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Application of H-point standard addition method for spectrophotometric determination of 2-tert-butyl 4-methylphenol in the presence of bis(4-metyl hydroxy phenyl) methane

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ABSTRACT

H-point standard addition method (HPSAM) has been applied for determination of 2-tert-butyl 4-methylphenol which acts as an intermediate in the presence of Bis (4-metyl hydroxy phenyl) Methane (product) in trace levels. Absorbance of the mixed spectra at the two pairs of wavelengths, 274.8 and 290.6 nm were monitored with the addition of standard solutions of 2-tert-butyl 4-methylphenol. The method is able to accurately determine intermediate in the intermediate/product ratio of 1:10 (w/w). Accuracy and reproducibility of the determination method on the various known amounts were evaluated in their binary mixtures. To investigate selectivity of the method and to ensure that no serious interferences were observed the effects of different species on the determination of 2-tert-butyl 4-methyl phenol were also studied. The recommended procedure was successfully applied to some synthetic mixtures.

KEYWORDS

2-Tert-butyl 4-methylphenol;
Bis (4-metyl hydroxy phenyl) methane;
UV-vis spectrophotometry;
HPSAM.

INTRODUCTION

Because of the sterically hindered group, tert-butylphenolic compounds have an antioxidizing action and also act as UV stabilisers. 2-Tert-butyl-4-methylphenol is used as an intermediate for the preparation of antioxidants and stabilizers. It is also used in fragrances. Antioxidant is a substance added in small quantities to hydrocarbons which are susceptible to oxidation, such as rubbers, plastics, foods, and oils to inhibit or slow oxidative processes, while being itself oxidized[1]. Antioxidants work in two different ways. In primary antioxidants (also called free-radical scavengers), antioxidative activity is implemented by the donation of an electron or hydrogen atom to a radical derivative. These antioxidants are usually hindered amines (p-Phenylene diamine, trimethyl dihydroquinolines, alkylated diphenyl amines) or substituted phenolic compounds with one or more bulky functional groups such as a tertiary butyl at 2,6 position commonly. Butylated hydroxytoluene (BHT) is a common example of hindered phenolic antioxidant. Primary antioxidants are free radical scavengers which combine with proxy radicals and break autocatalytic cycle. In secondary antioxidants (also called peroxide decomposers), activity is implemented by the removal of an oxidative catalyst and the consequent prevention of the initiation of oxidation. Examples of peroxide decomposer type of antioxidant

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are trivalent phosphorous and divalent sulfur containing compound such as sulfides, thiodipropionates, organophosphites and Bis (4-metyl hydroxy phenyl) Methane. Synergistic effect is expected when primary antioxidants are used together with secondary antioxidants as primary antioxidants are not very effective against the degradation by UV oxidation.

Being widely used antioxidants, several methods have been reported for their determinations. For example, 2-tert-butyl 4-methylphenol have determined by liquid chromatography[2], HPLC[3] and micellar electrokinetic chromatography[4].

Bis (4-metyl hydroxy phenyl) Methane is synthesized from 2-tert-butyl 4-methylphenol according to the SCHEME 1[5]. Because of the low solubility of the product (Bis (4-metyl hydroxy phenyl) Methane) in aqua media, separation of the product is very simple.

According to our knowledge, there isn't any proposed method for determination of antioxidants by spectrophotometry methods. Since UV-visible spectrophotometry is a rapid, sensitive and inexpensive analytical tool, it is appropriate for control of antioxidant preparations. However, the lack of specificity of the UV-visible absorption usually hinders the application of this technique in case of mixtures of absorbing species, due to spectral overlap.

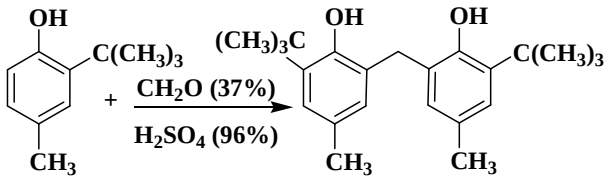
In the present work a very simple, sensitive, selective and low cost procedure for spectrophotometric determination of 2-tert-butyl 4-methylphenol in the presence of Bis (4-metyl hydroxy phenyl) Methane using H-point standard additions method is described. The method is based on the determination of the absorbances in an appropriate wavelength pair.

EXPERIMENTAL

Chemicals

2-tert-butyl 4-methylphenol and Bis (4-metyl hydroxy phenyl) Methane were purchased from Merck (Darmstadt, Germany).

A 1.0×10^{-3} mol/l 2-tert-butyl 4-methylphenol solution was prepared by dissolving 0.0164 g 2-tert-butyl 4-methylphenol (99%) in n-hexane and the solution was diluted to 100 ml in a 100-ml volumetric flask. More dilute solutions were prepared by serial dilution with n-hexane.



2-Tert-butyl-4-methyl phenol

Bis(4-methyl-2-tert-buthyl-hydroxy phenyl) methane

SCHEME 1: Chemical reaction between 2-tert-butyl 4-methylphenol and formaldehyde

A 1×10^{-3} mol/l Bis (4-metyl hydroxy phenyl) Methane solution was prepared by dissolving 0.034 g in n-hexane and diluting to 100-ml in a volumetric flask. More dilute solutions were prepared by serial dilution with n-hexane.

Apparatus

UV-vis absorption spectra are measured on an Agilent UV-Vis spectrophotometer, PerkinElmer (Lambda 25), with the use of 1.0 cm quartz cells.
A Pentium IV (2.53 MHz) computer controlled all of the setting and data processing.

Recommended procedure

An aliquot of the solution containing 2-tert-butyl 4-methylphenol and/or Bis (4-metyl hydroxy phenyl) Methane and 1.5 ml sulfuric acid solution (5 M) were added into a 10 ml volumetric flask and made up to the mark with n-hexane. The solution was then allowed to stand for 10 min at room temperature. After that a portion of the solution was transferred into a quartz cell to measure its absorbance at appropriate wavelength pair (274.8 and 290.6 nm for determination of 2-tert-butyl 4-methylphenol. The concentration range of 2-tert-butyl 4-methylphenol for construction of HPSAM calibration graph was 10–40 μmol/l.

RESULTS AND DISCUSSION

The absorption spectra of 2-tert-butyl 4-methylphenol and Bis (4-metyl hydroxy phenyl) Methane under certain experimental conditions are shown in figure 1. As can be seen the maximum wavelengths of two compounds are very close to each other and their spectra are highly overlapped. Therefore, determination of 2-tert-butyl 4-methylphenol in the presence of

Bis (4-metyl hydroxy phenyl) Methane is impossible by classical spectrophotometry. Therefore, it is necessary to use a chemometrics method to solve this problem.

H-point standard addition method

Consider an unknown sample containing an analyte X and an interferent Y. In this special system, 2-tert-butyl 4-methylphenol and Bis (4-metyl hydroxy phenyl) Methane were considered as the analyte and interferent, respectively. The determination of concentration of X by HPSAM under these conditions requires the selection of two wavelengths λ_1 and λ_2, at which the interferent species, Y, has the same absorbance.[6,7] Then, known amounts of X are successively added to the mixture and the resulting absorbances are measured at the two wavelengths and expressed by the following equations:

$$A_{(\lambda_1)} = b_0 + b + M_{\lambda_1} C_i \quad (2)$$

$$A_{(\lambda_2)} = A_0 + A + M_{\lambda_2} C_i \quad (3)$$

where, $A_{(\lambda_1)}$ and $A_{(\lambda_2)}$ are the analytical signals measured at λ_1 and λ_2, respectively. b_0 and A_0 ($b_0 \neq A_0$) are the original analytical signal of X at $A_{(\lambda_1)}$ and $A_{(\lambda_2)}$, respectively. b and A are the analytical signals of Y at $A_{(\lambda_1)}$ and $A_{(\lambda_2)}$, respectively. $M\lambda_1$ and $M\lambda_2$ are the slopes of the standard addition calibration lines at λ_1 and λ_2, respectively and Ci is the added X concentration. The two straight lines obtained intersect at the so-called H-point ($-C_H$, A_H).

At H-point, since $A_{(\lambda_1)} = A_{(2)}$, $C_i = C_H$, from Eqs. (2) and (3) it follows that:

$$b_0 + b + M_{\lambda_1}(-C_H) = A_0 + A + M_{\lambda_2}(-C_H) \quad (4)$$

$$-C_H = [(A_0 - b_0) + (A - b)]/(M_{\lambda_1} - M_{\lambda_2}) \quad (5)$$

From Eq. (5), if the component Y, is the known interferent and the analytical signal corresponding to Y, *b* (at λ_1 or λ_2) do not change with the additions of analyte, X, that is, b=A=constant, so:

$$-C_H = (A_0 - b_0)/(M_{\lambda_1} - M_{\lambda_2}) = -b_0 / M_{\lambda_1} \quad (6)$$

$$-A_0 / M_{\lambda_2} \quad (7)$$

where, $C_H = C_X$ corresponds to the analyte concentration in the mixture, because $-C_H$ depends only on variables related to the analyte[8].

If the value of $-C_H$ is included in Eq. (2), A_H, the ordinate value of the intersection point, will be described as follows:

$$A_H = b_0 + b + M_{\lambda_1}(-C_H) \quad (8)$$

as $b_0 = M_{\lambda_1} C_H$ then $A_H = b$

and similarly, $A_H = A$ (9)

Hence, A_H value is only related to the signal of the interferent Y at the two selected wavelengths. To evaluate the interferent concentration from the ordinate value of the H-point (A_H), a calibration graph or the absorbance value of an interferent standard is needed. Similarly, for determination of Y by HPSAM under these conditions, selection of two wavelengths λ_1 and λ_2, at which the species X, has the same absorbance is possible.

Wavelength selection

To select the appropriate wavelength pair for using HPSAM the following principles should be applied. At these selected wavelengths the analyte signals must be linear with concentrations and the interferent signal must be equal remains unchanged by changing the analyte concentration, the analytical signal obtained from a mixture containing the analyte and the interfering should be equal to the sum of the individual signals of the two components. In addition, the difference in the slopes of the two straight lines measured at two selected wavelengths (λ_1 and λ_2) must be as large as possible in order to get good accuracy and sensitivity[8-11].

For determination of 2-tert-butyl 4-methylphenol in the presence of Bis (4-metyl hydroxy phenyl) Methane, we selected one pair of wavelength on the Bis (4-metyl hydroxy phenyl) Methane spectra. In this case there were several pairs of wavelengths. As it is observed from figure 1, the best wavelength pair was 274.8 and 290.6 nm. Standard solutions of 2-tert-butyl 4-methylphenol and Bis (4-metyl hydroxy phenyl) Meth-

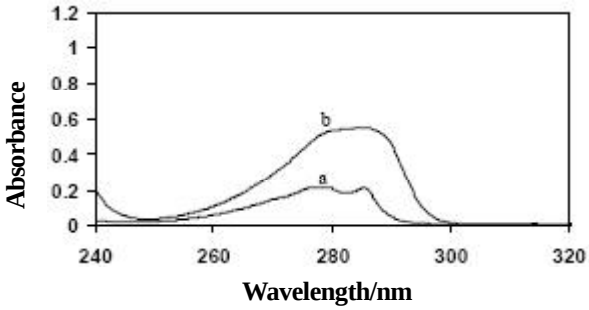


Figure 1:. Absorption spectra of (a) 100 μmol/l 2-tert-butyl 4-methylphenol (b) 100 μmol/l Bis (4-metyl hydroxy phenyl) Methane in n-hexane as a solvent

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ane were initially tested to validate the applicability of the chosen wavelength. Figures 2,3 are H-point standard addition calibration lines constructed at two selected wavelengths (274.8-290.6 nm) for determination of 2-tert-butyl 4-methylphenol in the present of Bis (4-metyl hydroxy phenyl) Methane. According to the characteristics of HPSAM at the H-point, C_H is independent of interferent concentration, but A_H is dependent of the interferent.

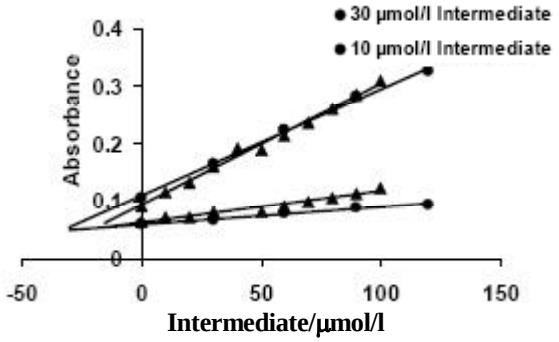

Figure 2: H-point standard addition plot for fixed Bis (4-metyl hydroxy phenyl) Methane concentration (10µmol/l) and different concentrations of 2-tert-butyl 4-methylphenol at wavelengths of 274.8 and 290.6 nm

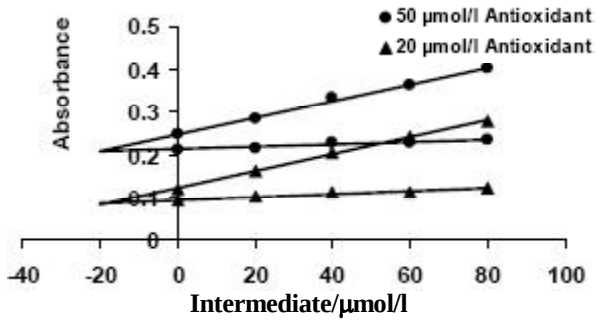

Figure 3: H-point standard addition plot for fixed 2-tert-butyl 4-methylphenol concentration (20 µmol/l) and different concentration of Bis (4-metyl hydroxy phenyl) Methane at wavelengths of 274.8 and 290.6 nm

Accuracy

Several synthetic samples with a different concentration ratio of 2-tert-butyl 4-methylphenol and Bis (4-metyl hydroxy phenyl) Methane were analyzed by using the suggested method. As can be seen from TABLE 1, the accuracy of the results is satisfactory in all cases.

TABLE 1: Determination of 2-tert-butyl 4-methylphenol in the presence of Bis (4-metyl hydroxy phenyl) Methane in some synthetic mixtures

A-C equation	R^2	Added/ µmol/l		Found/ µmol/l
		Intermediate	Product	Intermediate
A274.8 = 0.0020C + 0.1235	0.9976	20	20	18.50
A290.6 = 0.0004C + 0.0939	0.9404			
A274.8 = 0.0020C + 0.2490	0.9963	20	50	21.05
A290.6 = 0.0030C + 0.2132	0.9095			
A274.8 = 0.0019C + 0.1094	0.9972	30	10	31.62
A290.6 = 0.0030C + 0.0588	0.9903			
A274.8 = 0.0019C + 0.1611	0.9987	60	10	63.75
A290.6 = 0.0003C + 0.0591	0.9896			
A274.8 = 0.0017C + 0.2173	0.9963	10	50	9.39
A290.6 = 0.00006C + 0.2019	0.9020			

TABLE 2 : Results of the replicate measurements for determination of 2-tert-butyl 4-methylphenol in the presence of bis (4-metyl hydroxy phenyl) methan

A-C equation	R^2	Present in the sample/ µmol/l		Found/µmol/l
		Intermediate	Product	Intermediate
A274.8 = 0.0164C + 0.2476	0.9954	10.0	10.0	8.58
A290.6 = 0.0064C + 0.1655	0.9920			
A274.8 = 0.0165C + 0.2370	0.9916	10.0	10.0	9.05
A290.6 = 0.0062C + 0.1570	0.9840			
A274.8 = 0.0161C + 0.2477	0.9994	10.0	10.0	10.82
A290.6 = 0.0060C + 0.1620	0.9936			
Average				9.48
Standard deviation				1.18
A274.8 = 0.0147C + 1.7917	0.9985	50.0	10.0	53.17
A290.6 = 0.0060C + 1.2792	0.9942			
A274.8 = 0.0168C + 1.8898	0.9949	50.0	10.0	49.62
A290.6 = 0.0068C + 1.2909	0.8250			
A274.8 = 0.0167C + 1.9369	0.9810	50.0	10.0	54.14
A290.6 = 0.0064C + 1.3340	0.9020			
Average				52.31
Standard deviation				2.38

The good agreement between these results and known values indicates the successful applicability of proposed method for determination of two species when the concentration ratio of 2-tert-butyl 4-methylphenol and Bis (4-metyl hydroxy phenyl) Methane vary to 1:10.

Reproducibility of the method

To check the reproducibility of the method four replicate experiments for the analysis of mixtures were done (TABLE 2). A good standard deviation was obtained for two species in the mixtures.

Limit of detection

Limit of detection was calculated as LOD= $3S_{CH}$ [9], which S_{CH} is the standard deviation of several (n = 6) replicated measurements of zero concentration of analyte with the HPSAM. The corresponding value obtained for 2-tert-butyl 4-methylphenol was 0.25 μmol/l.

CONCLUSION

The suggested method shows that application of HPSAM can be well adopted for resolving binary mixtures of 2-tert-butyl 4-methylphenol and Bis (4-metyl hydroxy phenyl) Methane. The proposed method provides satisfactory results in synthetic and real mixtures. The method also offers good selectivity, accuracy and precision that did not report in the previous literatures.

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