

PRESERVATION OF PARABENS IN WATER SAMPLES

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INTRODUCTION

Parabens are mainly used as preservatives in the cosmetics, and in pharmaceutical and food products due to their antibacterial and antifungal properties. Their wide range of applications favors their indirect transfer into the environment. Their potential adverse effects led to their inclusion into the French monitoring program of aquatic environment as emerging contaminants. In order to help the laboratories improving their analytical skills regarding these emergent contaminants, BIPEA organizes proficiency testing schemes (PTSs) according to ISO 17043 standard [1] for the quantification of butyl-, ethyl-, methyl- and propylparaben in freshwater.

Parabens degradability in water by hydrolysis and photolysis raises the issue of their stability throughout the PT, especially for the samples with long delivery time or laboratories unable to perform their analyses at reception. In order to meet PT samples homogeneity and stability requirements, BIPEA conducted a comparative study on parabens preservation by ascorbic acid and nitric acid.

This study presents an experimental PT for which parabens-spiked samples were proposed to the laboratories with each preservation agent separately, and a dedicated homogeneity and stability study performed by INERIS. It aims at determining whether preservation with nitric acid may be more efficient than one with ascorbic acid.

METHODOLOGY

The design of this experimental PT can be schematized by 3 main steps: preparation of the samples, analyses by the laboratories and statistical treatment of the data.

SAMPLES PRODUCTION

For this PT, samples were prepared from surface water. The surface water was homogenized using a homogenization tank, and divided into samples by a quasi-simultaneous filling of bottles. Then each bottle was individually spiked with butylparaben (BuP), ethylparaben (EtP), methylparaben (MeP) and propylparaben (PrP) at different concentrations. Finally half of the samples were preserved with 1 g/l of ascorbic acid, and the other half with 1 ml of nitric acid concentrate (at 65%). Theoretical concentrations for each paraben and each preservative are given in Table 1. Sample total volume was 1 L. Amber glass bottles were used in order to minimize any sorption on bottle wall or any photolysis that may occur until analysis by the participants.

ANALYSES

Samples were shipped at (5±3) °C to the laboratories participating to the test. A reply form was made available to allow the laboratories to return their analysis results and some complementary information such as sample temperature upon receipt, date of the beginning of the analysis, and method used. Given the stability of the product, the participants were invited to analyze the samples as soon as possible after the reception.

At the same time as the test, INERIS performed an experimental study to verify the homogeneity and stability of the four parabens in the samples. Eight samples were analyzed at day 0 for the homogeneity; and three samples were analyzed after 1, 3 and 7 days for stability assessment.

STATISTICAL TREATMENT

The statistical treatments of the PT quantitative results were conducted according to ISO 13528 standard [2]. The assigned values (x_{pt}) were estimated using the robust means of the results. The proficiencies of each laboratory were evaluated with tolerance values, TV, being 60 % of the assigned value for each parameter. The results x could be evaluated and classified through z-scores :

$z \leq |2|$: satisfactory, $|2| \leq z < |3|$: questionable and $z \geq |3|$: unsatisfactory

$$\text{Where : } Z = \frac{x - x_{pt}}{\left(\frac{TV}{2}\right)}$$

RESULTS and DISCUSSION

This experimental PT was set up in March 2018 gathering 9 laboratories. The laboratories mainly used tandem mass spectrometry, MS/MS. Theoretical concentrations for each paraben and each preservative - ascorbic acid and nitric acid - are given in Table 1 and the main statistical parameters of this PT are given in Table 2.

The results for each paraben were relatively dispersed with coefficients of variation ranging from 26% to 40%. Considering these latter, less discrepancy among the participants was observed for EtP and MeP in the samples preserved with nitric acid. For BuP and PrP, similar results dispersion were observed for both preservation method.

Assigned values were compared with theoretical concentrations, C_{th} (Figure 1.). All assigned values underestimated the spiking values regardless of the preservation method. With nitric acid, relative differences between x_{pt} and C_{th} ranged from -14% to -24%. x_{pt} values were closer to C_{th} when nitric acid was added to the samples, especially for EtP and MeP.

At the same time as the PT, some samples were analyzed by INERIS for a homogeneity and stability study. Each result was compared to the spiking value by calculating the relative difference, in %, between the individual measurement and the theoretical concentration. Results are shown in Figure 2. and Figure 3.

For the homogeneity study, eight samples were analyzed at day 0. For each paraben and each preservation method, these results were less dispersed than the PT results. Nevertheless the same trend as in the PT results was observed: results for samples preserved with nitric acid were closer to the theoretical concentrations, and this for all parabens, especially for MeP.

For the stability study, three samples were analyzed after 1, 3 and 7 days. For the samples with ascorbic acid, and for all parabens, relative difference with the spiking concentration started increasing (in absolute value) from day 1. Remarkably relative difference reached about -70% for MeP after 7 days. In the contrary, such "loss" was not observed for the samples with nitric acid: results were relatively steady over time, even for MeP.

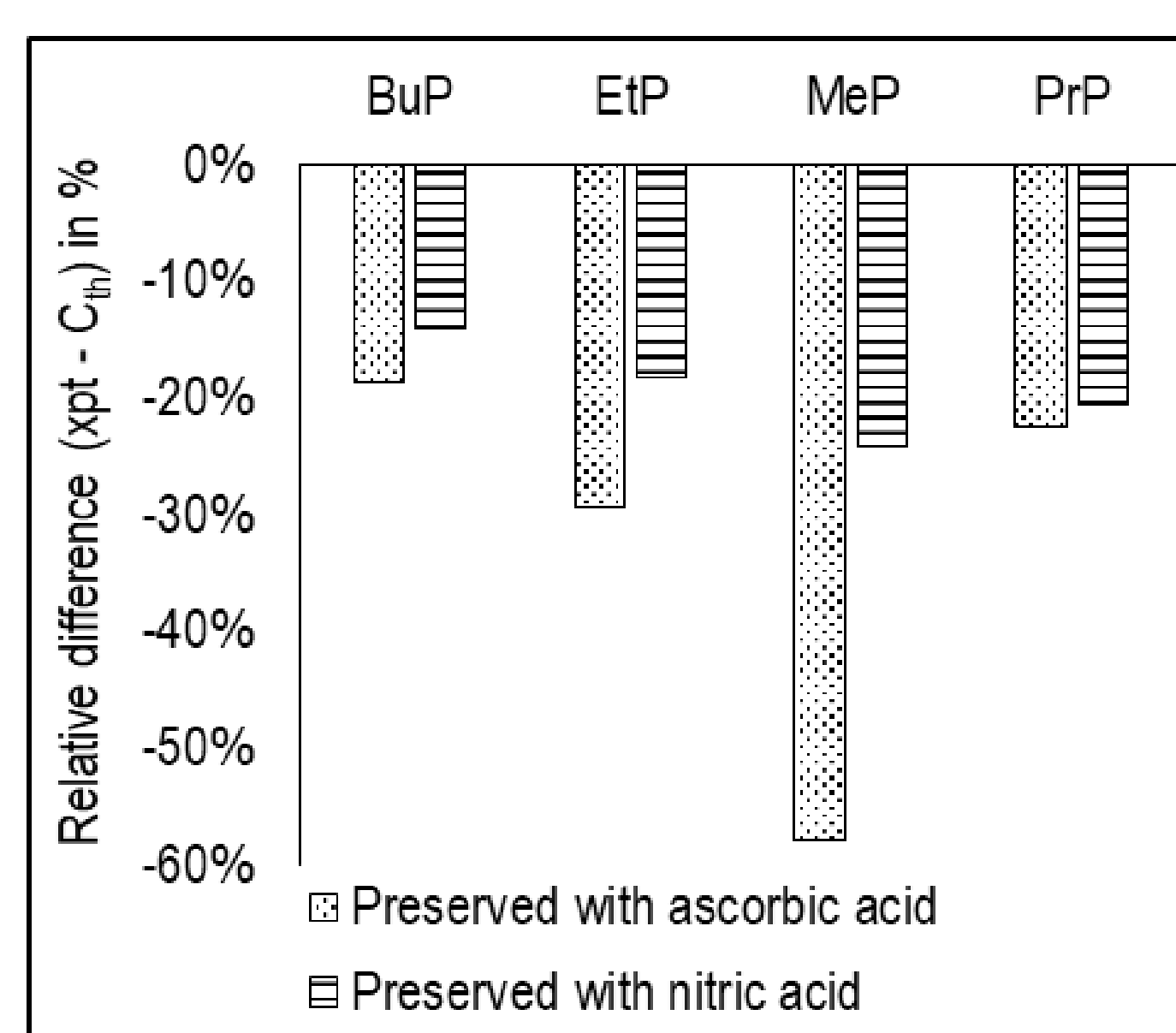


Figure 1. Relative differences, in %, between the assigned values x_{pt} and the theoretical concentrations C_{th} for each paraben and each preservative

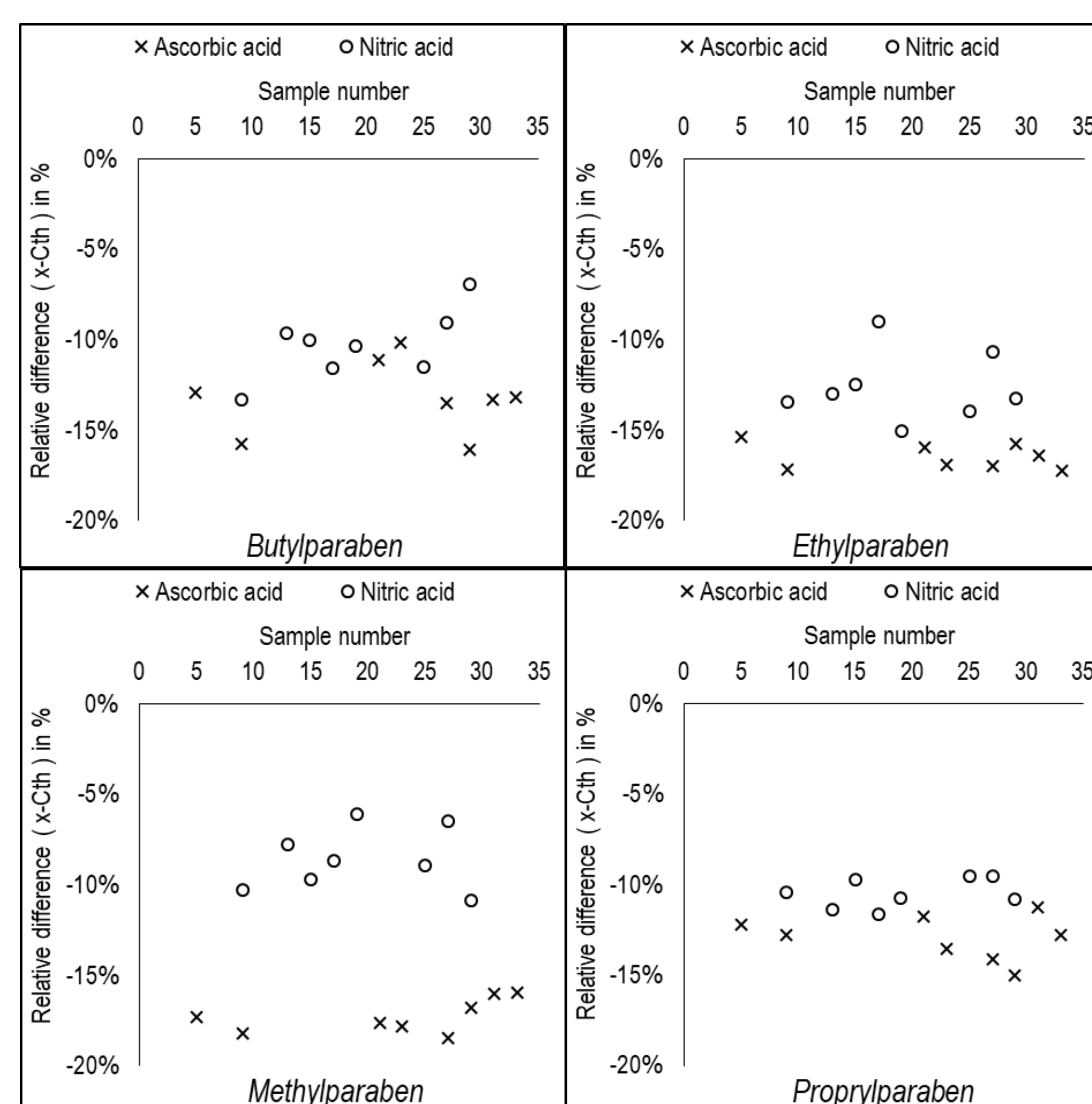


Figure 2. Results of the homogeneity study performed for each paraben and each preservative, ascorbic acid and nitric acid

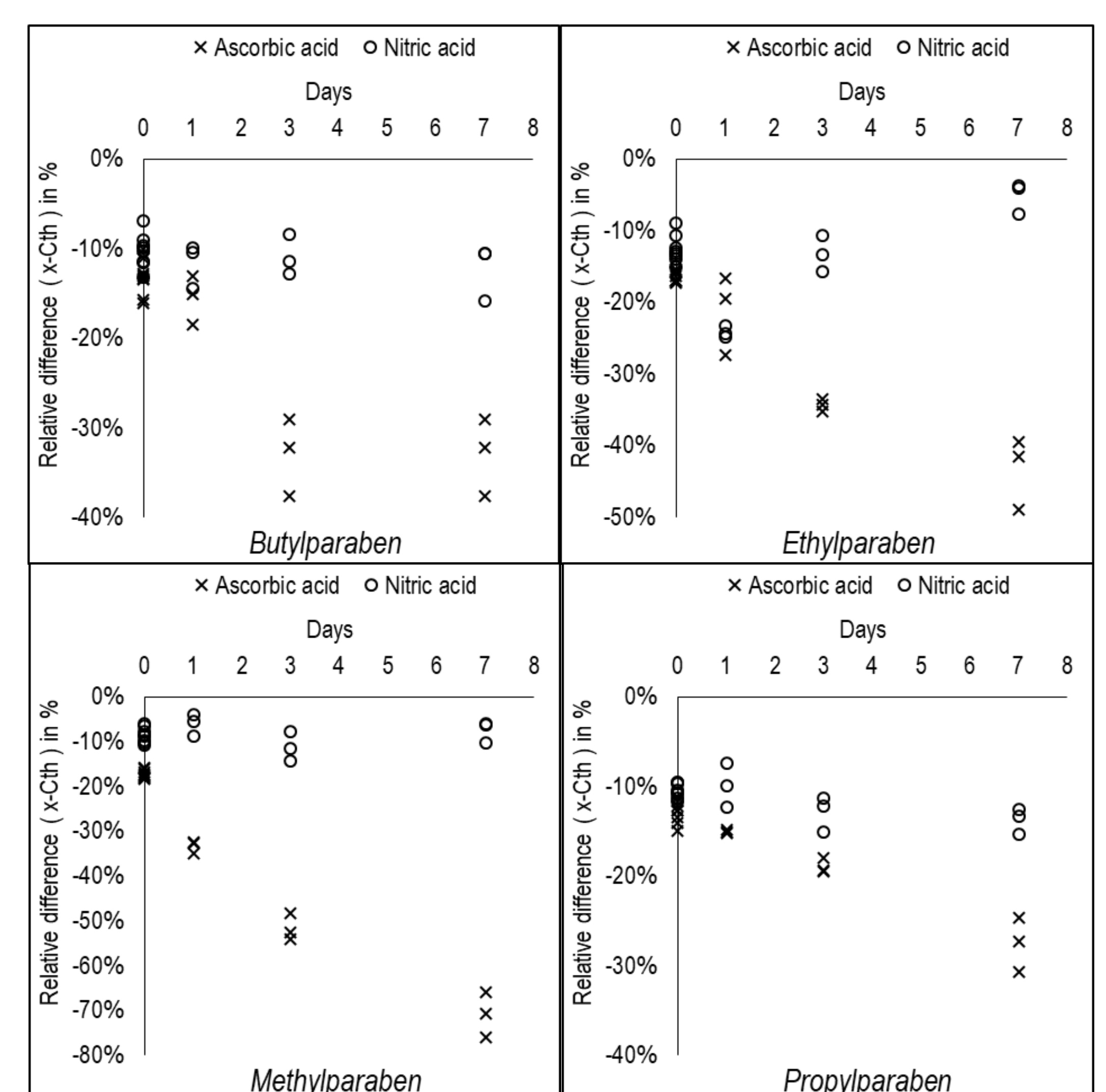


Figure 3. Results of the stability study performed for each paraben and each preservative, ascorbic acid and nitric acid

Spiked paraben	Unit	Concentration in samples preserved with ascorbic acid	Concentration in samples preserved with nitric acid
Butylparaben	µg/L	0.307	0.192
Ethylparaben	µg/L	0.333	0.208
Methylparaben	µg/L	0.384	0.240
Propylparaben	µg/L	0.358	0.224

Table 1. Theoretical concentrations in the samples for each paraben and each preservative

Statistical parameter	Concentration in samples preserved with ascorbic acid				Concentration in samples preserved with nitric acid			
	BuP	EtP	MeP	PrP	BuP	EtP	MeP	PrP
Number of returned results	7	8	8	8	7	8	8	8
Assigned values for proficiency testing (x_{pt}) (in µg/L)	0.250	0.235	0.162	0.278	0.165	0.170	0.182	0.178
Number of results taken into account for x_{pt} estimation	6	7	6	7	7	8	8	8
Robust standard deviation of the results $s(x_{pt})$	0.099	0.077	0.062	0.077	0.060	0.045	0.051	0.047
Coefficient of variation (%) CV (x_{pt})	40	33	38	28	36	26	28	26

Table 2. Summary of the PT quantitative results

CONCLUSION

An experimental PT was implemented in order to compare in real conditions ascorbic acid and nitric acid, for ensuring parabens stability in PT water samples over time.

Overall assigned values were closer to the spiking concentrations when nitric acid was used. A homogeneity and stability study performed on these PT samples confirmed that preservation with nitric acid allowed a higher recovery rate of the parabens in water samples, especially of MeP. It also indicated that nitric acid ensured more stable samples over seven days.

REFERENCES

- [1] ISO 17043:2015, Conformity assessment - General requirements for proficiency testing.
- [2] ISO 13528:2015 - Statistical methods for use in proficiency testing by interlaboratory comparisons