

**DETERMINATION OF THE HMX AND RDX CONTENT IN SYNTHESIZED ENERGETIC MATERIAL BY HPLC, FT-MIR, AND FT-NIR SPECTROSCOPIES****Elizabeth C. Mattos\* e Enézio D. Moreira**

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Recebido em 28/4/03; aceito em 8/3/04; publicado na web em 27/05/04

DETERMINATION OF THE HMX AND RDX CONTENT IN SYNTHESIZED ENERGETIC MATERIAL BY HPLC, FT-MIR, AND FT-NIR SPECTROSCOPIES. A new method has been developed for determining the content of mixtures of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), the HMX/RDX ratio, in explosive compositions by Fourier transform infrared spectroscopy (FT-IR), in the regions MIR (mid infrared) and NIR (near infrared) with reference values obtained by chromatographic analysis (HPLC). Plots of relative MIR ( $A_{917} / A_{783}$ ) or NIR absorbance values ( $A_{4412} / A_{4317}$ ) versus HMX/RDX ratio determined by HPLC analysis revealed good linear relationships.

Keywords: energetic material; FT-MIR-NIR; HPLC.

**INTRODUCTION**

Energetic compounds, such as HMX and RDX, have been employed in several applications, propellants compositions, energetic binder explosive, etc<sup>1</sup>. The synthesis of HMX and RDX is performed by nitration of hexamine<sup>2,3</sup>. The formation of a by-product BMX (a mixture of RDX and HMX)<sup>4</sup> occurs in the process.

The synthesis of these high energetic solids is an important research developed in the CTA (Aerospace Technical Center)<sup>3</sup> and rapid methods for the quality control of laboratory synthesized products are necessary because these products, in suitable ratios, will be used in plastic bonded explosive (PBX) researches. Therefore, it is important to know the HMX and RDX contents in energetic compositions.

In a previous publication<sup>5</sup>, materials obtained during the synthesis of HMX were characterized by FT-IR transmission spectroscopy and/or Fourier transform infrared photoacoustic spectroscopy (FT-IR/PAS). The characterized species during the synthesis of HMX were  $\alpha$ -HMX,  $\beta$ -HMX, and HMX/RDX mixtures.

Different methods employing several techniques have been developed for determination of the HMX and RDX contents<sup>6</sup>. Some previous investigations of MIR methods have used Nujol mulls but this technique is susceptible to errors due to variations in mulling. The solution IR methods are not recommended when a great amount of HMX or RDX is used in energetic compositions due to the very low solubility of the explosive, at room temperature, in solvents suitable for IR analysis.

High performance liquid chromatography (HPLC) is used for the investigation of explosives in large extent<sup>7</sup>. Acetonitrile solvent is often employed to determine the HMX and RDX contents in energetic composition<sup>8</sup>. Although the HPLC method gives good results, there are several time consuming steps related to the sample preparation or measurements. An HPLC analysis takes three hours.

Considering that the acetonitrile is not suitable for IR solution analysis, an alternative method for determining HMX and RDX is proposed using another IR transmission technique (potassium bromide pellet).

In addition, NIR-spectroscopy has grown to become one of the most important tools for on-line analysis in process technology and quality control. It is sensitive like the MIR-spectroscopy and it is better applied to industrial environments<sup>9</sup>. Fast measurements of energetic materials showed that NIR-spectroscopy could also be used during the manufacture control of propellants and explosives<sup>10</sup>.

In the MIR/NIR method the solid samples are prepared for spectrometric analysis such as received, as KBr pellet. Several steps are eliminated and although the data of MIR and NIR methods represent the median of five analysis, the time spent in the analysis is smaller than that involved in the HPLC method.

Then, this paper presents a new quantitative method for determination of the HMX/RDX ratio based on HPLC data (reference values) and NIR and MIR spectroscopy (KBr technique). BMX samples, with its HPLC reference values, were used to develop the MIR/NIR methodology. The advantages of the methods here presented are that they involve few steps, and do not require complex sample preparation.

**EXPERIMENTAL PART**

The nitration of hexamine to yield crude HMX is conducted in a stirred jacketed reactor. The reactor is served by three head tanks, which are used to control the quantity and the addition rate of the three reactants, (a) acetic anhydride, (b) hexamine/acetic acid solution, and (c) nitric acid/ ammonium nitrate solution<sup>2,4</sup>.

The reactants are added into the reactor at carefully controlled rates in accordance with a programmed sequence. The temperature is maintained controlled during the process. At the end of the reaction period a volume of water is added and the mixture is simmered for a period to precipitate the HMX. An increase in the temperature causes

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the majority of unwanted by-products to be destroyed. The solid HMX is filtered hot and washed with water. The filtrate contains the by-product BMX that is later precipitated. It is necessary to control the content of BMX samples, because during the nitration of hexamine part is converted in RDX, and this has influence in the yield of reaction.

Chromatographic analyses were carried out in a model 481 HPLC Waters system, which was equipped with a 6000 A pump and a Lambda – Max 481, LC Spectrophotometer UV detector at 230 nm. A  $\mu$  Bondapak C<sub>18</sub> 125Å column, 10  $\mu$ m, 3.9 x 300 mm was used; methanol/water mixture 40/60 at a flow rate of 1.2 mL/min was used as mobile phase.

The total injection volume was 10  $\mu$ L (injector: U6 K universal of Waters). Acetonitrile was used as solvent for the explosives samples. The concentration of the substances in the sample solutions used was 10 mg/L. The internal standard used was o-nitroaniline (ONA). The evaluation of the data was done with a Waters system data module 730 (Pw = 16 and NR = 75). FT-IR analyses were performed on a 2000 Spectrum Perkin-Elmer spectrometer (resolution 4  $\text{cm}^{-1}$ ; gain 1; range 5200 to 3891  $\text{cm}^{-1}$  (NIR analysis) and 4000 to 400  $\text{cm}^{-1}$  (MIR analysis); 40 scans. The samples were analyzed by potassium bromide (KBr) technique (0.8: 400 mg in MIR analysis and 7:400 mg in NIR analysis). In this technique, a small amount, usually 1 to 3 mg, of finely ground solid sample, is mixed with approximately 400 mg powdered potassium bromide and then pressed in an evacuated die under pressure. The resulting discs are transparent and yield good spectra.

## RESULTS AND DISCUSSION

### Characterization of HMX/RDX by HPLC

The structures of HMX and RDX are illustrated in Figure 1.

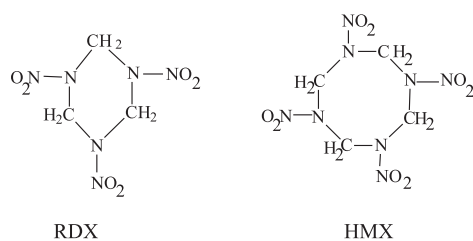


Figure 1. Structure for HMX and RDX

Substance characterization with HPLC analysis is done by the comparison of retention times of the standard o-nitroaniline and explosives (HMX and RDX). Figure 2 shows a typical chromatogram where the substances RDX and HMX appear very well separated

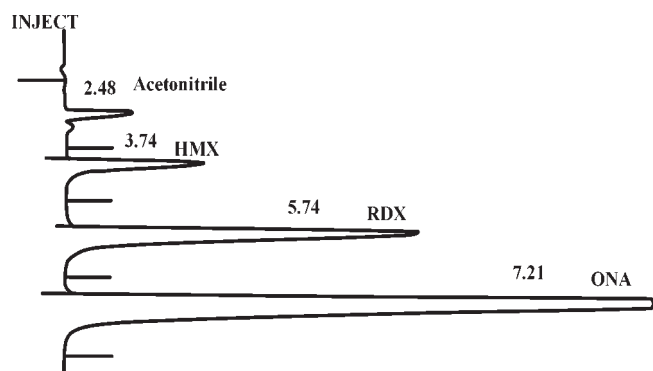


Figure 2. HPLC chromatogram of HMX/RDX (sample BMX SU 10/99)

under the conditions used. The data represent the average of the percentage composition of three analysis (Table 1), showing a maximum standard deviation of 1.30.

Table 1. HPLC data of explosives samples

Sample code	HMX content (wt-%)	RDX content (wt-%)	Standard deviation
BMX SU 16/99	28.74	71.26	1.30
BMX SU 08/99	24.00	76.00	0.05
BMX SU 12/99	22.60	77.40	0.35
BMX SU 10/99	17.15	82.85	0.08
BMX SU 05/99	15.00	85.00	0.20
BMX SU 01/99	11.60	88.40	0.06
BMX SU 14/99	8.60	91.40	0.07
BMX SU 12/00	6.10	93.90	0.04

### Quantitative analysis of HMX/RDX by FT-MIR

The FT-MIR spectra of HMX, RDX and HMX/RDX samples with different contents are shown in Figure 3. An increasing in the intensity of the absorption<sup>11-13</sup> at 783  $\text{cm}^{-1}$  ( $\delta$  and  $\gamma$   $\text{NO}_2$ ) is observed as the RDX content increases, associated with the decreasing of the ring<sup>13</sup> absorption intensity at 917  $\text{cm}^{-1}$  ( $\nu$  ring) as the HMX content decreases. These features may be a suitable analytical method to quantify the HMX/RDX content in the samples of BMX.

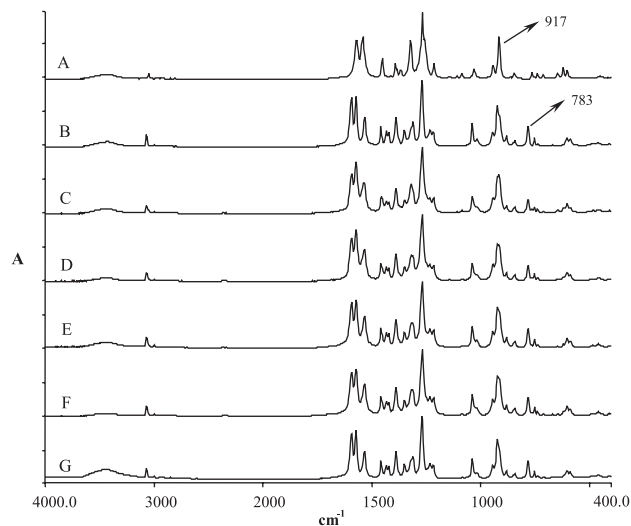


Figure 3. Overlaid FT-MIR spectra of A) HMX (100%), B) RDX (100%); HMX/RDX mixtures in increasing RDX order: C) BMX SU 16/99 (0.403), D) BMX SU 12/99 (0.292), E) BMX SU 10/99 (0.207), F) BMX SU 05/99 (0.176), G) BMX SU 14/99 (0.094) samples (HMX/RDX characteristics related to sample codes are indicated in Table 1)

When more than one constituent is present, the FT-IR quantitative determination becomes more complex. This quantitative determination requires a measurement of peak heights from the infrared spectra and a calculation of the ratios between peaks. The ratio method is used for calculation of blends when one is unable to measure with accuracy the thickness of the sample<sup>14</sup>. Therefore, in the FT-MIR quantitative analysis of HMX/RDX samples, the absorbance values at 917  $\text{cm}^{-1}$  (HMX) were related to those corresponding to the  $\delta$  and  $\gamma$   $\text{NO}_2$  absorption at 783  $\text{cm}^{-1}$  (RDX). The baseline points at 986 and 820  $\text{cm}^{-1}$  were considered in the calculations of absorbance values for the ring absorption at 917  $\text{cm}^{-1}$ . The calculations of absorbance

values for  $\delta$  and  $\gamma$  NO<sub>2</sub> absorption at 783 cm<sup>-1</sup> considered the baseline points at 820 and 720 cm<sup>-1</sup>.

Based upon in this simple examination of Beer's law, in accordance to the methodology used by Gedeon *et al.*<sup>14</sup>, an understanding of the limitations for the use of KBr pellets technique in quantitative analysis can be undertaken. To apply Beer's law to this analysis, the data obtained must be plotted versus the composition ratios of the explosives. The same method was used for NIR analyses.

Table 2 presents the  $A_{917}/A_{783}$  ratio as function of HMX/RDX ratio (wt-%), obtained by HPLC. The absorbance values represent the median ( $\mu$ ) of five analysis. According to Hórák<sup>15</sup>, with a low number of experimental values it may happen that the values of parameters  $\hat{\mu}$  and  $\hat{\sigma}$  thus determined are subject to larger errors, which are difficult to determine due to a non-uniform distribution of random errors in the set. Then a difference assessment is made. The values of  $\mu$  were determined by the median  $\hat{x}$  instead of the arithmetic mean. The standard deviation,  $\hat{\sigma}_\mu$  of the median absorbance is calculated as follows<sup>15</sup>:

$$\hat{\sigma}_\mu = \frac{\hat{\sigma}}{\sqrt{n}} \quad (1)$$

where  $\hat{\sigma}$  is the assessed standard deviation of the basic set and is a quantitative measure of the precision for each individual measurement;  $n$  is the number of experiments.

$$\hat{\sigma} = K_R \cdot R \quad (2)$$

where  $K_R$  is the coefficient for the calculation of the average standard deviation from the variation range (for five experiments,  $K_R = 0.430$ )<sup>15</sup>; and  $R$  is the difference between the largest and the smallest element ( $X_n - X_1$ ).  $\hat{\sigma}_\mu$  is an evaluation of the precision of this median, that is, an evaluation of the result obtained from the treatment of a finite set of measurements which are repeated under completely identical conditions. The relative error for each sample was determined as follows:

$$\text{relative error (\%)} = \left( \frac{\hat{\sigma}_\mu}{\mu} \right) \times 100 \quad (3)$$

Figure 4 shows the plot  $A_{917}/A_{783}$  versus HMX/RDX ratio (wt-%). From the calibration curve (Table 2) taken by FT-IR/HPLC analysis, the following relationship ( $R=0.994$ ) is proposed:

$$y = 1.552 + 2.493 x \quad (4)$$

where  $y$  is the median relative absorbance ( $A_{917}/A_{783}$ ) and  $x$  is the HMX/RDX ratio.

To calculate the HMX and RDX content, the median absorbance value ( $A_{917}/A_{783}$ ) must be related to the equation 4 to found relative concentration [HMX/RDX]. After, the equation 5 must be used:

$$[\text{HMX}] + [\text{RDX}] = 100\% \quad (5)$$

### Quantitative analysis of HMX/RDX by FT-NIR

The FT-NIR spectra (region 5200 to 3891 cm<sup>-1</sup>) of HMX, RDX and HMX/RDX samples with highest contents HMX or RDX are shown in Figure 5. The criteria employed for the wavelength selections in the NIR method was similar to the one used in the MIR method. The analysis of the NIR spectra of HMX and RDX and its main peaks showed that the band at 4317 cm<sup>-1</sup> is characteristic of RDX, and the band at 4412 cm<sup>-1</sup>, although near to RDX a band, was choosed as characteristic of HMX. According to Goddu<sup>17</sup>, these analytical absorptions are in the C-H combination band region. Then, both of these values were selected as the analytical peaks for the NIR methodology.

An increase in the intensity of the absorption at 4317 cm<sup>-1</sup> is observed as the RDX content increases. On the other hand, the increase of the absorption intensity at 4412 cm<sup>-1</sup> is observed when the HMX content increases. These features are the basis of a suitable analytical method to quantify the HMX/RDX content in the mixtures of these explosives.

For FT-NIR quantitative analysis in HMX/RDX samples, the absorbance values at 4412 cm<sup>-1</sup> (HMX) were related to those corresponding to the absorption at 4317 cm<sup>-1</sup> (RDX). The baseline points at 4554 cm<sup>-1</sup> and 4240 cm<sup>-1</sup> were established in calculations of the absorbance values.

Table 3 presents the  $A_{4412}/A_{4317}$  ratio as function of HMX/RDX ratio (wt-%) as obtained by HPLC. The absorbance values represent

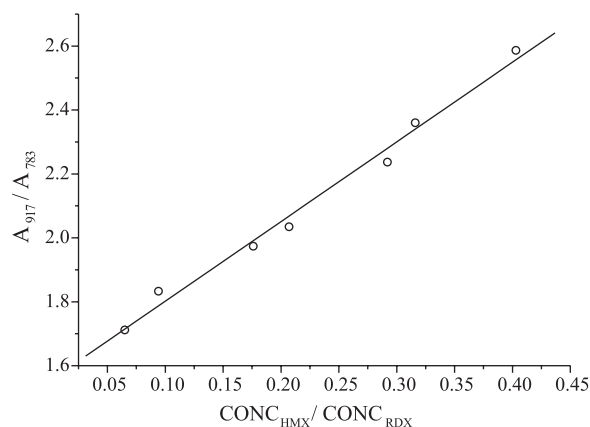
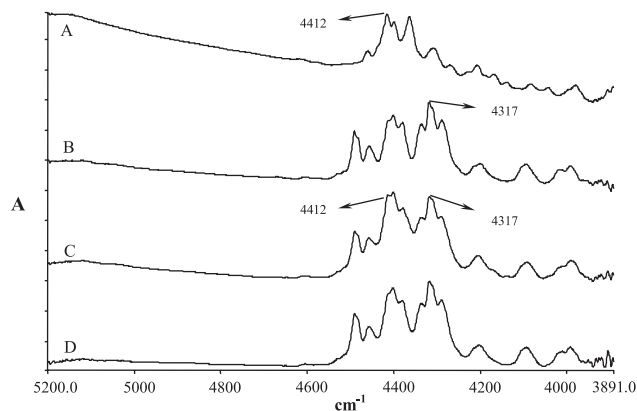


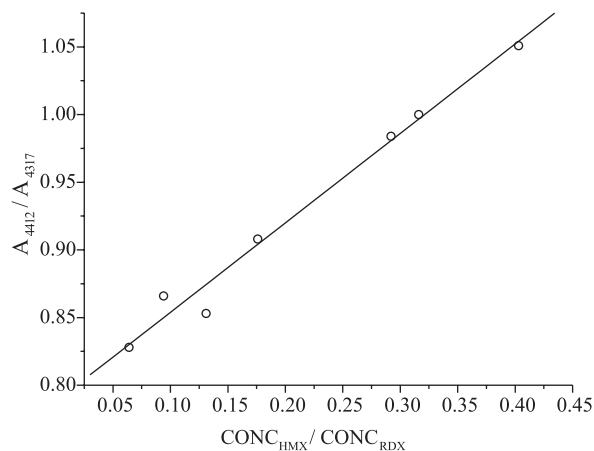
Figure 4. Plot of absorbance  $A_{917}/A_{783}$  versus HMX/RDX ratio (wt-%)

Table 2. FT-MIR data of HMX/RDX samples with different contents

Sample code	Conc.HMX/Conc.RDX	$A_{917}/A_{783}$ (median)	Standard deviation ( $\hat{\sigma}_\mu$ )	Relative error (%)
BMX SU 16/99	0.403	2.587	0.074	2.85
BMX SU 08/99	0.316	2.360	0.015	0.63
BMX SU 12/99	0.292	2.237	0.038	1.68
BMX SU 10/99	0.207	2.035	0.009	0.45
BMX SU 05/99	0.176	1.974	0.031	1.57
BMX SU 14/99	0.094	1.833	0.010	0.52
BMX SU 12/00	0.065	1.712	0.007	0.43



**Figure 5.** Overlaid partial FT-NIR spectra of A) HMX (100%), B) RDX (100%), C) BMX SU 16/99 (0.403), D) BMX SU 14/99 (0.094) samples (HMX/RDX characteristics related to sample codes are indicated in Table 1)



**Figure 6.** Plot of absorbance  $A_{4412}/A_{4317}$  versus HMX/RDX ratio (wt-%)

**Table 3.** FT-NIR data of HMX/RDX samples with different contents

Sample code (run)	Conc.HMX/ Conc.RDX	$A_{4412}/A_{4317}$	Standard deviation ( $\hat{\sigma}_\mu$ )	Relative error (%)
BMX SU 16/99	0.403	1.051	0.001	1.01
BMX SU 08/99	0.316	1.000	0.003	0.30
BMX SU 12/99	0.292	0.984	0.001	0.66
BMX SU 05/99	0.176	0.908	0.001	1.02
BMX SU 14/99	0.094	0.866	0.001	1.38
BMX SU 01/99	0.131	0.853	0.001	1.72
BMX SU 12/00	0.065	0.828	0.001	0.12

**Table 4.** Precision Data from MIR and NIR analysis

Sample code	Conc. HMX/RDX by HPLC method (reference values for MIR and NIR method)	Conc. HMX/RDX by MIR method	Conc. HMX/RDX by NIR method	Relative error (MIR) (%)	Relative error (NIR) (%)
BMX SU 16/99	28.74 / 71.26	29.34 / 70.66	28.47 / 71.53	2.85	1.01
BMX SU 08/99	24.00 / 76.00	24.48 / 75.52	24.30 / 75.10	0.63	0.30
BMX SU 12/99	22.60 / 77.40	21.56 / 78.44	22.83 / 77.16	1.68	0.66
BMX SU 10/99	17.15 / 82.85	16.23 / 83.77	—	0.45	—
BMX SU 05/99	15.00 / 85.00	14.46 / 85.54	15.32 / 84.67	1.57	1.02
BMX SU 14/99	8.60 / 91.40	10.13 / 89.87	10.55 / 89.45	0.52	1.38
BMX SU 01/99	11.60 / 88.40	—	8.95 / 91.05	—	1.72
BMX SU 12/00	6.10 / 93.90	6.07 / 93.96	5.70 / 94.30	0.43	0.12

the median ( $\mu$ ) of five analysis. The standard deviation,  $\hat{\sigma}_\mu$ , of the median absorbance and relative error were calculated as in MIR analysis. Figure 6 shows the plot of  $A_{4412}/A_{4317}$  versus HMX/RDX ratio (wt-%). From the calibration curve (Table 3) taken by FT-IR/HPLC analysis, the following relationship ( $R=0.991$ ) is proposed:

$$y = 0.788 + 0.661 x \quad (6)$$

where  $y$  is the median relative absorbance ( $A_{4412}/A_{4317}$ ) and  $x$  is the HMX/RDX ratio.

To calculate the HMX and RDX content, the median absorbance value ( $A_{4412}/A_{4317}$ ) must be related to the equation 6 to found relative concentration [HMX/RDX]. After, the equation 5 must be used.

The precision data obtained from analyses by both procedures

(MIR and NIR) are shown in Table 4. The samples BMX SU 10/99 (NIR analysis) and BMX SU 01/99 (MIR analysis) were used as test samples for the curves.

## CONCLUSIONS

A new method by FT-MIR/NIR has been developed and compared to HPLC for determining the content of mixtures of HMX and RDX, high energetic compounds used in explosive compositions.

Since the main subject of this work was to provide a rapid method for quality control of laboratory synthesized HMX, one can consider that MIR and NIR methods fulfilled these requirements. NIR and MIR methods should be used where more accuracy and precision is required, since that deviations from the accurate values do not usually

exceed 1-2% of the transmittance scale, according precision limits of used spectrometer. It was also observed that both MIR and NIR methods applied to this determination are comparable to each other in ease of use and faster and cleaner (without cleaning of the glassware) than the HPLC techniques. HPLC, MIR and NIR analysis showed good agreement. Based upon results obtained on BMX references values the present method can be used for control of the BMX compositions unknowns.

#### ACKNOWLEDGMENTS

We thank Mr. Gilson da Silva for suggestions on the final manuscript.

#### REFERENCES

1. Chan, M. L.; Roy, E. M.; Turner, A.; *US pat. 5,316,600* **1994**.
2. Robbins, R.; Boswell, B. C.; *US pat. 3,770,721* **1973**.
3. Mattos, E. C.; *Tese de Mestrado*, Instituto Tecnológico de Aeronáutica, Brasil, 2001.
4. Royal Ordnance, Explosives Division: Bridgwater, 1987, Commercial in Confidence; report unpublished.
5. Mattos, E. C.; Viganó, I.; Dutra, R. C. L.; Diniz, M. F.; Iha, K.; *Quim. Nova* **2002**, *25*, 722.
6. Grindlay, J. W.; *Anal. Chem.* **1972**, *44*, 1676.
7. Kaiser, M.; *Propellants, Explos., Pyrotech.* **1998**, *23*, 309.
8. Mattos, E. C.; Dutra, R. C. L.; Diniz, M. F.; Otani, C.; Iha, K.; *Anais do III Encontro Técnico de Materiais e Química*, Rio de Janeiro, Brasil, 1999.
9. Kathryn, A. B. L.; *Appl. Spectrosc.* **1993**, *28*, 231.
10. Eisenreich, N.; Kull, H.; Hertz, J.; *25<sup>th</sup> International Annual Conference of ICT*, Karlsruhe, Germany, 1994.
11. Litch, H. H.; *2<sup>o</sup> Symposium on Chemistry Problems with the Stability of Explosives*, Tyninge, Sweden, 1970.
12. Achuthan, C. P.; Jose, C. L.; *Propellants, Explos., Pyrotech.* **1990**, *15*, 271.
13. Smith, A. L.; *Applied Infrared Spectroscopy*; John Wiley & Sons: New York, 1979.
14. Gedeon, B. J.; Ngyuen, R. H.; *128<sup>th</sup> Meeting of rubber Division*, Cleveland, Ohio, 1985.
15. Hórák, M.; Viték, A.; *Interpretation and Processing of Vibrational Spectra*, John Wiley & Sons: New York, 1978.
16. Dutra, R. C. L.; Lourenço, V. L.; Diniz, M. F.; Azevedo, M. F. P.; Barbosa, R. V.; Soares, B. G.; *Polym. Bull.* **1996**, *36*, 593.
17. Goddu, R. F.; *Adv. Anal. Chem. Instr.* **1960**, *1*, 347.