentration of the ethanol in water CRM and the methodology employed (individual or batch), was found to be 1. Even for individual or for batch methodology it was possible to estimate the measurement uncertainty related to ethanol evaporation for all concentrations of ethanol in water CRM. The fact that the experiment was performed under reproducible conditions has provided a more accurate assessment of the parameters studied, making possible the assessment of the homogeneity of the measurements of the different technicians in different days.

7. REFERENCES

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