

*Dedicated to the memory of
Professor Maria Brezeanu (1924–2005)*

SIMULTANEOUS ESTIMATION OF SOME POLYMER ADDITIVES BY THE SPECTROTOMETRIC METHOD

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The aim of this study was to propose a simple method for estimation, by UV-molecular absorption spectrometry, of the main polymer additives (the antioxidant and the vulcanization accelerator), present in rubber materials. The proposed procedure works without any separation step of the polymer additives from each other. 2-(2'-Hydroxy-5'-methylphenyl)-benzothiazole (HMB) was selected as antioxidant and 2-mercaptobenzothiazole (MBT), as vulcanization accelerator. Rubber mixtures containing the cited polymer additives were manufactured specially for this study. First derivative signal, measured at 234 nm, was used for the elimination of the mutual interferences of the other additives in the HMB estimation, while the determination of MBT was made on the basis of the absorbance measured at 325 nm. Beer's law was valid in the concentration range of 0.10-30 µg HMB/mL and 0.05-15 µg MBT/mL, respectively. The proposed spectrometric method was applied for HMB and MBT determination in synthetic mixtures of rubber additives and in rubber samples.

INTRODUCTION

The range of application for polymeric materials is increasing and, consequently, the number of additives available to improve polymer properties increases proportionately. Thus, besides the polymer and sulphur, a rubber mixture contains (as secondary constituents) one or more vulcanization accelerators, an antioxidant, a plasticizer and filling material. Antioxidants and accelerators are important additives in polymers. Generally, their analysis may be carried out by the examination of extracts. Thus, gas chromatography (GC),¹ gas chromatography–mass spectrometry (GC-MS),² thin layer chromatography (TLC),³ HPLC,⁴ size-exclusion and paper chromatography¹ are used for estimation of rubber additives after their extraction from the polymeric matrix. Also, for the determination of low levels of rubber antioxidants, many other high techniques were proposed, such as: supercritical fluid extraction combined with GC-MS,⁵ supercritical fluid and enhanced solvent extraction,⁶ size exclusion chromatography with UV, RMN and MS detection,⁷ capillary liquid chromatography.⁸ Other techniques are based on the analytical properties of thermal degradation products of additives such as: pyrolysis (Py),⁹ Py-GC and Py-GC-MS,^{10,11} or differential calorimetry.¹² Rubber additives are also evaluated by Fourier transform infrared spectrometry.¹³ Most of the analytical researches on rubber additives reported the high reactivity and low stability of antioxidants. These factors and the low concentrations of rubber additives normally used (0.01-5%), severely limit the analytical techniques which can be applied to the sample without prior separation of the antioxidants and accelerators from the polymer matrix and from the other additives.

The aim of our study was to find a method for the determination of the antioxidant and the accelerator, in ternary mixtures, without any separation step from each other and from the plasticizer. Although,

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chromatographic or coupled techniques are characterized by high selectivity, sensitivity and are giving reliable results, they still do not satisfy all the requirements for a routine analysis, mainly because of their complicated process design, time consumption or the need for expensive instruments. Taking into account that the polymer additives have UV spectrometric properties, we have proposed a simple spectrometric method for their estimation. Thus, the first derivative spectra allow to determine HMB at $\lambda = 234$ nm, while the measurement of the absorbance at 325 nm was used for the determination of the vulcanization accelerator MBT, in binary and ternary synthetic mixtures. Furthermore, we tested the proposed method for HMB and M determination in some rubber samples.

RESULTS AND DISCUSSION

Absorption spectra of the polymer additives

The analysis of polymer additives could be performed after their preliminary separation from the polymer matrix. Usually, such separations are made by solid/liquid extraction.¹¹ The liquid phase obtained after extraction contains also other polymer additives besides the plasticizer. All these additives have UV- molecular absorption spectra. But, UV spectrometry is not a good tool for the determination of polymer additives, since it is non-specific and subject to many interferences.¹⁴ Fig. 1 presents the UV-conventional absorption spectra of HMB (2-(2'-Hydroxy-5'-methylphenyl)-benzothiazole), MBT (2-Mercaptobenzothiazole) and SA (Stearic acid), in the wavelength range of $\lambda = 220$ –350 nm. As we observe, the spectra of HMB and MBT overlap considerably between 220 and 300 nm, while the spectrum of SA is insignificant in the whole wavelength range explored. The large overlap of the UV spectra of HMB and MBT prevents the use of direct absorbance measurements for HMB estimation, in the presence of the other additives.

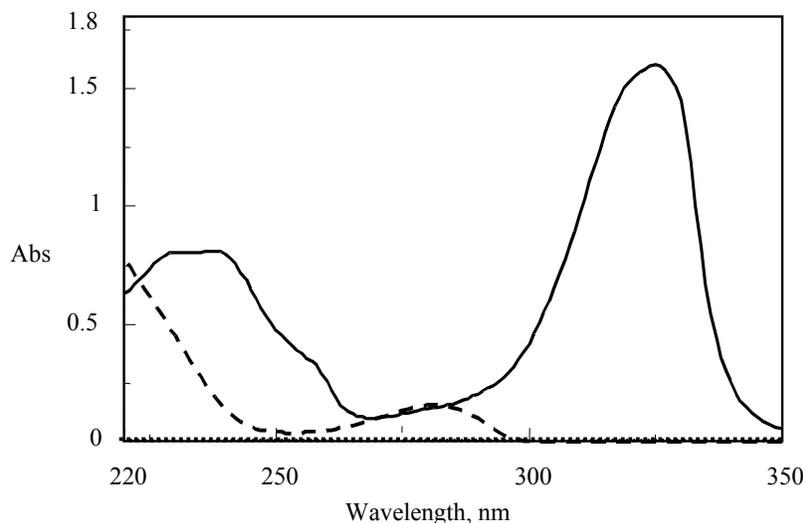


Fig. 1 – UV molecular absorption spectra of some polymer additives.
MBT (—); HMB (- - -); SA (.....); $c_{\text{MBT}} = c_{\text{HMB}} = 10$ $\mu\text{g/mL}$; $c_{\text{SA}} = 250$ $\mu\text{g/mL}$.

Derivative spectral characteristics of the investigated additives

Interferences in the direct ultraviolet molecular absorption spectrometry could be minimized or even avoided by applying the derivative spectrometry.^{15,16} The most common technique used for quantitative analysis is the zero-crossing method (ZCM).¹⁷ This method involves a measurement of the amplitude of the total derivative spectrum at an abscissa value (λ) corresponding to the zero-crossing point (ZCP) of the interfering components. So, at this wavelength, the derivative signal attributed to the interferences passed

through zero. In our study, preliminary tests were made to select the more convenient order of the derivative and working wavelength. Fig. 2 presents the overlapped first derivative spectra of HMB, MBT and SA. As we observe, the first derivative spectrum of MBT crosses the zero line at 234 nm while at the same wavelength the signal of SA is insignificant. Also, the simple measurement of the absorbance at 325 nm can be used for the estimation of MBT in the presence of the other additives. The main spectral characteristics, used for estimation of HMB and MBT, are presented in Table 1. Calibration graphs were linear in the concentration range 0.05-15 μg MBT/mL and 0.10-30 μg HMB/mL respectively. The intercepts for the calibration graphs were almost passing through the origin. The limit of quantification (LOQ), for the two analytes, were determined as the lowest concentration determined with an acceptable level of precision (so, with a coefficient of variance (CV) values less than 5%).

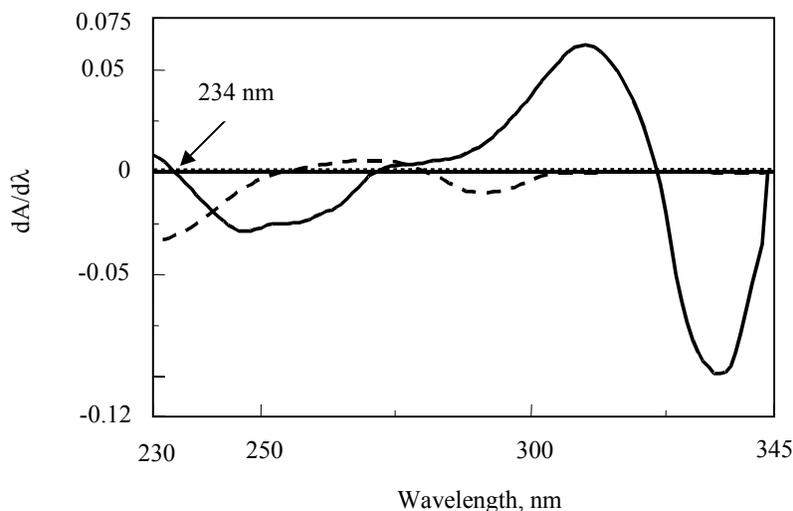


Fig. 2 – First derivative spectra of the studied polymer additives.
MBT (—); HMB (- - -); SA (·····); $c_{\text{MBT}} = c_{\text{HMB}} = 10 \mu\text{g/mL}$; $c_{\text{SA}} = 250 \mu\text{g/mL}$.

Table 1
Spectral characteristics of HMB and MBT

Analyte	Characteristics of calibration graphs					Conformance to Beer's law $\mu\text{g/mL}$
	Function	λ^a , nm	Linear regression equation	LOQ, $\mu\text{g/mL}$	Correlation coefficient, R^2	
MBT	$A = f(c)$	325	$y = 0.1609x + 0.0011$	0.1	0.9998	0,05-15
HMB	$dA/d\lambda = f(c)$	234	$y = -0.0024x - 0.0059$	0.5	0.9970	0.10-30

a) Wavelength at which the measurement of the analytical signal was made

The extension of the calibration graph over its linear range may be established by applying the procedure described above.¹⁸ For this purpose, the following parameters were calculated: A_i/c_i , M , S , $M \pm 2S$, where: c_i = concentration i of the analyte standard solution; A_i = analytical signal corresponding to the calculated concentration i ; S = standard deviation of A_i/c_i values; $M = \left(\sum_{i=1}^n A_i/c_i \right) / n$; n = number of standard solutions of the analyte. Then, the function $A/c = f(c)$ and the lines corresponding to M and $M \pm 2S$ values were overlapped on the same graph. The pairs of points (c , A/c) situated within the range $M \pm 2S$ indicate that the two analytes could be determined with a standard deviation of $\pm 2S$ between 0.5-40 $\mu\text{g/mL}$ for HMB and 0.1-25 $\mu\text{g/mL}$ for MBT (see Figs. 3 and 4). The main characteristics of the two extended calibration graphs are presented in Table 2. Although the antioxidant and the accelerator should be determined using the polynomial functions of the extended calibration graphs, for analytical purposes the linear ranges were used.

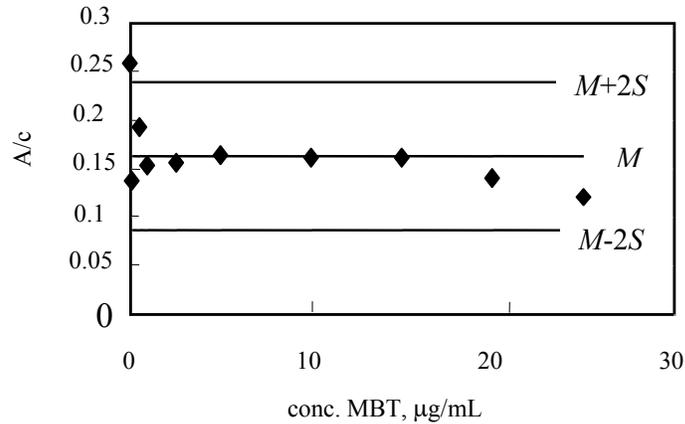
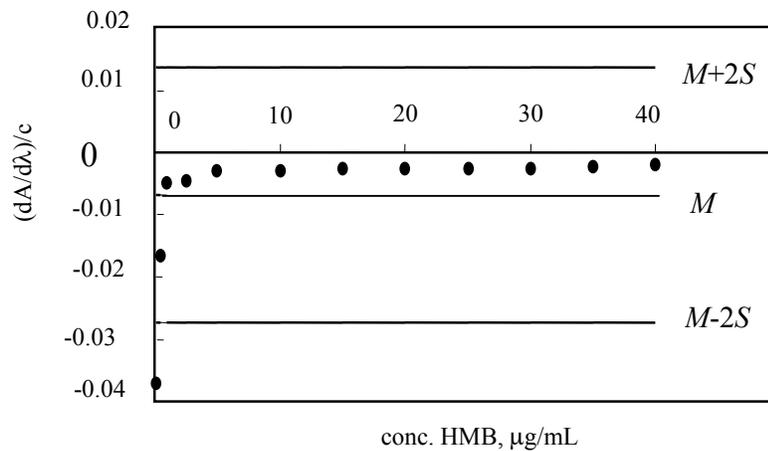
Fig. 3 – Correlation between A/c and c , for MBT.Fig. 4 – Correlation between $(dA/d\lambda)/c$ and c , for HMB.

Table 2

Characteristics of the extended calibration graphs

Analyte	Characteristics of extended calibration graphs			Working range, µg/mL
	Function	Polynomial equation	Correlation coefficient, R^2	
MBT	$A = f(c)$	$y = -0.0002x^3 + 0.0036x^2 + 0.146x + 0.0079$	0.9995	0,1-25
HMB	$dA/d\lambda = f(c)$	$y = 5E-08x^4 - 3E-06x^3 + 4E-05x^2 - 0.0025x - 0.0048$	0.9967	0.5-40

Determination of HMB and MBT in synthetic mixtures

As we have mentioned, the main interferent in the estimation of HMB could be the vulcanization accelerator MBT. In order to determine HMB and to verify if the proposed method was free from errors depending on the simultaneous presence of MBT, some binary synthetic mixtures were tested. Thus, a constant concentration of one of the two additives (5 µg/mL) was maintained in the presence of the other, over a range of concentrations between 5 and 15 µg/mL (to obtain a 1:1 to 1:3 ratio between the two investigated analytes). Then, the conventional spectra of binary mixtures, obtained against ethanol, were recorded and transformed in the first derivative. The concentrations of MBT and HMB were estimated as presented in the general procedure. As can be seen from Table 3, the concentration of the antioxidant and the vulcanization accelerator found are quite

consistent with those actually added to the binary mixture. The recoveries obtained were in the range of 100.7-102.0 % for MBT and of 94.4-97.5% for HMB; RSD were in the range of 0.89%-1.87% for MBT and of 3.42%-4.55% for HMB. On the basis of the obtained results and taking into account that in real rubber samples the mentioned additives are introduced together with stearic acid, a series of synthetic ternary mixtures were prepared and the proposed method applied for HMB and MBT estimation. In the prepared mixtures, the ratios were as in real samples (HMB-MBT-SA = 1:2:3). The results obtained are summarized in Table 4. As we observe, the proposed spectrometric method applied to ternary mixtures of rubber additives allows the determination of HMB and MBT, one in the presence of the other constituents, in the investigated concentration range. The recoveries obtained were in the range of 102.0-104.0 % for MBT and of 95.6-97.5% for HMB; RSD were in the range of 0.85%-2.11% for MBT and of 3.87%-4.25% for HMB.

Table 3

Results of HMB and MBT determination in binary mixtures by use of the proposed spectrometric methods

Ratio MBT/HMB	MBT, $\mu\text{g/mL}$		Recovery \pm RSD, % (n=3)	HMB, $\mu\text{g/mL}$		Recovery \pm RSD, % (n=3)
	in sample	found		in sample	found	
1:1	5	5.07	101.4 \pm 0.98	5	4.87	97.40 \pm 3.71
1:2	5	5.10	102.0 \pm 1.22	10	9.75	97.50 \pm 3.42
1:3	5	5.10	102.0 \pm 1.87	15	14.51	96.73 \pm 4.19
2:1	10	10.15	101.5 \pm 0.89	5	4.75	95.00 \pm 4.26
3:1	15	15.10	100.7 \pm 0.95	5	4.56	94.40 \pm 4.55

Table 4

Results of HMB and MBT determination in ternary mixtures^a

HMB, $\mu\text{g/mL}$		Recovery \pm RSD, % (n=3)	MBT, $\mu\text{g/mL}$		Recovery \pm RSD, % (n=3)
in sample	found		in sample	found	
5	4.78	95.60 \pm 3.95	2.5	2.60	104.00 \pm 2.11
10	9.75	97.50 \pm 3.87	5	5.10	102.00 \pm 1.99
15	14.54	96.93 \pm 4.25	7.5	7.65	102.00 \pm 0.85

a) Ratio HMB:MBT:SA = 1:2:3

Application

To evaluate the analytical applicability of the proposed method, it was tested to the determination of HMB and MBT in real samples, manufactured, extracted and then prepared according to the general procedure. We mention that, as we previously found, stearic acid introduced into the rubber samples, and which is to be extracted together with the other additives in acetone, does not interfere in the estimation of HMB and MBT. As is shown in Table 5, the amount of HMB extracted from rubber samples, and found spectrometrically, is less than the amount of HMB introduced in the rubber samples. It could be assumed that this behavior arises from the fact that antioxidants are labile unstable compounds;¹⁴ so, any loss of material is liable to be significant since the quantity of antioxidant present is initially so low. This results in a decrease of HMB in extract.

Table 5

Results of HMB and MBT determination in real samples^a

Sample	MBT, g/100g of sample		Recovery \pm RSD, % (n=3)	HMB, g/100g of sample		Recovery \pm RSD, % (n=3)
	in sample	found		in sample	found	
Vulcanized rubber	0.58	0.55	94.82 \pm 2.15	1.16	0.97	83.62 \pm 4.05

a) The rubber samples were manufactured according to the general procedure

EXPERIMENTAL

Materials

All the chemicals used were of analytical-reagent grade (Merck) and all the solutions were prepared in ethanol. One type of elastomer was used, namely nitrile rubber (NR). The specimen of elastomer was manufactured specifically for this study. The rubber extraction was made in acetone. As vulcanization accelerator, 2-mercaptobenzothiazole (MBT) was selected. The antioxidant used was 2-(2'-Hydroxy-5'-methylphenyl)-benzothiazole (HMB). As plasticizer, stearic acid (SA) was used. Stock solutions containing 100 µg polymer additive/mL were prepared in ethanol. Working solutions were obtained by appropriate dilutions of the stock solutions with ethanol.

Apparatus

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

Procedure

Procedure for spectra measurements

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 in the range 220-350 nm, against ethanol. For the determination of HMB, the value of the first derivative spectra was measured at the selected "zero-crossing" wavelength of the first derivative spectra of the other polymer additives existing in mixtures ($\lambda = 234$ nm) and compared with the calibration graph. The vulcanization accelerator (MBT) was estimated on the basis of its absorbance, measured at $\lambda = 325$ nm, and compared with its proper calibration graph.

Preparation of rubber mixtures

The rubber mixtures were manufactured with the additives in a certified formula. Thus, the ingredients were added to obtain a formulation which could be manufactured under normal industrial conditions, in the following proportions: elastomer (nitrile rubber), 100; zinc oxide, 5; silicon oxide (Zeosil 45), 40; chalk, 20; sulphur, 1.2; MBT, 1; HMB, 2; SA, 3. Preparation of the mixtures takes place at a temperature of approximately 60°C and the vulcanization process itself at around 160°C, under pressure.

Extraction

Extraction was performed on a weighed amount of the rubber specimen (2.5 g, cut into small pieces), in a Soxhlet extractor for 24 hours, with a defined volume of acetone, at the boiling temperature of the solvent. In order to minimize the decomposition and loss of the antioxidant during extraction, this was made under nitrogen. After evaporation to dryness in a vacuum, the obtained extract was dissolved in ethanol, filtered and then diluted, in order to be recovered with ethanol in a 100 mL calibrated flask. A portion of this solution (0.5 mL) was diluted to 25 mL with ethanol and the spectrum recorded.

Conformance to Beer's law

Into each of a series of 10 mL calibrated flasks, known volume of polymer additive solution (HMB or MBT) was transferred, diluted to the mark with ethanol and mixed. The absorption spectra of these solutions were recorded. The values of the absorbance at 325 nm were used for preparation of calibration graph for the vulcanization accelerator estimation. Then, the first derivative was applied and the analytical signal attributed to HMB was measured at $\lambda = 234$ nm.

CONCLUSION

Spectrometry, as a fast, simple and easy accessible technique, seems to be an efficient method, which may be used for the routine analysis of polymer additives, including vulcanization agents such as antioxidants and accelerators. In order to estimate the content of the main vulcanization agents without their preliminary separation from each other, the conventional (for accelerator MBT) and the derivative spectrometric methods (for antioxidant HMB) were applied. From the obtained results, it follows that the proposed methods for the determination of MBT and HMB are satisfactory in terms of accuracy and precision. Thus, the recoveries obtained were of 94.82% for MBT and of 83.62% for HMB; RSD were of $\pm 2.15\%$ for MBT and of 4.05% for HMB. Also, the proposed methods allow the estimation of percent of accelerator and of unmodified antioxidant, from the rubber sample, available after extraction in acetone.

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