

FIRST DERIVATIVE SPECTROMETRY FOR DETERMINATION OF A RUBBER ANTIOXIDANT

Zenovia Moldovan* and Laurenția Alexandrescu

abstract: The aim of our study was to develop a simple method for quantitative estimation of an amine antioxidant, namely 2,2,4 – trimethyl – 1,2 – dihydro – quinoline (TMHQ), used in the manufacture of industrial rubber. In order to avoid the influence of other polymer additives, the analysis of TMHQ was made by derivative spectrometry. Thus, by applying the first derivative spectrum of TMHQ, Beer's law has been valid in the concentration range 0.25-10 μ g TMHQ /mL. Measurements were made at 254 nm. At this wavelength, the first derivative spectra of the other polymer additives cross the zero line.

Introduction

Aromatic amines are widely used as rubber antioxidants in industry. Almost all methods reported for the estimation of the antioxidants are usually based on their separation from the other additives, after extraction from the polymer [1]. As an inexpensive alternative to the separatory techniques (HPLC [2], GC-MS [3], MS-HPLC [4], capillary liquid chromatography [5]), we have reported in recent papers [6÷8] a simple method for estimation of the antioxidant, by derivative spectrometry. As a continuation of these studies, the present work is concerned with the determination of TMHQ in presence of other additives, by first derivative spectrometry.

Experimental

Reagents

All the chemicals used were of analytical-reagent grade (Merck) and all the solutions were prepared in ethanol. The following vulcanization accelerators were selected: 2-cyclohexylbenzothiazil sulphenamide (CBS) and diphenylguanidine (DPG). The antioxidant used was 2,2,4 – trimethyl – 1,2 – dihydro – quinoline (TMHQ). As plasticizer, stearic acid (SA) was used. Stock solutions containing 100 μ g polymer additive/mL were prepared in ethanol. Working solutions were obtained by appropriate dilutions of the stock solutions with ethanol.

* Department of Analytical Chemistry, University of Bucharest, 90-92 road Panduri, Bucharest, ROMANIA

Apparatus

All absorption spectra and derivatives were recorded with a Jasco-V 530 UV-VIS double beam spectrophotometer, equipped with a pair of 1-cm path length quartz cells and interfaced to a compatible computer running a spectrophotometric software. This equipment allows a direct derivatization up to the third-order. The suitable wavelength at which derivative spectrum crosses the zero-line was linearly approximated from two neighbouring measurements. Suitable settings were: slit width, 1 cm; scan speed, 200 nm/min.

Procedure

Suitable volumes of stock solutions containing 100 μg polymer additive/mL were placed into the 10-mL calibrated flasks and brought to volume with ethanol. Also, mixtures of stock solutions containing suitable amounts of the investigated polymer additives were placed into the 10-mL standard flasks and diluted to the mark with ethanol. The absorption spectra of the samples were recorded between 220 and 350 nm, against ethanol. For the estimation of TMHQ, the value of the first derivative spectra was measured at the selected "zero-crossing" wavelength of the first derivative spectra of the other additives commonly presented in mixtures with TMHQ ($\lambda = 254$ nm).

Results and Discussion

Spectral characteristics of the polymer additives

In Fig. 1 the absorption spectra of the investigated polymer additives are shown. The spectra of TMHQ, CBS and DPG overlap considerably, while the spectrum of SA is insignificant in the 220 – 350 wavelength range. So, UV conventional spectrum of TMHQ is not suitable for its determination in presence of CBS and DPG.

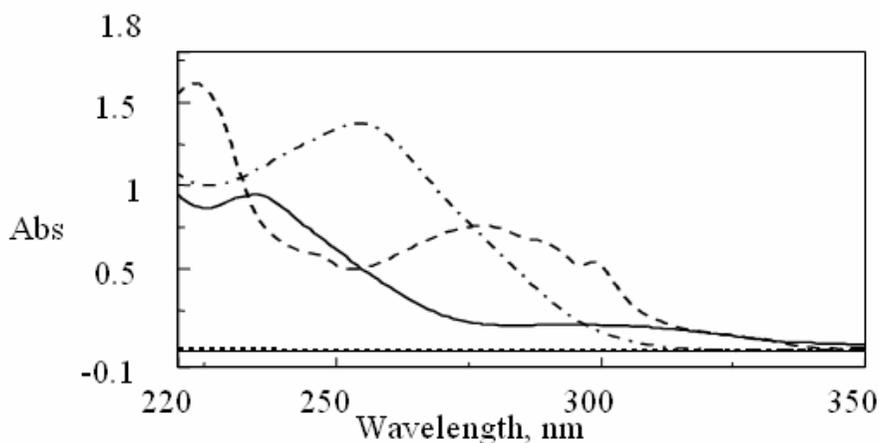


Fig. 1. Conventional UV spectra of some polymer additives.
TMHQ (—); CBS (---); DPG (- · - · -); SA (·····); $c_{\text{TMHQ}} = c_{\text{DPG}} = c_{\text{CBS}} = c_{\text{SA}} = 10 \mu\text{g/mL}$

First derivative absorption spectra of the polymer additives

Fig. 2 shows the first derivative synchronous spectra of the polymer additives in ethanol, recorded against the reagent blank. As we observe, at 254 nm the derivative signal of the accelerators CBS and DPG passes through zero, while that attributed to SA is zero. This point can be used for the determination of TMHQ in presence of CBS, DPG and SA, by applying the quantitative zero-crossing method [9]. Thus, when the first-derivative signals of the interferents (here CBS and DPG) are zero, the derivative spectrum of the analyte (TMHQ) is a function only of its concentration.

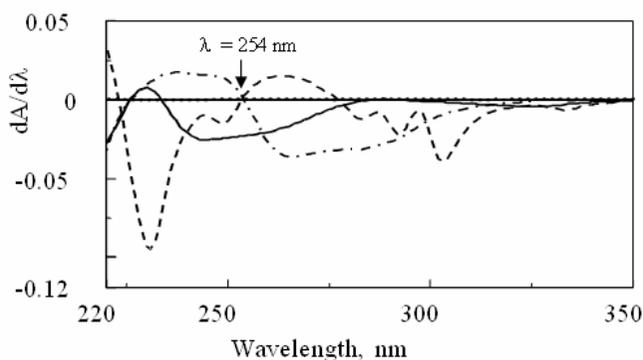


Fig. 2. First derivative spectra of some polymer additives
TMHQ (—); CBS (---); DPG (- · - · -); SA (····); $c_{\text{TMHQ}} = c_{\text{DPG}} = c_{\text{CBS}} = c_{\text{SA}} = 10 \mu\text{g/mL}$

Conformance to Beer's law

As is shown in Fig. 3, a reproducible straight line dependence of $dA/d\lambda$ signal with the concentration of TMHQ was obtained in the range 0.25-10 $\mu\text{g/mL}$.

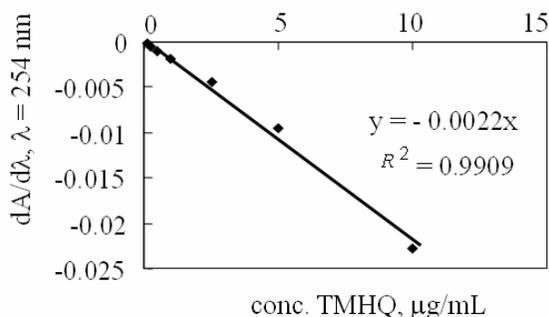


Fig. 3. Conformance to Beer's law, for the antioxidant TMHQ

Determination of TMHQ in synthetic mixtures

As preliminary tests, the spectrometric method has been applied to the quantitative analysis of TMHQ in several binary mixtures with each interferent, in different ratios. Table 1 summarizes the results calculated from the calibration graph. As it can be seen from Table

1, the determination of the antioxidant TMHQ can be easily and selectively performed in the presence of the other additives. Only DPG has a significant effect on the determination of TMHQ at a 4-fold excess with respect to TMHQ. In real samples, the studied polymer additives are added in the following ratio: TMHQ-CBS-DPG-SA = 1:2:2:3. For testing the validity of the proposed method, synthetic samples whose composition corresponds to real samples were prepared and general procedure applied for TMHQ determination. Table 2 shows the results obtained. As we observe, the first order derivative spectrometry applied to complex mixtures of rubber additives allows the determination of TMHQ in presence of three other constituents, in the concentration range 0.25-5 $\mu\text{g/mL}$, with a relative error not greater than + 6 %.

Table 1. Results of TMHQ determination in ternary mixtures by the use of the first derivative (mean values for three independent measurements; RSD = relative standard deviation)

TMHQ in sample, $\mu\text{g/mL}$	TMHQ found by first derivative *, $\mu\text{g/mL}$	RSD, %	Interferent, $\mu\text{g/mL}$
2.50	2.50	–	
2.50	2.44	– 2.40	CBS
2.50	2.40	– 4.00	10
2.50	2.50	–	
2.50	2.62	+ 4.80	DPG
2.50	2.75	+ 10.00	10
2.50	2.50	–	
2.50	2.50	–	SA
2.50	2.50	–	10

* Measurements were performed at $\lambda = 254 \text{ nm}$.

Table 2. Results of TMHQ determination in multicomponent mixtures by the use of the first derivative (mean values for three independent measurements; RSD = relative standard deviation)

TMHQ in sample, $\mu\text{g/mL}$	TMHQ found by first derivative *, $\mu\text{g/mL}$	RSD, %	Interferents, $\mu\text{g/mL}$ CBS DPG SA		
0.25	0.25	–	0.50	0.50	0.75
0.50	0.50	–	1.00	1.00	1.50
1.00	1.00	–	2.00	2.00	3.00
2.50	2.57	+ 2.80	5.00	5.00	7.50
5.00	5.29	+ 5.80	10.00	10.00	15.00
10.00	7.20	– 28.00	20.00	20.00	30.00

* Measurements were performed at $\lambda = 254 \text{ nm}$.

Conclusion

The first derivative spectrometric method proposed for determination of TMHQ is simple and permits its determination in multicomponent mixtures. Also, the preliminary step of separation of the polymer additives from each other is avoided. In our following

experiments, the determination of the antioxidant in real rubber samples, containing the studied polymer additives, will be performed.

REFERENCES

1. Wheeler, D.A. (1968) *Talanta* **15**, 1315-34.
2. Ruiz, M.A., Garcia-Moreno, E., Barabas C. and Pingarron, J.M. (1999) *Electroanalysis* **11**, 470-4.
3. Marinac, L., Jimenez, A., Vilaplanab, J., Lopez J. and Berenguera, V. (1998) *J. Chromatog. A* **819**, 289-96.
4. Egsgaard, H., Larsen, E., Pedersen W. and Carlsen, B. L. (1992) *Trends Anal. Chem.* **11**, 164-8.
5. Molanderaa, P., Hauglanda, K., Hegnab, D.R., Ommundsenb, E., Lundanesa E. and Greibrokka, T. (1999) *J. Chromatog. A* **864**, 103-9.
6. Moldovan, Z. and Alexandrescu, L. (2002) *Anal. And Bioanal. Chem.* **374**, 46-50.
7. Moldovan, Z. and Alexandrescu, L. (2003) *Rev. Roum. Chim.* **48**, 279-85.
8. Moldovan, Z. and Alexandrescu, L. (2002) *Acta Chim. Slov.* **49**, 909-16.
9. O'Haver, T.C. and Green H.L. (1976) *Anal. Chem.* **48**, 312.