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PRESERVATION OF PARABENS IN WATER SAMPLES

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Abstract

Parabens are preservatives widely used in cosmetics, pharmaceutical and food products due to their antibacterial and antifungal activity. Their ubiquity in surface water and their potential adverse effects on human health and environment led to their inclusion into the French monitoring programme of aquatic environment. In order to help the laboratories improving their analytical skills regarding these chemicals, BIPEA organises since November 2016 proficiency testing schemes (PTS) according to ISO 17043 [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 sample preservation by ascorbic acid and nitric acid. It included (i) an experimental PT for which parabens-spiked samples were proposed to the laboratories with each preservation agent separately, and (ii) a dedicated homogeneity and stability study performed by the French National Institute for Industrial Environment and Risks (INERIS).

Overall preservation with nitric acid implied less dispersed results and closer to the spiking concentrations, especially for methylparaben, and a greater stability over time.

Key words

Parabens; preservation; proficiency testing schemes; water quality control.

1 INTRODUCTION

Parabens are esters of parahydroxybenzoic acid. Due to their antibacterial and antifungal properties, they are mainly used as preservatives in the cosmetics, and in pharmaceutical and food products. Recent studies showed that they may have potential adverse effects on human health and on environment. In fact these substances may exert weak oestrogenic activity [2, 3, 4] and may present potential hazard on reproduction [5].

Their wide range of applications favors their indirect transfer into the environment, especially through the urban wastewater containing residues of cosmetics [6] and the industrial wastewater [7]. Their ubiquity in surface water and their potential adverse effects led to their inclusion into the French monitoring programme of aquatic environment as emerging contaminants. In order to help the laboratories improving their analytical skills regarding these emergent contaminants, BIPEA organises since November 2016 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 fact an experimental stability study was conducted on PT samples with parabens (butyl-, ethyl-, methyl- and propylparaben) and preserved with ascorbic acid only, before the present work. This study, performed according to the ISO 13528 standard [8], demonstrated the stability for butylparaben and the instability for the others parabens over a period of 22 days.

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 with ascorbic acid.

2 EXPERIMENTAL

The design of this experimental PT included three main steps: manufacturing of the samples, analyses by the laboratories and statistical treatment of the data, with the estimation of an assigned value.

2.1 Manufacturing of the samples

For this PT, samples were prepared from surface water that was characterized by an accredited laboratory (see Table 1). 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 2. 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.

2.2 Analysis of the samples

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. Moreover, participants were invited to enter in the reply form 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 analyse the samples as soon as possible after the reception.

Table 1. Characteristics of the raw surface water

Parameter	Unit	Method	Results
pH	pH unit	EN ISO 10523	8.2
Conductivity at 25 °C	µS/cm	EN 27888	760
Suspended solids	mg/L	EN 872	30
Nitrates	mg NO_3/L	EN ISO 10304-1	23
Chlorides	mg Cl/L	EN ISO 10304-1	27
Sulphates	mg SO_4/L	EN ISO 10304-1	79
Calcium	mg Ca/L	EN ISO 11885	140
Magnesium	mg Mg/L	EN ISO 11885	21
Sodium	mg/L	EN ISO 11885	12
Haze	FNU	EN ISO 7027	22
Total Organic Carbon	mg/L	EN 1484	4.0
Hydrogen carbonates	mg/L	EN ISO 9963-1	347

Table 2. Theoretical concentrations in the samples for each paraben and each preservative

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

2.3 Statistical treatment

The statistical treatment of the PT data was performed according to the ISO 13528 standard [8]. 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, (see Eq. 1): result with $z \leq |2|$ is considered as satisfactory, result with $|2| \leq z \leq |3|$ is considered as questionable, and result with $z \geq |3|$ is considered as unsatisfactory, where:

$$z = \frac{x - x_{pt}}{\frac{TV}{2}} \quad (1)$$

2.4 Homogeneity and stability study

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 analysed at day 0 for the homogeneity; and three samples were analysed after 1, 3 and 7 days for stability assessment.

3 RESULTS

This experimental PT was set up in March 2018 gathering 9 laboratories. One laboratory gave semi-quantitative results for all chemical compounds, one laboratory gave results for EtP, MeP and PrP only, while the rest of the participants gave results for all substances. Except the laboratory with semi-quantitative results and using mass spectrometry, the laboratories used tandem mass spectrometry, MS/MS. In addition to the detection method, the participants could provide their extraction method. Four of them carried out a direct injection, two performed a solid/liquid extraction, and one used an on-line preconcentration. The low number of participants did not allow to compare relevantly the extraction and detection techniques.

Table 3. Main statistical parameters 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 value 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 $CV(x_{pt})$ (in %)	40	33	38	28	36	26	28	26

The main statistical parameters of this PT are given for each paraben and each preservation method - ascorbic acid and nitric acid - in Table 3. It should be noted that the number of results taken into account for the estimation of the assigned value is not always the same, and relatively low.

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 compared to those preserved with ascorbic acid. For BuP and PrP, similar results dispersion were observed for both preservation method.

Assigned values were compared with theoretical concentrations, C_{th} (Fig. 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% while with ascorbic acid they ranged from -19% to -58%. x_{pt} values were closer to C_{th} when nitric acid was added to the samples, especially for EtP and MeP.
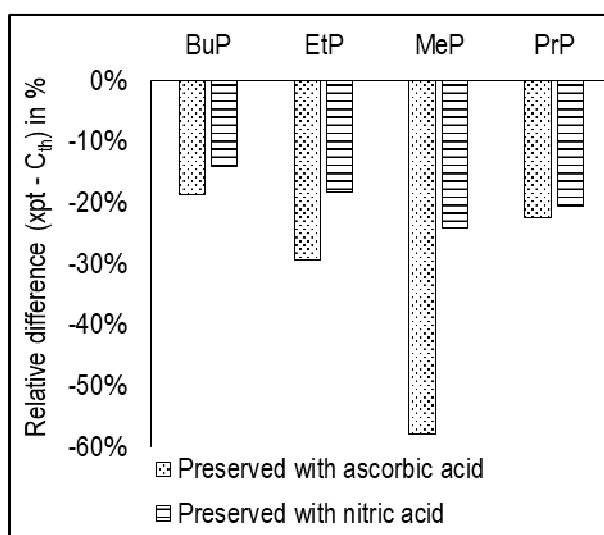

Fig.1. Relative differences, in %, between the assigned values x_{pt} and the theoretical concentrations C_{th} for each paraben and each preservative

At the same time as the PT, some samples were analysed 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 theroretical concentration. Results are shown in Fig. 2. and Fig. 3.

For the homogeneity study, eight samples were analysed 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 analysed 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.
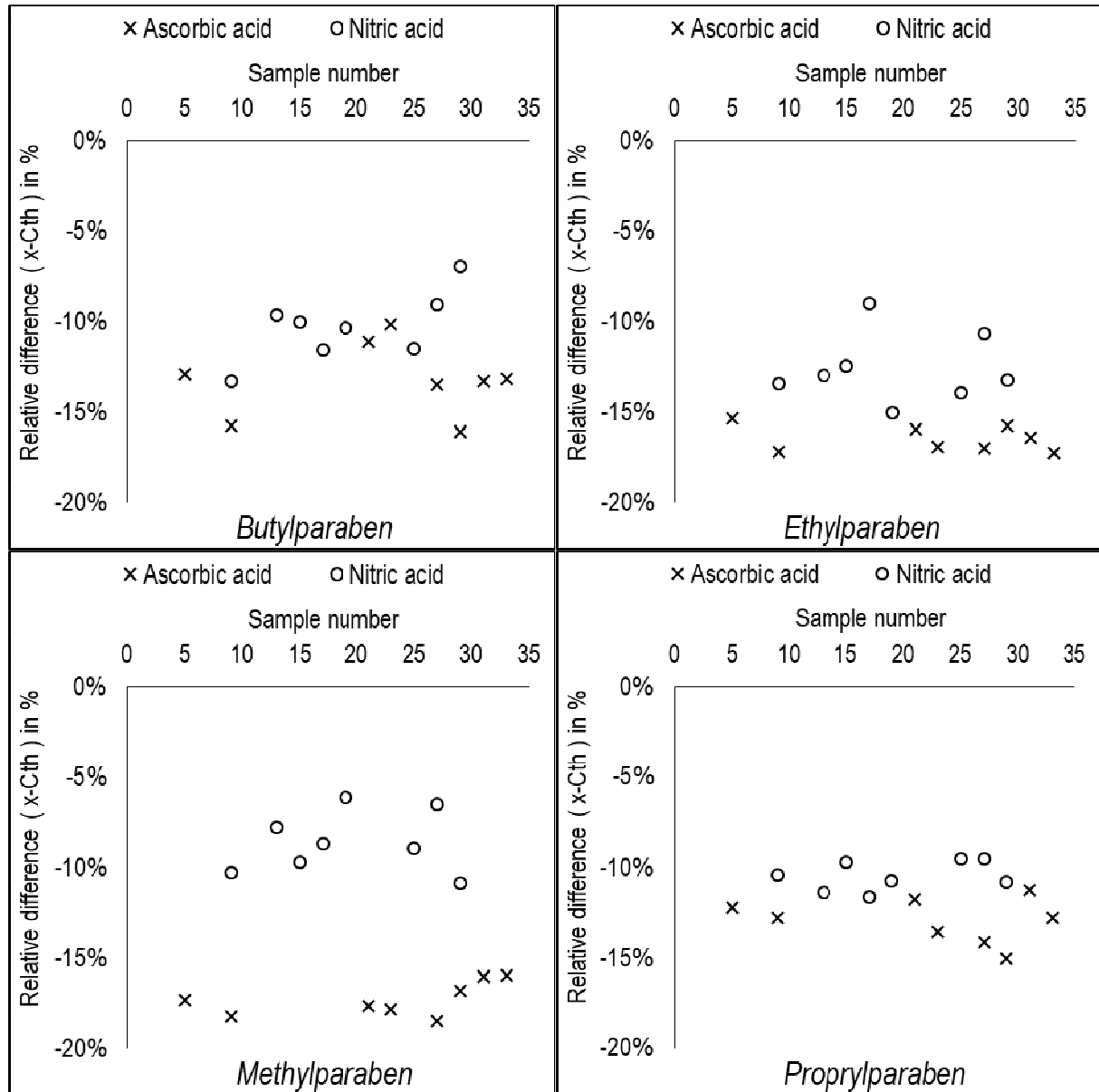

Fig. 2. Results of the homogeneity study performed for each paraben and each preservative, ascorbic acid and nitric acid
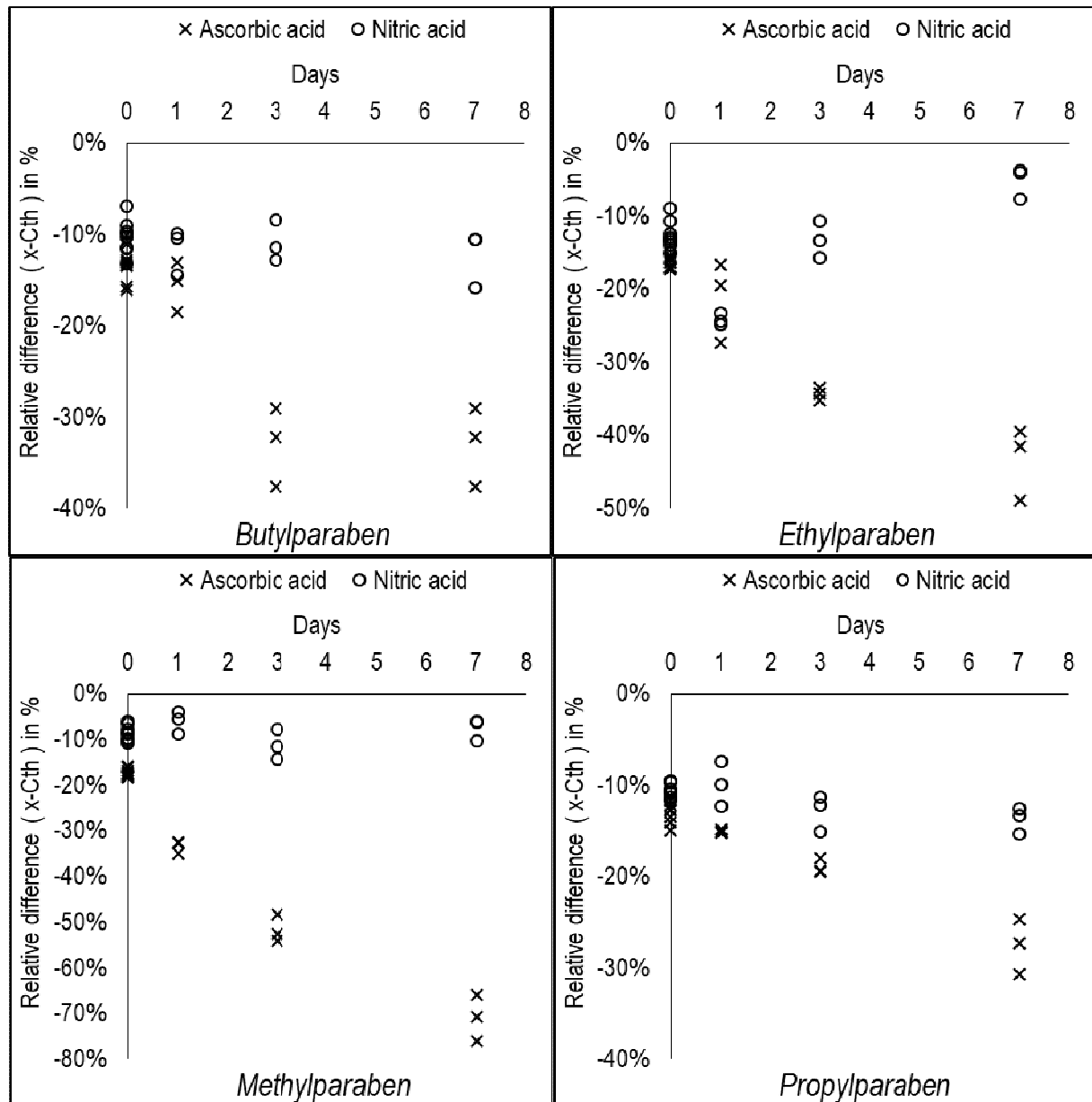
Fig. 3. Results of the stability study performed for each paraben and each preservative, ascorbic acid and nitric acid

4 CONCLUSION

Parabens are emerging contaminant considering their ubiquity in the environment and their potential effects. Need for PTS with these substances is also emerging. An experimental PT was implemented in order to compare in real conditions two preservatives, ascorbic acid and nitric acid, for ensuring parabens stability in PT water samples over time.
Less dispersion was observed among the participants for EtP and MeP in the samples preserved with nitric acid. Overall assigned values were closer to the spiking concentrations when nitric acid was used, especially for EtP and MeP. 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.

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