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Simultaneous Determination of Chlorophenols from Quaternary Mixtures Using Multivariate Calibration

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Abstract: Multi-component quantitation method was used for chlorophenols determination from quaternary mixtures in water solutions. For multicalibration of spectrophotometer three series of standard samples were prepared using 2,4,6-trichlorophenol, 2,6-dichlorophenol, 2,4-dichlorophenol, 4-chlorophenol, 2-chlorophenol, and phenol in the concentration range of 0.5-12.5 mg/L. The mean recoveries from mixed samples containing 3.0-4.0 mg/L CPs were 96-98% and for 1.0 mg/L, 88-97.66%. Relative standard deviation determined for the same concentrations ranged between 4.65-5.21% and 7.48-9.86%, respectively. The method is not expensive and is useful for the analysis of different aromatic compounds from mixtures.

Keywords: chlorophenols, multicalibration, spectrophotometry, recovery

1. Introduction

Some compounds present a high degree of uv-vis spectra overlapping. So, their simultaneous determination with conventional spectrophotometric methods is not possible. Despite of this difficulty have been developed methods that allow quantitation both of organic and inorganic compounds from mixtures: multicomponent quantitative analysis (MCA) [1-3], rank anihilation factor analysis (RAFA) [4, 5], and derivative UV spectroscopy (DS) [6, 7].

In the last years multicomponent quantitative analysis together with classical least-squares (CLS) or partial least-squares (PLS) methods were used in UV–visible spectrophotometry [8-11]. Using a set of multicomponent samples of known concentrations and their corresponding instrument data, a multivariate calibration model must be realized. This method was applied for the determination of 2-5 compounds from their mixtures. Its main advantage is the speed of analysis.

The selection of the optimum wavelengths or of spectral ranges is needed for the improvement of this procedure. E.g., for the analysis of 4-dihydropyridine (DHP) calcium anatagonists and its photoproducts (amlodipine, nicardipine, nimodipine and nitrendipine), the following spectral ranges were used: 220–240, 340–380 and 210–240 nm. The recoveries for DHP and its degradation products were 99.09% and 97.85%, respectively. These results were compared with those obtained using UV derivative spectrophotometry.

Multivariate calibration spectrophotomery was also applied for the determination of some dyes used as additives from cosmetics: the recovery of Quinoline Yellow (C.I. 47005), Sunset Yellow (C.I. 15958), Tartrazine (C.I. 19140) and Brilliant Blue FCF (C.I. 42090), ranged between 91.0 -108.0% [10,11].

Chlorophenols (CPs) are discharged in the environment due to their huge production. They are present in drinking-water as a result of humic acids and phenol chlorination during disinfection, as by-products of the reaction of chlorine or hypochlorite with phenolic acids, as biocides, or as degradation products of phenoxy herbicides. Data from 40 Canadian treatment plants indicate that chlorophenol levels in drinking-water are generally low and may vary from one location to another. Maximum levels determined for some CPs were: 2-chlorophenol, 65 ng/L; 2,4-chlorophenol, 72 ng/L; 2,4,6-trichlorophenol, 719 ng/L. In drinking water from the Ruhr area of Germany were determined 2,4-DCP, 36 ng/L and 2,4,6-TCP, 1 ng/L [12].

The analysis of some chlorophenols from quaternary mixtures in water solutions using multivariate calibration spectrophotometry, is presented in this paper.

2. Experimental

Stock solutions of 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and phenol (Fischer, purity greater than 98%) 100 mg/L, were prepared in distilled water at pH =7.0 ± 0.015, using standard buffer consisting of 0.1 M NaOH + 0.1M KaH_2PO_4 . Concentrations of working solutions prepared by two successive dilutions ranged between 0.50 - 12.5 mg/L.

All chlorophenols present specific absorption maxima in the field of 269-311 nm, fig. 1. It may be seen that the overlapping of their uv spectra take place in great extent. For multicomponent analysis of chlorophenols both mixed and pure solutions were used, as standards for UV-Vis instrument calibration. After different trials there were determined mixed standards useful for the calibration, that allow the analysis of these compounds from quaternary mixtures, tables 1 and 2. E.g., in case of the analysis of

2,4,6-TCP, 2,6-DCP, 2,4-DCP and 4-CP, for calibration were used five mixed standards with concentrations presented in table 1 (set a), and one pure standard for each chlorophenol containing the same concentration as in the last mixed standard, no. 5: 2,4,6-TCP, 10.0 mg/L; 2,6-DCP, 2.5 mg/L; 2,4-DCP, 10.0 mg/L; and 4-CP, 5.0 mg/L, table 1. So, nine standards were used for the instrument calibration in order to determine these four CPs from mixtures.

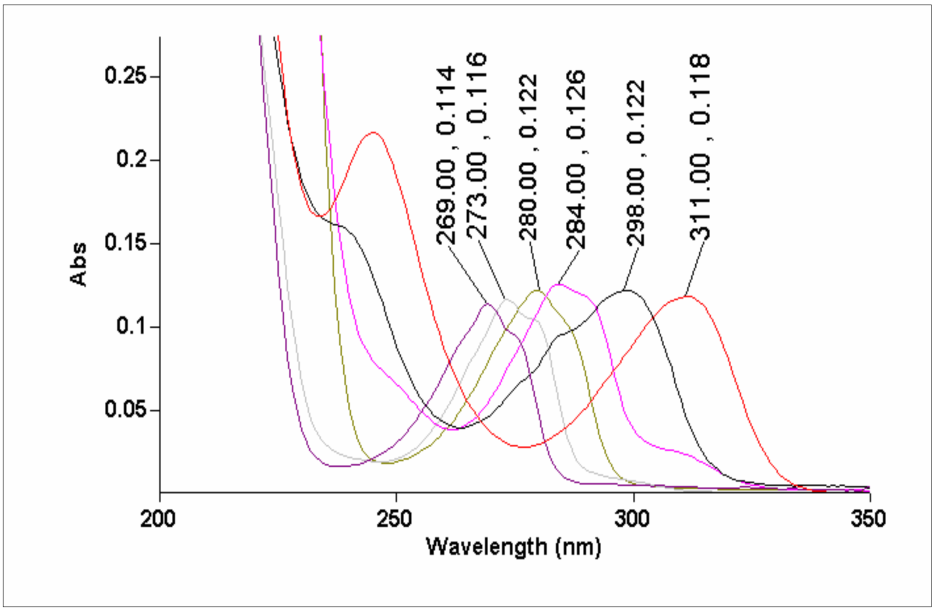

Figure 1. UV spectra for phenol (6.8 mg/L), 2-CP (8.0 mg/L), 4-CP (10.0 mg/L), 2,4-DCP (10.0 mg/L), 2,6-DCP (6.0 mg/L), 2,4,6-DCP (6.0 mg/L), in distilled water at pH = 7.0

TABLE 1. Standard samples in distilled water containing four CPs , used for calibration

set / sample	Chlorophenols, mg/L				set / sample	Chlorophenols, mg/L			
a	2,4,6-TCP	2,6 -DCP	2,4 -DCP	4 - CP	b	2,4,6 -TCP	2,6 -DCP	2,4 -DCP	2 - CP
1	1.0	-	1.0	0.5	6	0.75	0.5	1.25	1.0
2	2.0	0.5	2.0	1.0	7	1.5	1.0	2.5	2.0
3	4.0	1.0	4.0	2.0	8	3.0	2.0	5.0	4.0
4	8.0	2.0	8.0	4.0	9	6.0	4.0	10.0	8.0
5	10.0	2.5	10.0	5.0	10	7.5	5.0	12.5	10.0

TABLE 2. Standard samples in distilled water containing four CPs used for calibration

set / sample	Chlorophenols, mg/L			
c	2,4,6-TCP	2,6-DCP	2,4-DCP	phenol
11	0.75	0.5	1.25	1.0
12	1.5	1.0	2.5	2.0
13	3.0	2.0	5.0	4.0
14	6.0	4.0	10.0	8.0
15	7.5	5.0	12.5	10.0

For 2-CP and phenol analysis from quaternary mixtures two similar series of standards were prepared like above (set b and c), in which 4-CP was successively replaced with 2-CP and phenol, tables 1 and 2..The measurement of absorptions took place at the following wavelengths: phenol, 269 nm; 2-CP, 273 nm; 4-CP-280 nm; 2,4-DCP, 284 nm; 2,6-DCP-298 nm; 2,4,6-TCP, 311 nm.

To estimate chlorophenols recoveries, other series of 23 mixed samples containing four CPs were prepared, with the following concentrations: 2,4,6-trichlorophenol = 1.0 -4 mg/L; 2,6-dichlorophenol = 0.8 - 2.0 mg/L;

2,4-dichlorophenol = 0.8-3.0 mg/L; 4-chlorophenol = 1-3 mg/L; 2-chlorophenol = 1-2 mg/L; phenol = 2-10 mg/L, tables 3-5. Also, for statistic analysis in case of three samples (1, ll, lll) containing four chlorophenols were used five replicates for each of them, and standard deviation, relative standard deviation (%) and confidence interval were computed with MS Excel.

The following instruments were used: Shimadzu 1700 UV-Vis spectrophotometer with the facility for multi-component quantitation, Kern ABT 220–5DM analytic balance and Thermo Orion pH-meter.

3. Results and Discussion

The recovery of chlorophenols from different quaternary mixtures is presented in tables 3-5. The determination of 2,4,6-trichlorophenol was not significant influenced by its concentration: for 1.5-4.0 mg/L it was obtained 87.3-92.5%. Similar results were recorded for 2,4-dichlorophenol, 4-chlorophenol and 2,6-dichlorophenol, table 3.

TABLE 3. The analysis of CPs from mixed samples using multicomponent analysis

sample	2,4,6-TCP			2,6-DCP			2,4-DCP			4-CP		
	A	B	R, %	A	B	R,%	A	B	R,%	A	B	R,%
1	1.5	1.31	87.3	2.0	1.9	95	1.0	1.12	112	2.0	1,73	86.5
2	3.0	2.75	91.6	1.0	0.93	93	1.0	1.06	106	1.0	0.74	74
3	3.0	2.91	96.6	1.0	1.06	106	2.0	2.18	109	2.0	1.80	90
4	3.0	2.81	93.6	1.0	0.90	10	3.0	3.25	108	1.0	0.78	78
5	4.0	3.81	95.25	1.0	0.98	98	2.0	2.24	112	2.0	1.72	86
6	4.0	3.67	92.5	1.0	0.88	88	1.0	1.10	110	3.0	2.7	90

A = added concentration, mg/L; B = determined, mg/L; R = recovery, %

TABLE 4. The recovery of CPs from mixed samples using multicomponent analysis

sample	2,4,6-TCP			2,6-DCP			2,4-DCP			2-CP		
	A	B	R,%	A	B	R,%	A	B	R,%	A	B	R,%
1	1.2	1.04	86.6	0.8	0.62	75	0.8	0.72	90	-	-	-
2	1.2	1.31	109	0.8	0.75	93.7	0.8	0.96	120	-	-	-
4	3.0	3.05	101	1.0	0.92	92	3.0	3.4	113	1.0	1.2	120
5	3.0	2.68	89.3	1.0	0.82	82	3.0	3.3	110	1.0	0.87	87
6	3.0	2.61	87	1.0	0.93	83	2.0	2.3	115	2.0	1.87	93.5
7	3.0	2.8	93.3	1.0	1.09	109	2.0	2.4	120	2.0	2.1	105
8	4.0	3.64	91	-	-	-	3.0	3.3	110	1.0	1.1	110
9	4.0	3.7	92.5	-	-	-	3.0	3.6	120	1.0	1.3	130

A = added concentration, mg/L; B = determined, mg/L; R = recovery, %.

TABLE 5. The recovery of CPs from mixed samples using multicomponent analysis

sample	2,4,6-TCP			2,6-DCP			2,4-DCP			Phenol		
	A	B	R,%	A	B	R,%	A	B	R,%	A	B	R,%
1	1.0	1.13	105	1.0	1.02	102	3.0	3.15	105	-	-	-
2	1.0	0.97	97	1.0	1.07	107	-	-		2.0	2.1	105
3	1.0	1.13	103	1.0	1.02	102	3.0	3.28	109	2.0	2.14	107
4	3.0	2.83	94.3	-	-	-	1.0	1.1	110	-	-	-
5	4.0	3.5	87.5	-	-	-	1.0	0.77	77	10	9.8	98
6	4.0	3.67	91.7	1.0	1.08	108	2.0	2.25	112	-	-	-

A= added concentration, mg/L; B = determined, mg/L; R = recovery, %.

From the other two series of mixtures closed recoveries were determined for 2,4,6-TCP, 86.6-92.5%, and 87.5-105%, respectively, tables 4 and 5. There was not observed a influence due to the mixture content on chlorophenols recovery: by analysis of samples with different compositions containing 0.8-2.0 mg/L 2,6-dichlorophenol its recovery ranged between 75-109%.

Statistic evaluation of CPs analysis from mixtures containing four compounds using five replicates is presented in table 6. There was some influence of chlorophenol concentrations on the relative standard deviation: when 2,4,6-TCP was the major compound like in sample l, for 4.0 mg/L were determined 4.65% and for 1.0 mg/L, 9.86%, in sample lll. The values of RSD corresponding to the other compounds in concentrations of 1.0 mg/L each other, were closed 7.48-9.86% and were not appeared to be influenced by different concentrations of the major compounds. In case of 4-CP, 2,4-DCP, and phenol for 2.0-3.0 mg/L closed values were obtained for relative standard deviation, 6.25-7.81%.

The mean recoveries determined both for the major compounds, 96-98% and the minor compounds, 88-97.6%, from the above samples revealed good results using the multicalibration method. These are similar with those reported for the analysis of 4-dihydropyridine (DHP) calcium antagonists together with its photoproducts, and of some dyes used as additives for cosmetics [8, 11].

TABLE 6. Determination of CPs content from samples l-lll using five replicates

CPs	mg/L	mean	mean recovery (%)	SD	RSD (%)	C.I. P=95%
2,4,6-TCP (l)	4.0	3.84	96.0	0.179	4.65	0.156
2,6-DCP (l)	1.0	0.88	88.0	0.066	7.48	0.058
2,4-CP (l)	1.0	0.934	93.4	0.078	8.41	0.069
4-CP (l)	3.0	2.93	97.6	0.192	6.55	0.168
2,4,6-TCP(ll)	3.0	2.91	97.0	0.152	5.21	0.133
2,6-DCP (ll)	1.0	0.901	90.1	0.085	9.45	0.074
2,4-DCP (ll)	3.0	2.94	98.0	0.184	6.25	0.161
2-CP (ll)	1.0	0.914	91.4	0.089	9.8	0.078
2,4,6-TCP(lll)	1.0	0.976	97.6	0.096	9.86	0.084
2,6-DCP (lll)	1.0	0.93	93.0	0.088	9.54	0.077
2,4-DCP (lll)	3.0	2.93	97.8	0.201	6.84	0.176
phenol (lll)	2.0	1.92	96.0	0.150	7.81	0.131

SD = standard deviation, RSD = relative standard deviation, C.I.= confidence interval

4. Conclusions

The multicalibration method allows the determination of chlorophenols from quaternary mixtures in water solutions with good results. The mean recoveries from mixed samples containing 3.0-4.0 mg/L CPs were 96-98% and for 1.0 mg/L, 88-97.66%. Relative standard deviation determined for the same concentrations ranged between 4.65-5.21% and 7.48-9.86%, respectively. The method is not time consuming, is useful for the analysis of different aromatic derivatives from their mixtures and must be developed for on-line monitoring of water treatment.

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