EVALUATION OF UNCERTAINTY IN THE DETERMINATION OF INORGANIC CONTAMINANTS IN *CACHAÇA* BY ATOMIC ABSORPTION SPECTROMETRY (AAS)

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Abstract: *Cachaça* is a widely consumed beverage in Brazil with a growing foreign market in recent years, demanding that the manufacturing process be carefully determined based on practices with proven quality, making it necessary to assess the levels of its contaminants. This study aims to evaluate the uncertainty in the determination of inorganic contaminants in *cachaça* by AAS.

Keywords: uncertainty, inorganic contamination, *cachaça*, AAS

1. INTRODUCTION

Cachaça, a drink made from fermenting and distilling the molasses from the sugar cane, was discovered by the slaves of the sugar mills in the mid-sixteenth century and was considered a beverage of low status before the society[1]. Today is the third most consumed beverage in the world, with about 5,000 brands, 30,000 producers and a annual producing volume of around 1.3 billion liters with 75% of this total coming from industrial and 25% from craft producters[2,3].

The increased consumption of *cachaça* require standardized product and proven on physical-chemical properties. Brazilian Ministry of Agriculture (MAPA) provides evaluation criteria to fix identity and quality characteristics of *cachaça*[4]. The quantification of inorganic contaminants, arsenic (As), copper (Cu) and lead (Pb), is of fundamental importance because they are harmful elements that can cause health disorders on high levels.

The aim of this study was to survey the sources of uncertainty, the estimated standard uncertainty, combined standard uncertainty and expanded uncertainty in the determinations of arsenic, lead and copper in *cachaça*.

2. RESULTS AND DISCUSSION

The methodology used was implemented[6] in accordance with the maximum levels (ML) established by MAPA[4] and was validated according DOC-CGCRE-08-INMETRO[7] which included determination of performance parameters selectivity, linearity, sensitivity, limit of detection, limit of quantification, precision and accuracy[6]. Table 1 presents the methodologies used in determination of arsenic, lead and copper in *cachaça*. The expanded uncertainties were estimated according to the Guide to the Expression of Uncertainty and Measurement[8] and EURACHEM[9].

The detailed analyses of factors influencing the analytical results can be represented in the diagram cause and effect, known as “fishbone” (Figure 1). Relevant sources for the uncertainty assessment have been simplified into three groups: the uncertainty associated with the analytical curve, method accuracy and standard solution preparation. On arsenic determination it was also considered the uncertainty associated with sample preparation of *cachaça*.

Table 1 - Analytical methods used in determining the As, Cu and Pb in *cachaça*

	Arsenic	**Copper**	**Lead**
Analytical technique	Atomic absorption spectrometry with hydride generator (HGAAS)	Atomic absorption spectrometry with flame (FAAS)	Atomic absorption spectrometry with graphite furnace (GFAAS)
Equipment	AAnalyst 100 coupled with MHS10 from PERKIN ELMER	AAnalyst 400 from PERKIN ELMER	5100ZL coupled with HGA600 from PERKIN ELMER
Sample preparation	Reduction of the sample in water bath to eliminate ethyl alcohol. Taken up with HCl 4.5 N	Direct determination using standard solutions prepared in alcoholic 50% v/v	Direct determination using standard solutions prepared in nitric acid 0.2% v/v
ML	100 µg/L	5 mg/L	200 µg/L
Calibration standards	3 ng to 40 ng	0.25 mg/L to 4.0 mg/L	10 µg/L to 100 µg/L

The standard uncertainty were calculated and identified as type A (accuracy) and type B (preparation of standards, calibration curve and sample preparation). The combined standard uncertainty was calculated from appropriated combination of their variances Figure 2 shows the values of standard uncertainty contribution from each source.

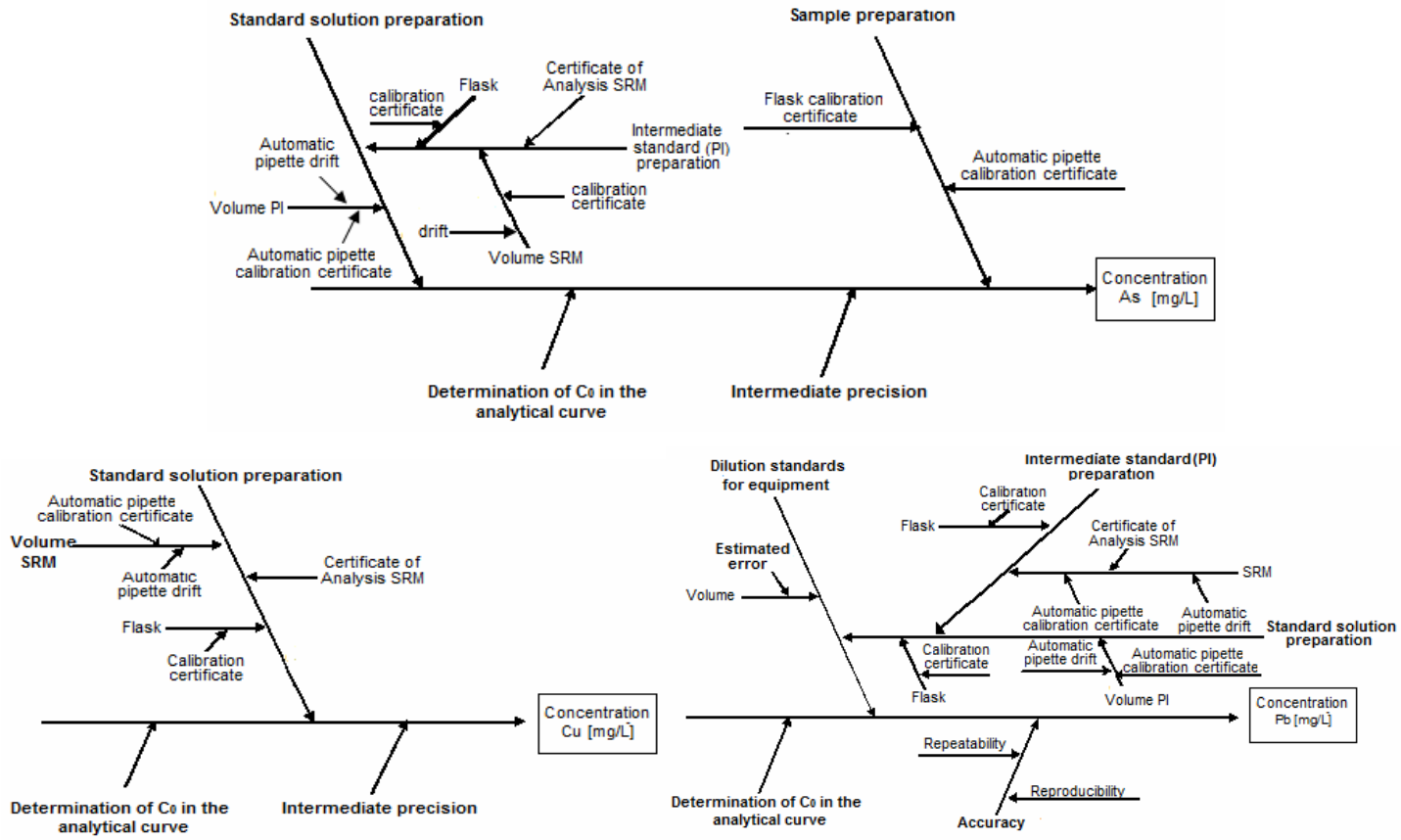

Figure 1 - Diagram cause and effect of the uncertainty sources associated with the measurement process As, Cu and Pb

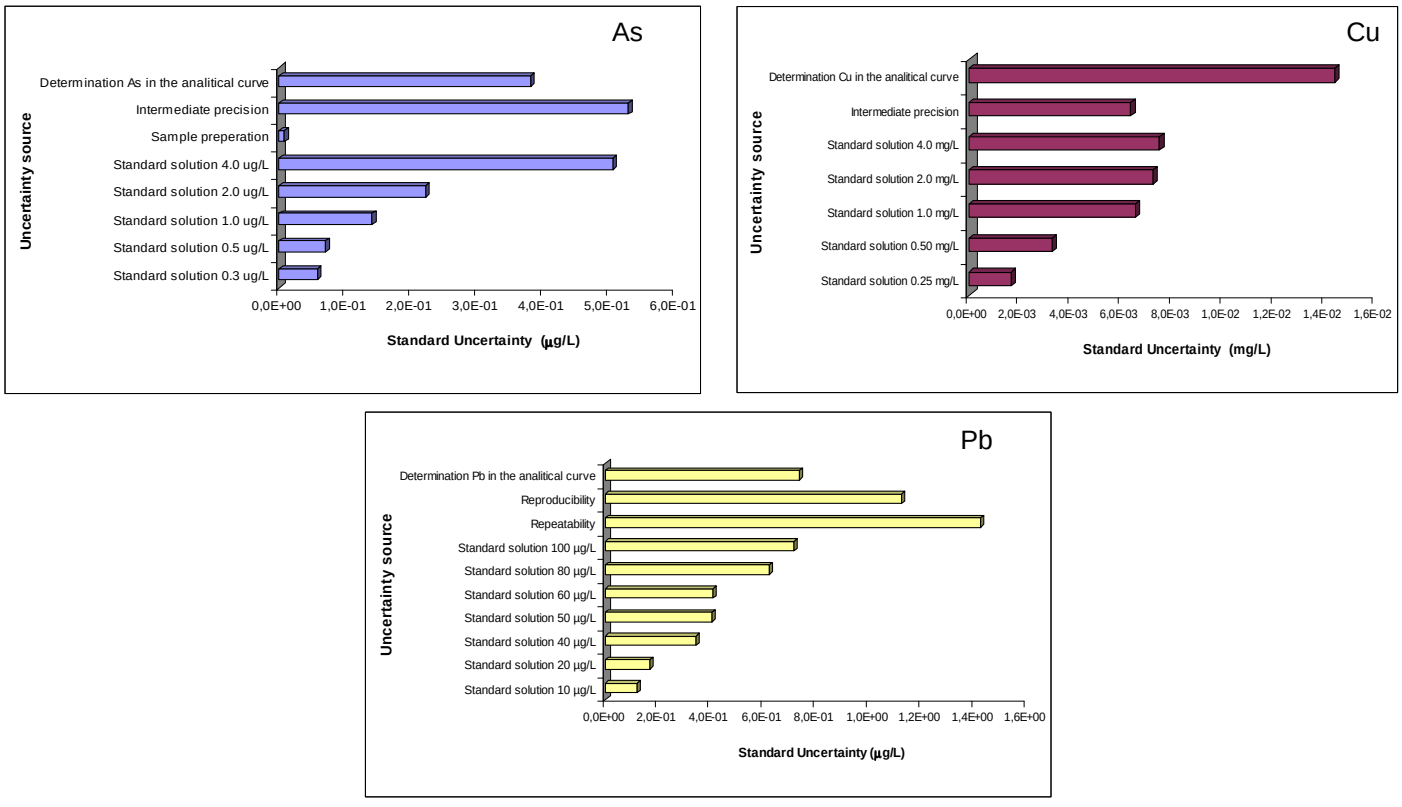

Figure 2 – Contribution of the uncertainty sources in the measurement of As, Cu and Pb

Table 2 - Results of the combined standard uncertainty ν_{eff}, k and the expanded uncertainty for a sample *cachaça*

Element	Combined Standard Uncertainty	ν_{eff}	k	Concentration	Expanded uncertainty (Probability ≅ 95%)	Unit
As	0.87	360	2.00	18.9	4.9	µg/L
Cu	0.02031	1455	2.00	1.030	0.041	mg/L
Pb	2.29	18	2.15	37.9	1.8	µg/L

The expanded uncertainty were obtained by multiplying an expansion factor k associated with a confidence interval of 95.45%. These factors were calculated following Welch-Satterwaite (ν_{eff})[8] which determines the number of effective degrees of freedom using the Student t distribution (Table 2).

3. CONCLUSIONS

Although Normative Instruction No. 13 of MAPA[4] does not established acceptable values for the uncertainties, the expanded uncertainties calculated values showed satisfactory results for the methodology used, around 4% for As, 9% for Cu and 13% for Pb following others references on literature[10].

It was observed when high level elements are determined, copper for example, the main source of uncertainty contribution is the analytical curve, which represents over 50%. However for methodologies of determination of low levels elements, Arsenic and Lead, the preparation of standard solutions, the accuracy and the analytical curve are the main contributors for uncertainty. It was also noted that the sample preparation, for the arsenic case, contributes only 0.01% for uncertainly, which is negligible.

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