SPECTROPHOTOMETRIC MULTICOMPONENT ANALYSIS APPLIED TO PRIORITY POLLUTANT
CHLOROPHENOLS. STANDARD SPECTRA BY MULTIVARIATE CALIBRATION.

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ABSTRACT

A multicomponent analysis method is proposed for the determination
of chlorophenols, applying diode array derivative spectrophotometry. The method
is based on formation of ion-pairs with tetrabutylammonium nitrate as counte-
rion and extraction in chloroform at pH 9.1. Prediction and quantitative deter-
mination (concentration range 3-15 mgl^{-1}) of two, three and four component mix-
tures were possible using multivariate calibration of first derivative spectra.

INTRODUCTION

Chlorophenols are widely used in pesticide formulations. The presen-
ce of chlorophenols in water, soil, food and animal feed stuffs presents a
potential hazard owing to their toxicity. Spectrophotometric determination
of these phenols is of limited use because of overlapping of their absorption
bands (1). The need for reliable determination of chlorophenols has led to the
development of a number of sophisticated analytical methods (2-5) mainly using
chromatographic techniques (HPLC and GC). However, in laboratories where large
number of samples must be processed rapidly a method with sufficient sensitivi-
ty and selectivity, which can be used for preliminary screening, has obvious
advantages.

This paper describes the development of a method for the determina-
tion of chlorophenols using diode array derivative spectrophotometry. The me-
thod is based on formation of ion-pairs with tetrabutylammonium nitrate as
counterion and extraction in chloroform at pH 9.1.

Prediction and quantitative determination of two, three and four com-
ponent mixtures was possible using multivariate calibration (6) of first deri-
vative spectra and multicomponent analysis computer programme based on least
squares linear regression.

EXPERIMENTAL PART

Reagents

Pentachlorophenol (99% pure, Carlo Erba) o-chlorophenol (99% pure, Carlo Erba), 2,4-dichlorophenol (99% pure, Aldrich-Chemic), 4-chloro-3 methyl phenol (99% PURE? Aldrich-Chemie) and 2,4,6-trichlorophenol (98% pure, Carlo Erba) were used for preparing 150 and 50 mgl^{-1} stock solutions. Standard working solutions of the chlorophenols were prepared by suitable dilution of the stock solutions with water. A 5000 mgl^{-1} stock solution of tetrabutylammonium nitrate (98% pure, Fluka Chemie AG) was also used.

The pH was adjusted with a 0.1M phosphate buffer (pH 9.1). Spectrophotometric grade chloroform (Carlo Erba) was used for extraction. All chemicals used were analytical grade and water was obtained using a Milli Q apparatus.

Apparatus

A detection system consisted of a diode array HP 8452 A spectrophotometer equipped with 1 cm path length silica cell. The spectrophotometer was interfaced to an HP Vectra AT computer and a HP Think Jet printer.

Procedure

Aliquots of chlorophenol solutions containing two, three or four chlorophenols in the 3-15 mgl^{-1} range were transfered into a 10 ml beaker and the following reagents were added: 3 ml of the tetrabutylammonium nitrate solution and 3 ml of the phosphate buffer solution; the volume was made up to the mark with water. This solution was treated with 10 ml of chloroform in a 100 ml extraction funnel and stirring for 3 min. The absorbance of the organic extract was measured between 280-400 nm against the blank.

RESULTS AND DISCUSSION

The first derivative standard spectra of chlorophenols (2-chlorophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol and pentachlorophenol) has been obtained from twenty quaternary mixtures containing chlorophenols in concentrations between 3-15 mgl^{-1}. Binary and ternary mixtures have been resolved using first derivative standard spectra of twenty binary and ternary mixtures containing chlorophenols in the concentration range 3-9 mgl^{-1}. The multicomponent computer programme allows the determination of each phenol in such mixtures in the wavelenght range 280-400 nm with relative errors below 5.4%. Results obtained from quaternary mixtures are shown in the table. As it can be seen the overlapping of ionic pair spectra in the range 280-400 nm does not prevent simultaneous determination of the four chlorophenols whose errors is acceptable for particular aplication.

MULTIVARIATE-MULTICOMPONENT D&TERMINATION OF QUATERNARY CHLOROPHENOLS MIXTURES

Mixture composition, results and errors

,4-dichlorophenol, mgl^{-1}			4-chloro-3methyl phenol, mgl^{-1}			2,4-dichlorophenol, mgl^{-1}			pentachlorophenol, mgl^{-1}		
dded*	Found	Error, %	Added*	Found	Error, %	Added*	Found	Error, %	Added*	Found	Error, %
.0	4.9	1.4	5.0	5.0	0.0	9.0	9.4	4.8	7.0	7.2	2.3
.0	9.1	1.5	11.0	11.1	1.0	9.0	8.7	3.5	5.0	4.9	1.4
.0	9.3	3.1	11.0	11.3	2.9	13.0	13.1	0.3	7.0	7.1	1.4
5.0	15.6	4.0	15.0	15.2	1.7	9.0	9.2	2.1	7.0	7.2	2.6
3.0	13.2	1.5	9.0	9.0	0.0	9.0	9.2	2.1	5.0	4.9	1.0
.0	5.1	2.6	11.0	10.8	1.6	3.0	2.9	0.3	9.0	9.1	1.2
.0	6.8	2.7	7.0	6.9	3.0	9.0	9.3	3.6	9.0	8.9	1.3

Mean of three determinations.

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