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RESULTS OF COLLABORATIVE INTERLABORATORY STUDY TO ESTIMATE THE PERFORMANCE CHARACTERISTICS OF THE GAS CHROMATOGRAPHIC METHOD FOR SOME ALKYL PHENOLS FROM WATER

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Abstract. 4-*tert*-octylphenol and 4-nonylphenol are two major metabolites of alkyl phenol polyethoxylates which are widely used in different industrial and commercial applications as non-ionic surfactants. In order to ensure the ecological security by controlling the concentrations of these pollutants in water it was developed a gas chromatographic method after extraction with dichloromethane at pH = 3.5. The estimation of the performance characteristics of the method was performed by a collaborative interlaboratory study. Each participant laboratory has analysed a set of five water samples with 4-*tert*-octylphenol and 4-nonylphenol in different levels of concentration. The results obtained after the statistic processing of the experimental data showed that the standard deviations of repeatability and reproducibility are lying in the normal domains for a chromatographic method. Consequently, the proposed method can be used by any environmental laboratory which performs the control of the level of pollution with these two compounds.

Keywords: alkyl phenols, 4-*tert*-octylphenol, analysis, gas chromatography, water.

AIMS AND BACKGROUND

The continuous control of the pollution level from different categories of water and the comparison of the obtained concentration values with the maximum accepted limits involve the use of analytical methods with a high level of repeatability and reproducibility.

In accordance with the European Directives concerning environmental pollution, the discharges of dangerous priority substances were normed also in our country according to HG 118/2002. For 4-*tert*-octylphenol and 4-*n*-nonylphenol the maximum accepted concentrations in natural water sources were established at 0.01 μg/l, respectively 0.30 μg/l.

The methods developed in the laboratory for the analysis of octyl phenols and nonyl phenols in water consist in the extraction of the sample with methyl-

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ene chloride at pH 3-3.5, followed by the gas-chromatographic analyses of the organic extract. The chromatographic separation of the compounds is performed on a low polar capillary column and the detection is done with a flame ionisation detector (FID).

In order to test the performances of these new methods developed, was initiated an interlaboratory collaborative scheme. In this way it was possible to observe if the methods have deficiencies and also to make proposals for modification/ improvement of the analytical techniques.

EXPERIMENTAL

The testing scheme applied in this study was in accordance with the requirements of the Guide SO/IEC 43/1(Ref. 1) and from standard ISO 5725:1994, Parts 2 and 6 (Ref. 2).

The samples to be tested were divided into sub-samples and sent simultaneously to the laboratories participant in the scheme[3]. The samples were put in glass containers, tightly closed and kept in cooling boxes at 4°C and in the dark till when they were distributed.

Each laboratory had to test 5 representative samples corresponding to the following concentration ranges: 0.02–0.07 mg/l for 4-*t*-octylphenol and 0.06-0.15 mg/l for 4-*n*-nonylphenol, with two duplicates for each level of concentration.

The results were collected by the coordinator laboratory and evaluated using the statistical calculation model[4] specific for the precision experiments.

The next steps were as follows:

– a critical examination of the results given by the participants at the scheme in order to identify and treat adequately the extreme results and other irregularities by applying the graphical method (the Mandel test *h* and *k*) and also the numerical calculation method – (the Cochran test).

For the Mandel test of interlaboratory coherence (*h)* the following formula was used:

$$h_{ij} = \frac{\bar{y}_{ij} - \bar{\bar{y}}_j}{\sqrt{\frac{1}{p_j - 1} \sum_{i=1}^{p_j} (\bar{y}_{ij} - \bar{\bar{y}}_j)^2}} \tag{1}$$

where $\bar{y}_{ij}$ is the mean value in the cell; $\bar{\bar{y}}_j$ – general mean of the tests ($\hat{m}_j$).

For the Mandel test of intralaboratory coherence (*k*) the following formula was used:

$$\sqrt{\frac{\sum S_{ij}^2}{p_j}} \text{ for each level} \tag{2}$$

$k_{ij} = \dfrac{s_{ij}\sqrt{p_j}}{\sqrt{\sum s_{ij}^2}}$ for each laboratory, at every concentration level. (3)

The Cochran numerical test, as a measure of the variability inside the laboratory, was calculated with the following formula:

$$C = \frac{s_{\max}^2}{\sum\limits_{i=1}^{p} s_i^2} \tag{4}$$

where $s_{\max}$ is the highest value of the standard deviation from the set.

Determination of the precision values and of the mean values for each concentration level:

– standard deviation of repeatability, s_r^2:

$$s_{ij}^2 = \frac{\sum\limits_{i=1}^{p}(n_{ij}-1)s_{ij}^2}{\sum\limits_{i=1}^{p}(n_{ij}-1)}; \tag{5}$$

– interlaboratory standard deviation, s_L^2:

$$s^2_{Lj} = \frac{s^2_{dj} - s^2_{rj}}{\bar{n}_j} \tag{6}$$

where

$$s_{dj}^2 = \frac{1}{p-1}\sum_{i=1}^{p} n_{ij}(\bar{y}_{ij} - \bar{\bar{y}}_j)^2 = \frac{1}{p-1}\left[\sum_{i=1}^{p} n_{ij}(\bar{y}_{ij})^2 - (\bar{\bar{y}}_j)^2 \sum_{i=1}^{p} n_{ij}\right] \tag{7}$$

$$\bar{n}_j = \frac{1}{p-1}\left[\sum_{i=1}^{p} n_{ij} - \frac{\sum\limits_{i=1}^{p} n^2_{ij}}{\sum\limits_{i=1}^{p} n_{ij}}\right]. \tag{8}$$

– standard deviation of reproducibility:

$$s_{Rj}^2 = s_{rj}^2 + s_{Lj}^2 \tag{9}$$

– general mean:

$$\hat{m}_j = \bar{\bar{y}}_j = \frac{\sum\limits_{i=1}^{p} n_{ij}\bar{y}_{ij}}{\sum\limits_{i=1}^{p} n_{ij}} \tag{10}$$

The relation between s_r, s_R and $\hat{m}_j$ may be represented graphically and can be included in one of the following situation:

- $s_r = b\hat{m}_j$ – a straight line passing through the origin;

- $s_r = a + b\hat{m}_j$ – a straight line with positive ordinate at the origin;
- $\lg s_r = c + d\lg\hat{m}_j$ – an exponential relation.

RESULTS AND DISCUSSION

The results reported by the laboratories which participated in the scheme are presented in Tables 1 and 2.

Table 1. Initial results obtained in the interlaboratory study for 4-*te*rt-octylphenol

Laboratory	Concentration (mg/l)				
	1	2	3	4	5
1	0.026	0.027	0.034	0.05	0.066
	0.023	0.025	0.032	0.047	0.069
2	0.026	0.031	0.037	0.049	0.06
	0.028	0.034	0.039	0.046	0.063
3	0.02	0.028	0.034	0.043	0.065
	0.021	0.03	0.037	0.045	0.065
4	0.021	0.028	0.035	0.045	0.066
	0.022	0.029	0.036	0.045	0.063
5	0.023	0.027	0.03	0.044	0.061
	0.027	0.031	0.033	0.041	0.063

Table 2. Initial results obtained in the interlaboratory study for 4-*n*-nonylphenol

Laboratory	Concentration (mg/l)				
	1	2	3	4	5
1	0.063	0.078	0.097	0.125	0.154
	0.063	0.076	0.095	0.126	0.152
2	0.063	0.077	0.096	0.122	0.152
	0.061	0.075	0.098	0.122	0.154
3	0.067	0.074	0.094	0.127	0.155
	0.065	0.073	0.094	0.126	0.157
4	0.064	0.074	0.093	0.123	0.155
	0.062	0.075	0.095	0.124	0.154
5	0.061	0.071	0.092	0.122	0.156
	0.061	0.073	0.093	0.125	0.157

Using both statistical techniques – graphical method (the Mandel test) and the numerical calculation method (the Cochran test) there have not been found outliers or extreme values in the results reported by the participants at the interlaboratory comparison scheme concerning the test methods. The results are presented in Figs 1-4 and in Tables 3 and 4.

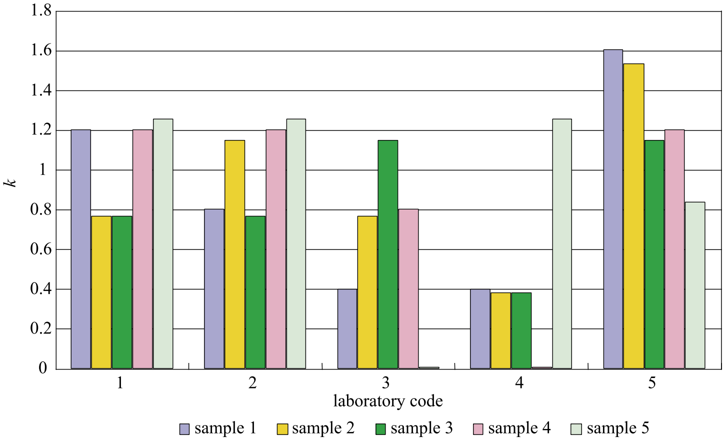

Fig. 1. Results of the Mandel test of intralaboratory coherence (*k*) for 4-*tert*-octylphenol

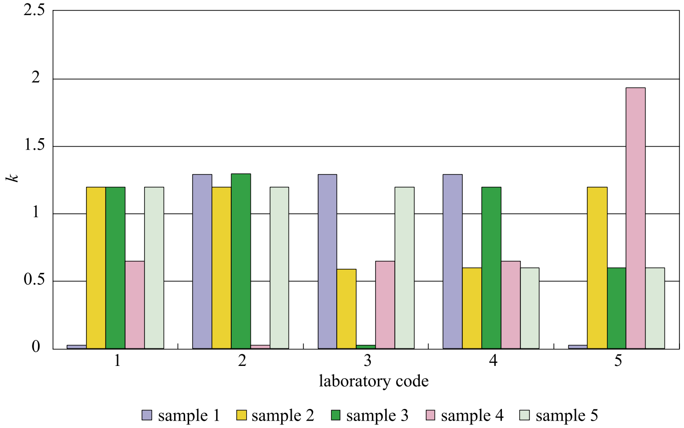

Fig. 2. Results of the Mandel test of intralaboratory coherence (*k*) for 4-*n*-nonylphenol

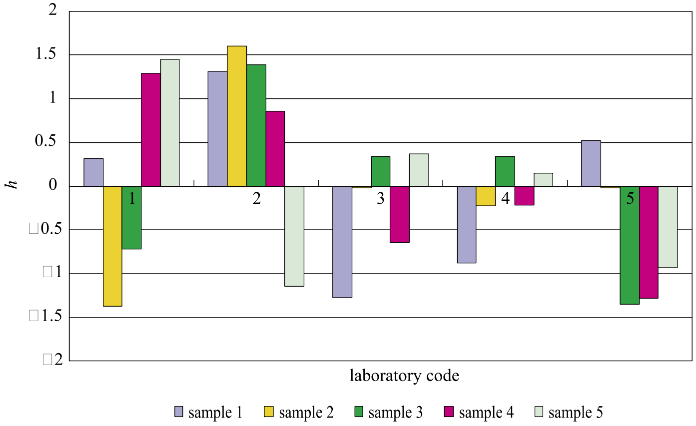

Fig. 3. Results of the Mandel test of interlaboratory coherence (*h*) for 4-*tert*-octylphenol

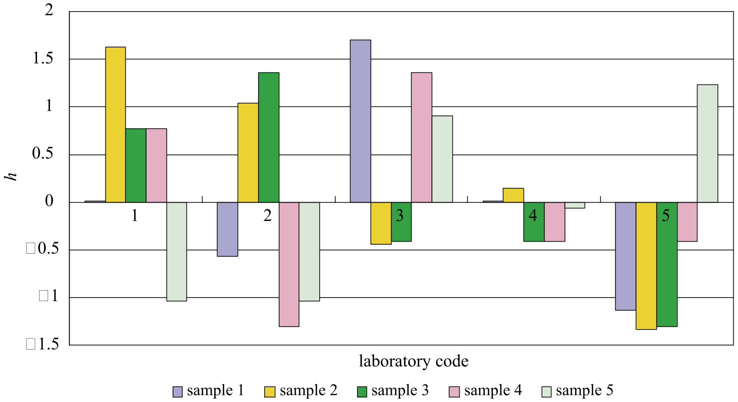

Fig. 4. Results of the Mandel test of interlaboratory coherence (*h*) for 4-*n*-nonylphenol

Table 3. Results of the Cochran numerical test for 4-*tert*-octylphenol

Level	1	2	3	4	5
$C_{\text{calc.}}$	0.145161	0.014706	0.166667	0.064516	0.070175

P=5 , *n*=2 , significance level 1% *C*=0.928; *P*=5 , *n*=2 , significance level 5% *C*=0.841

Table 4. Results of the Cochran numerical test for 4-*n*-nonylphenol

Level	1	2	3	4	5
$C_{\text{calc.}}$	0	0.035714	0	0.041667	0.035714

P=5 , *n*=2 , significance level 1% *C*=0.928; *P*=5 , *n*=2 , significance level 5% *C*=0.841

The experimental study furnished to the participant laboratories information about their analytical performance, respectively the repeatability of the interlaboratory determinations (with the Mandel test *k*) and the reproducibility of the results in case of interlaboratory determinations (with the Mandel test *h*).

Using the intralaboratory coherence test, *k,* it can be noticed that for both 4-*n*-nonylphenol and 4-*tert*-octylphenol the laboratories presented relatively small and constant variations for most of the concentration levels, and in some cases there were no variations at all (see Figs 1 and 2).

Concerning parameter *h,* laboratories presented positive and negative results, with relatively small variations (see Figs 3 and 4).

Also, in the case of the numerical Cochran test (test of the variability inside the laboratory) there have not been observed outliers or extreme results for none of the concentration levels. The values calculated for parameter '*C*' were compared with the critical values of the Cochran test for *P*=5, *n*= 2 and significance levels of 1% (0.928) and 5% (0.841). The values obtained for this parameter are situated in the range of 0.07–0.16 for 4-*tert*-octylphenol and 0.0-0.4 for 4-*n*-nonylphenol.

Because all the values obtained by the participant laboratories were in the range of the accepted values, were calculated the other statistical parameters: *m*, s_r, s_R, which are presented in Tables 5 and 6.

Table 5. Calculated values for *m*, s_r and s_R of the determination method for 4-*tert*-octylphenols

Level	*P* (participant laboratory)	*m* (the mean value) (mg/l)	s_r (standard deviation of the repeatability) (mg/l)	s_R (standard deviation of the reproducibility) (mg/l)
1	5	0.0237	0.002374	0.003018
2	5	0.029	0.002439	0.002784
3	5	0.0347	0.002187	0.002831
4	5	0.0455	0.002329	0.002856
5	5	0.06415	0.002233	0.002798

Table 6. Calculated values for *m*, s_r and s_R of the determination method for 4-*n*-nonylphenols

Level	*P* (participant laboratory)	*m* (the mean value) (mg/l)	s_r (standard deviation of the repeatability) (mg/l)	s_R (standard deviation of the reproducibility) (mg/l)
1	5	0.063	0.001477	0.00205
2	5	0.07425	0.001565	0.002018
3	5	0.0947	0.001511	0.001997
4	5	0.1242	0.001449	0.001973
5	5	0.1546	0.001565	0.001898

For the tested concentrations, the calculated values for the standard deviation of repeatability (s_r) remained relatively constant related to the increase of the general mean value: 0.002 mg/l for 4-*tert*-octylphenol and 0.0015 mg/l for 4-*n*-nonylphenol. The same behaviour can be observed for the standard deviation of reproducibility: 0.003 mg/l for 4-*tert*-octylphenol and 0.002 mg/l for 4-*n*-nonylphenol. In both cases, the values of the standard deviation are situated in the normal limits for a chromatographic method.

CONCLUSIONS

Using both statistical techniques – the graphical Mandel test and the numerical calculation method – the Cochran test – were not observed outliers or extreme values in the results reported by the laboratories which participated to the interlaboratory comparison scheme concerning the determination method for nonylphenols and octylphenols in water.

Concerning the precision's dependence on the general mean value, it was observed that on the tested concentration domain both standard deviations (s_r and s_R)

remained relatively constant related with the increase of the general mean value, both for nonylphenol and octylphenol.

The method performance parameters (repeatability and reproducibility) are situated in the accepted limits for a chromatographic method, so that the methods elaborated can be used by different environmental laboratories for the determination of nonylphenols and octylphenols from water.

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