ACID-BASE TITRATION TECHNIQUES: METROLOGICAL CONSIDERATIONS

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INTRODUCTION

Titrations are a group of techniques that have contributed considerably to the development of the chemical industry and to the development of the chemistry itself (1). Consultative Committee for Amount of Substance (CCQM) has recognized titration as one of the primary methods for determining amount of substance (2), which has attracted many attention by National Metrology Institutes (3). In several studies, the uncertainty estimation for acid-base titrations is carried out using Bottom Up approach, and it is recognized that the main sources of uncertainty comes from reference material purity, instrument resolutions, calibration, repeatability, molecular weight of the species and amount of titrant. (4,5). However, Wamplfler and Rösslen found that in comparison with Top Down Approach, the most of the studies underestimate the uncertainty up to 4 times. Some studies have shown that the detection of the end point is one of the main sources of error, so multiple strategies have been designed to perform the detection of this point through derivatives, mathematical transformation, and even graphical methods. Based on this, we evaluated different measurement systems for acid-base titrations in order to determine which have better metrological qualities (uncertainty and bias).
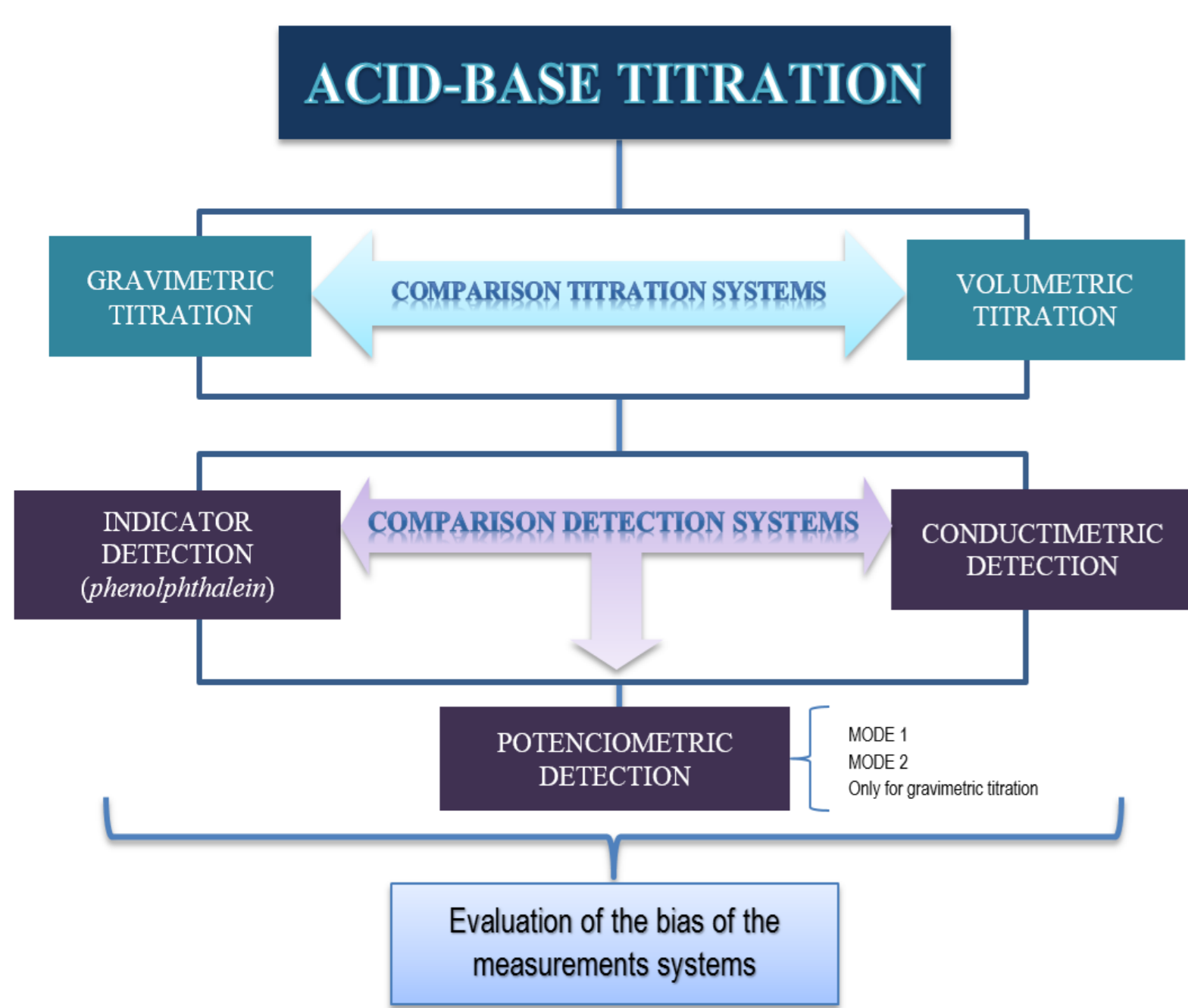
EXPERIMENTAL

Figure 1. General scheme of this study

The mathematical model that is proposed for the determination of the concentration of NaOH throught the primary reference material (PRM), is given by the following equation:

$$C_{NaOH} = \frac{W_{PRM}\, P_{PRM}\, MM_{PRM}}{Q_{NaOH} - Q_{EP}} \times 1000R$$

Table 1 presents the main sources of uncertainty measurement with the expression used for the estimation.

Identification	SOURCE	EXPRESSION USED FOR THE ESTIMATION
Weight (W_{PRM})	Resolution and calibration certificate	$u_{W_{PRM}} = \sqrt{u_{calibration}^2 + u_{resolution}^2}$
Purity (P_{PRM})	Certificate (SMU)	$u_{P_{PRM}} = U_{certificate} \times k^{-1}$ where k= 2
Molecular mass (MM_{MRP})	IUPAC	$u_{MM_{PRM}} = \sqrt{64u_{MM\,of\,C}^2 + 25u_{MM\,of\,H}^2 + 16u_{MM\,of\,O}^2 + u_{MM\,of\,K}^2}$
Titrant (Q^*_{NaOH})	Resolution, calibration certificate and temperature change	$u_{Q_{NaOH}} = \sqrt{u_{calibration}^2 + u_{resolution}^2 + u_{temperature\,change}^2}$
Titrant (Q^{**}_{NaOH})	Resolution and calibration certificate	$u_{Q_{NaOH}} = \sqrt{u_{calibration}^2 + u_{resolution}^2}$
R	Repeatability	$u_{Q_{NaOH}} = \frac{s}{\sqrt{n}}$
End point detection (Q_{EP})	Classic method (6,7): Resolution (for all systems)	$u_{Q_{EP}} = \frac{R}{2\sqrt{3}}$
	Proposed approach: change of titrant quantity close to the equivalence point	$u_{Q_{EP}} = \frac{\Delta Titrant}{\sqrt{3}}$

Table 1. Uncertainty sources and expression used for the estimation

The results were analyzed by the statistical program R using "Propagate" package (R Core Team (2016)).

RESULTS AND DISCUSSION

COMPARISON OF TITRATION SYSTEMS AND DETECTION SYSTEMS

Figure 2 plots relative standard uncertainties for the different titration systems evaluated, where it is observed that the uncertainties of the gravimetric methods present, in general, a decrease of 40% with respect to the volumetric titration. These differences are attributed to the better metrological characteristics of the mass instruments as compared to those of volumen.
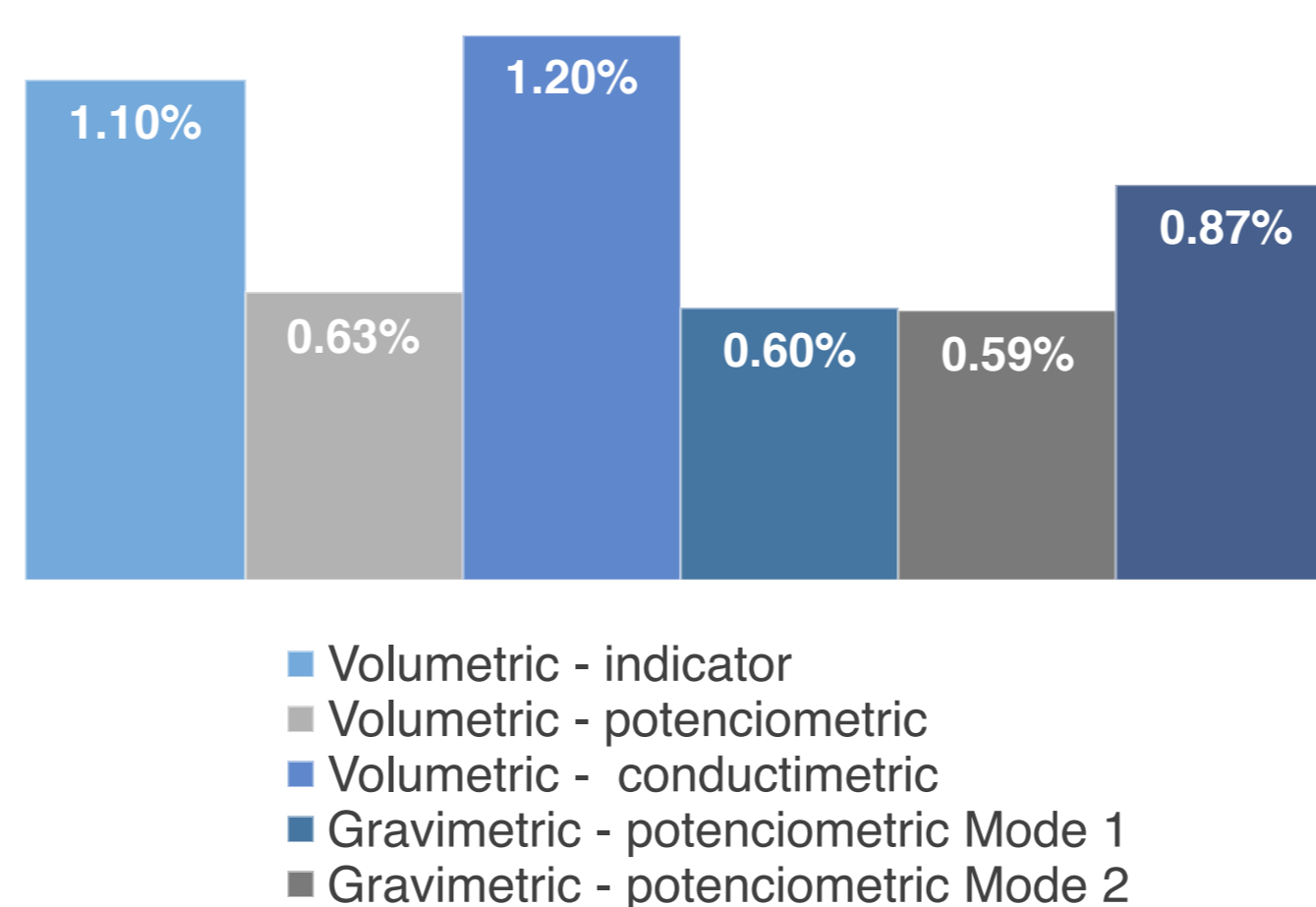

Figura 2. Uncertainty for the titration systems evaluated

Figures 3 and **4** the contribution of each uncertainty source are compared. The results presented can be summarized in the following way:

a. The contribution due to the molecular mass of the PRM and its weighing are practically negligible.

b. The source associated with repeatability is not the most significant component.
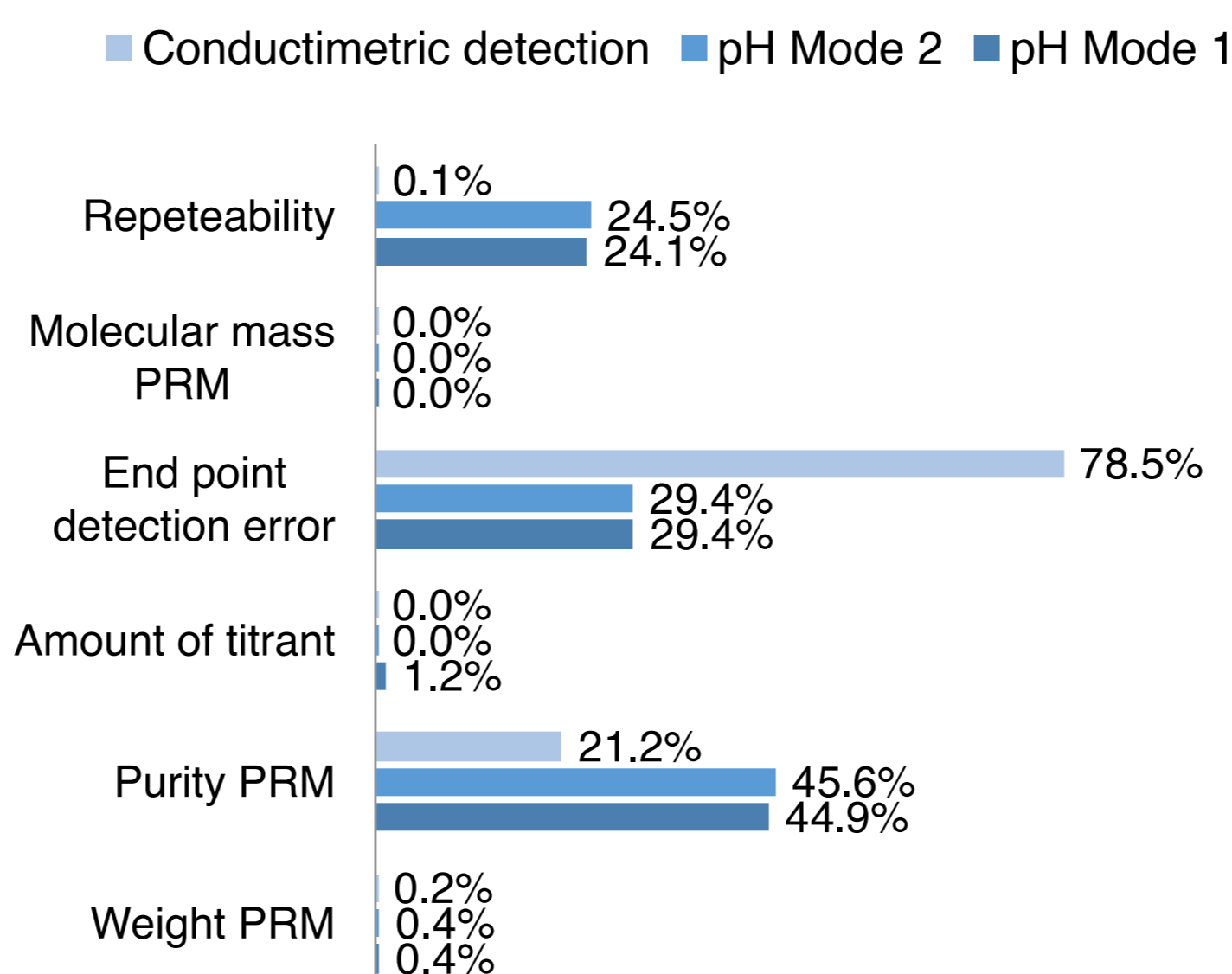

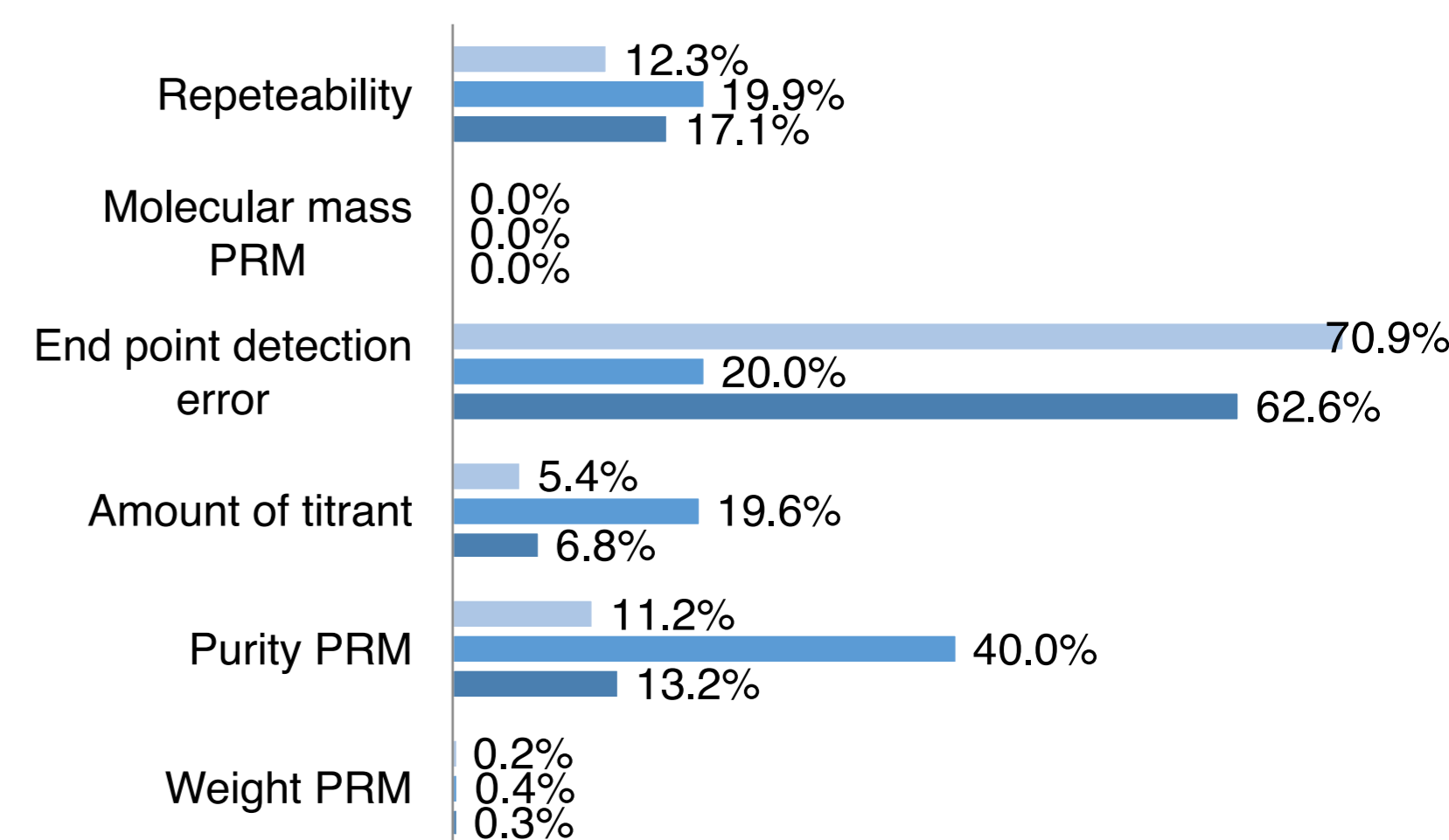Figura 3. Distribution of uncertainty sources for the gravimetric system.

Figura 4. Distribution of uncertainty sources for the volumetric system.

c. For conductimetric detection system, the most important uncertainty component is due to the error by detection of the end point.

d. For gravimetric titration with potentiometric detection the most important uncertainty is associated to the purity of CRM.

e. When applying the classical method (see **Table 1**), the uncertainty is underestimated or overestimated if R is different to the instrument resolution.

f. The proposed approach applies for all cases because it does not depend on the instrument resolution. The new approach only depend on the amount of titrant added near the end point

EVALUATION OF THE BIAS

Table 2 shows the results of bias for each system evaluated. According to the evaluation criterion (8), the non-significance of bias for all systems was obtained as a result.

TITRATION SYSTEM	BIAS (Relative error)
Volumetric - indicator	1.55%
Volumetric - potentiometric	0.05%
Volumetric - conductimetric	3.93%
Gravimetric - potenciometric Mode 1	0.00%
Gravimetric - potenciometric Mode 2	0.23%
Gravimetric -conductimetric	2.99%

The detection by conductimetry presents greater bias against the pontentiometric detection. This difference is mainly attibuted to the end point estimation.

CONCLUSION

In this study was found that less bias and uncertainties were obtained for the gravimetric method with potentiometric detection. A new approach was proposed for uncertainty evaluation associated to the end point detection. The results showed that with the classic approach (see **Table 1**) the uncertainty maybe until 6 times less that with the new approach.

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