

# Determination of CHN Content in Energetic Binder by MIR Analysis

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**Abstract:** Azide polymers samples were analyzed by FT-MIR in order to develop a quantitative methodology to determine the C, H and N content in energetic polymers used in propellants. The elemental analysis data were used as reference. The FT-MIR results show a good agreement with CHN analysis. A good linear relationship was obtained suggesting that the methodology developed in the CTA laboratory can be used for quality control of these energetic polymers.

**Keywords:** FT-IR, energetic binders, mid-IR region (MIR), C, H, N, O content.

## Introduction

The elastomeric binder of a composite system like propellants plays an important role in dispersing and immobilizing the fuel material and oxidizer. The materials used in the binder normally burn with lower energy than does the fuel material itself. Therefore the binder imposes limits on the energy content that can be recovered from the fuel material. In order to minimize this limitation some energetic binders can be used since they can release much more energy when they are burned together with the fuel material<sup>[1]</sup>. The energetic binders are the ones that have in their structure chemical groups with high energy content such as azide, nitrate, difluoroamine, nitro and nitroamine, etc.

A formulation using this energetic binder system can result in a propellant with better performance<sup>[2]</sup>. They are the so called modern solid propellants<sup>[3]</sup> and are expected to give higher burning rate and specific impulse when used for rockets.

One<sup>[4]</sup> of the aims of the joint project between CTA/IAE – Chemistry Division, Department of Analysis (Brazil) and ICT (Energetic Materials group) is to synthesize some energetic binders that can have several applications including the use in propellants. The following compounds, 3-Azidomethyl-3-methyl oxetane (AMMO), 3,3-Bis-azidomethyl oxetane (BAMO), 3-Bromomethyl-3-methyl oxetane

(BrMMO), Poly-AMMO, Poly-BAMO and Poly-BrMMO, have been characterized by several methods including MIR spectroscopy<sup>[5,6]</sup>.

To establish the relation between structure and properties of a composite solid propellants is important to know the structure of the elastomeric binder that has been used in the system. Therefore this study<sup>[7]</sup> has concentrated in the characterization in a wide spectral band of infrared, NIR/MIR/FIR, of all thermoplastic elastomers (TPE's) that has been synthesized at ICT, which will therefore, allows the identification of analytical bands for future quantitative and kinetic studies of these compounds.

A quantitative analytical method using MIR has been developed at CTA/IAE (Chemistry Division-analytical department) for CHN determination of the TPE's that has been synthesized at ICT (poly AMMO, poly BAMO and copolymers of poly AMMO/BAMO). The CHN elemental analysis has been used as reference.

## Experimental

The TPE's samples used in this study, as mentioned before have been synthesized at ICT (AK 81 Poly BAMO; AK 97 Poly BAMO; AK 96 Poly AMMO; AK 101 Poly AMMO; AK 98 Poly AMMO/BAMO; AK 120 Poly AMMO/BAMO;

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AK 109 Poly AMMO/BAMO) following a method that has already been described in the literature<sup>[4]</sup>.

The MIR spectra have been acquired at CTA using FT-IR spectrometer SPECTRUM 2000 PERKIN ELMER, in the region of 4000 to 400  $\text{cm}^{-1}$ , gain 1, resolution of 4  $\text{cm}^{-1}$  and 40 scans. The samples were analyzed by the KBr pellet technique (0.8:400 mg). Due to the uncertainty inherent to this technique, each sample has been analysed ten times in order to reach higher accuracy in the results.

For the quantitative analysis of the compounds using MIR, the values of the stretching frequencies at 2100  $\text{cm}^{-1}$  ( $\nu_a \text{N}_3$ ) have been related to the ones corresponding to C-O group at 1100  $\text{cm}^{-1}$ . The baseline points at 2358  $\text{cm}^{-1}$  and 1779  $\text{cm}^{-1}$  were established for the calculations of the absorbance values of the  $\text{N}_3$  groups at 2100  $\text{cm}^{-1}$  and the baseline points at 1779  $\text{cm}^{-1}$  and 841  $\text{cm}^{-1}$  established for calculations of the absorbance values of C-O absorption at 1100  $\text{cm}^{-1}$ . The values of the relative absorbance  $A_{2100}/A_{1100}$  represent an average value ( $\mu$ ) of 10 measurements of each sample.

For the calibration curve, the CHN values measured at ICT<sup>[8]</sup> for the compounds, have been used as reference.

## Results and Discussion

The chemical structure of the compounds and their starting materials that have been used in this work are presented in Table 1.

The frequencies and assignments of AMMO; BAMO; PolyAMMO and PolyBAMO are compiled in Table 2 and the spectra shown in Figures 1 to 3.

## MIR analysis of AMMO and BAMO

As it has been mentioned in previous paper<sup>[7]</sup>, the main difference between AMMO and BAMO chemical structures is the methyl group at AMMO and one additional azide group at BAMO, which can be visualized at the IR spectra (Figure 1). The assignments of the bands are in Table 3. The peak at 1382  $\text{cm}^{-1}$  ( $\delta_s \text{CH}_3$ ) is attributed to  $\text{CH}_3$  group and the peaks at 2100  $\text{cm}^{-1}$  ( $\nu_a \text{N}_3$ ), 2500  $\text{cm}^{-1}$  ( $2 \nu_s \text{N}_3$ ), 1250  $\text{cm}^{-1}$

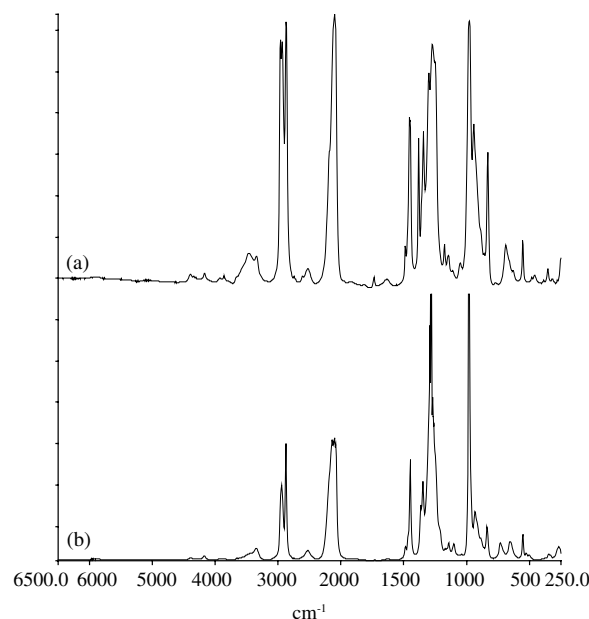


Figure 1. IR spectra of a) AMMO; and b) BAMO.

Table 1. Monomers and polymers studied in this work.

	Monomer	Polymer
AMMO		
BAMO		
Poly-AMMO /BAMO		

**Table 2.** Mid IR frequencies (4000-400  $\text{cm}^{-1}$ ) of the energetic binder<sup>[3-5]</sup>.

Poly(AMMO) ( $\text{cm}^{-1}$ )	AMMO ( $\text{cm}^{-1}$ )	BAMO ( $\text{cm}^{-1}$ )	Poly (BAMO) ( $\text{cm}^{-1}$ )	Tentative assignments
3340	3344	3345	3401	$(\nu_a + \nu_s)N_3 / \nu \text{ OH}$
-	2965	2945	2929	$\nu_a \text{ CH}_3 / \nu_a \text{ CH}_2$
2882	2873	2877	2874	$\nu_s \text{ CH}_3 / \nu_s \text{ CH}_2$
2542	2523	2524	2546	$2\nu_s N_3$
2125	2101	2102	2106	$\nu_a N_3$
1485	-	-	-	$\delta_a \text{ CH}_3$ and $\delta_s \text{ CH}_2$
1452	1455	-	-	$\delta_a \text{ CH}_3$ and $\delta_s \text{ CH}_2$
-	-	1449	1444	$\delta_a \text{ CH}_3$ and $\delta_s \text{ CH}_2$
-	1382	-	-	$\delta_s \text{ CH}_3$
1376	1344	1348	-	-
1299	1274	1279	1301	$\nu_s N_3$
-	1177	1143	1138	$\nu \text{ CN}$
1091	-	1102	1101	$\nu \text{ C-O/ring stretch}$
1047	-	-	-	$\nu \text{ C-O/ring stretch}$
-	980	981	-	$\nu \text{ C-O/ring stretch}$
943	944	-	-	$\nu \text{ C-O/ring stretch}$
-	-	934	934	$\nu \text{ C-O/ring stretch}$
884	-	-	-	$\nu \text{ C-O/ring stretch}$
-	833	839	-	Ring stretch / $\rho \text{ CH}_2$
665	689	733	-	$\rho \text{ CH}_2$
-	-	657	641	$\rho \text{ CH}_2$

$\nu$  – stretching;  $\nu_a$  – asymmetrical stretching;  $\nu_s$  – symmetrical stretching;  $\delta_a$  – in plane asymmetric bending;  $\delta_s$  – in plane symmetric bending;  $\rho$  – rocking vibration; and  $w$  – wagging.

( $\nu_s N_3$ , or  $\nu \text{ C-N}$ ) are attributed to azide group. It can also be observed that for BAMO the vibrational mode for  $N_3$  broadens and/or increase in the intensity, which can be attributed to the presence of two azide groups in the compound.

#### MIR analysis of AMMO and PolyAMMO

The main change observed in IR spectroscopy due to the polymerization of AMMO is the opening of the oxetane ring with the formation of the C-O bond. In the spectra of the polymer one can notice the absence of the band related to the ring at  $980 \text{ cm}^{-1}$  (ring stretching) and the appearance of the new bands typical of C-O ( $1000\text{-}1100 \text{ cm}^{-1}$  -  $\nu \text{ C-O}$ ), and OH ( $3340 \text{ cm}^{-1}$  -  $\nu \text{ OH}$ ) attributed to the end groups of the polymer (Figure 2).

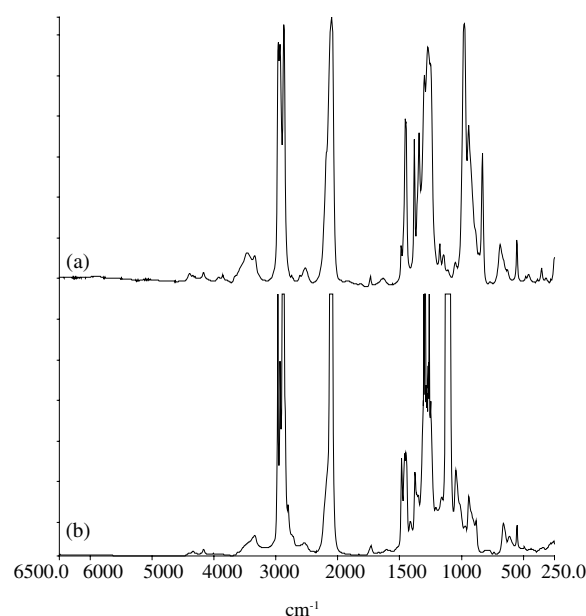
The broadening of the bands at the C-O group region (aliphatic ether) is due to the repetition of the units in the polymer (Figure 2).

#### MIR analysis of BAMO and PolyBAMO

The main changes observed in IR spectrum due to the polymerization of BAMO are basically the ones that have been observed for AMMO (ring opening and C-O formation) and shown in Figure 3.

#### Measurement of CHNO of the PolyAMMO and polyBAMO through MIR technique

The relative absorbance  $A_{2100}/A_{1100}$  and the CHN content (measured at the analytical department of ICT)<sup>[8]</sup> for all sev-

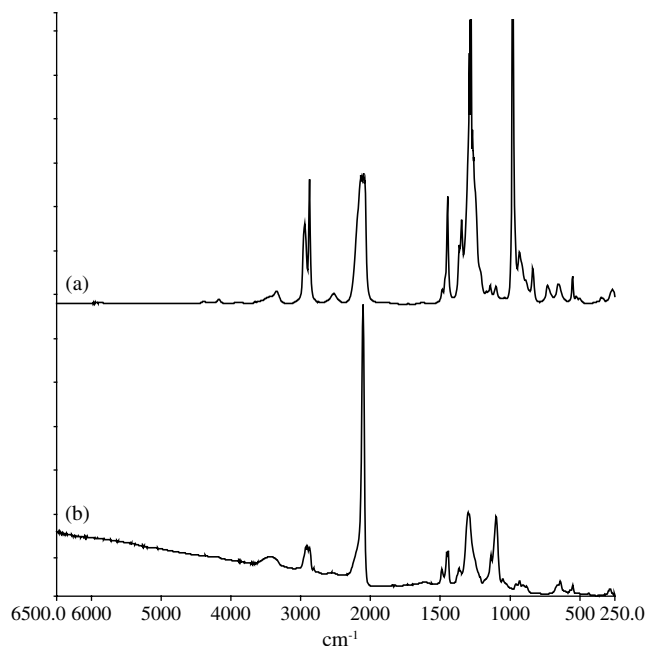
**Figure 2.** IR spectra of a) AMMO; and b) PolyAMMO.

en samples of polyAMMO and polyBAMO, are presented in Table 3. The standard deviation  $\sigma_\mu$ , of the average value of the absorbance is calculated according to the equation<sup>[9]</sup>:

$$\sigma_\mu = \sigma / \sqrt{n} \quad (1)$$

**Table 3.** MIR data of the energetic binders with different CHN contents.

Sample	%[C]	%[H]	%[N]	%[O]	%[N]/ %[C]	%[N]/ %[O]	Absorbance $A_{2100}/A_{1100}$	Standard deviate $\sigma_{\mu}$	Relative deviate (%)
AK 81 Poly (BAMO)	36.30	5.03	45.30	13.40	1.25	3.38	3.992	0.203	5.09
AK 97 Poly (BAMO)	36.38	4.77	43.56	15.29	1.20	2.85	3.858	0.071	1.84
AK 96 Poly (AMMO)	47.87	7.38	27.33	17.42	0.57	1.57	2.370	0.055	2.32
AK 101 Poly (AMMO)	46.74	7.16	27.85	18.25	0.60	1.53	2.616	0.016	0.61
AK 98 Poly (AMMO)/BAMO	41.88	5.73	39.30	13.09	0.94	3.00	3.403	0.033	0.97
AK 120 Poly (AMMO)/BAMO	43.65	6.34	32.33	17.68	0.74	1.83	2.781	0.032	1.15
AK 109 Poly (AMMO)/BAMO	44.41	6.23	32.96	16.40	0.74	2.01	2.776	0.032	1.15

**Figure 3.** IR spectra of a) BAMO and b) Poly BAMO.

$\sigma$  is the standard deviation and  $n$  the number of measurements.

$\sigma$  is represented by:

$$\sigma = K_R \cdot R \quad (2)$$

$K_R$  is the coefficient for the calculation of the standard deviation in a range of values and  $R$  is the difference between the higher and lower value

$$R = X_n - X_1 \quad (3)$$

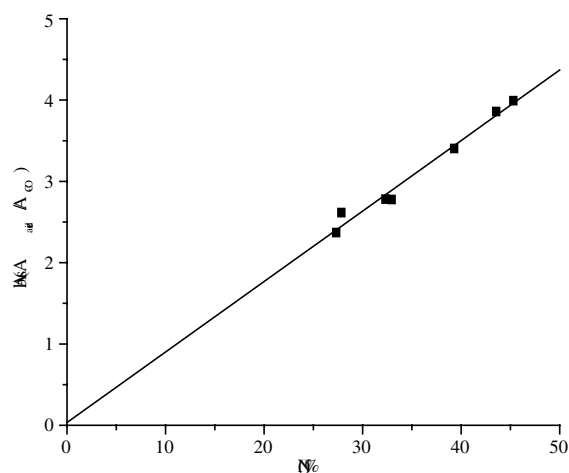
The relative error for each sample has been determined according to the following equation:

$$\text{Relative Error (\%)} = (\sigma_{\mu}/\mu) \times 100 \quad (4)$$

Figure 4 shows the analytical or calibration curve  $A_{2100}/A_{1100}$  vs. %N of the energetic binders. A good linear relationship was obtained ( $R = 0.990$ ) and is represented by the following equation:

$$y = 0.034 + 0.087x \quad (5)$$

Where:  $y$  is the average value of the absorbance  $A_{2100}/A_{1100}$  and  $x$  is the %N value.

**Figure 4.** Values of absorbance ( $A_{2100}/A_{1100}$ ) vs. %N by elemental analysis.

The curves of  $A_{2100}/A_{1100}$  vs. %N/C and  $A_{2100}/A_{1100}$  vs. %N/O have been also built to establish correlation with the content of C and O.

Figure 5 shows the calibration curve  $A_{2100}/A_{1100}$  vs. %N/C for the energetic binders. A good linear relation was obtained ( $R = 0.993$ ) and is represented by the following equation:

$$y = 1.131 + 2.297x \quad (6)$$

Figure 6 shows  $A_{2100}/A_{1100}$  vs. %N/O. A good linear relation was also obtained ( $R = 0.954$ ). The following equation represents the curve:

$$y = 1.245 + 0.809x \quad (7)$$

The average relative error inherent to the MIR method is equal to 1.48%, which is inside the precision of IR methods in general ( $\leq 2\%$ ), mentioned in the Literature<sup>[9]</sup>.

The 2,4-Toluene diisocyanate (TDI) was used to link the block PolyBAMO to block PolyAMMO in the copolymer synthesis Poly-AMMO/BAMO. Their structure is shown in Table 1. The contribution of TDI to the nitrogen content of the copolymer was also investigated. Therefore, it is lower than 1.0 wt. (%) weight of total nitrogen in the copolymer, then it does not play any important role in this method.

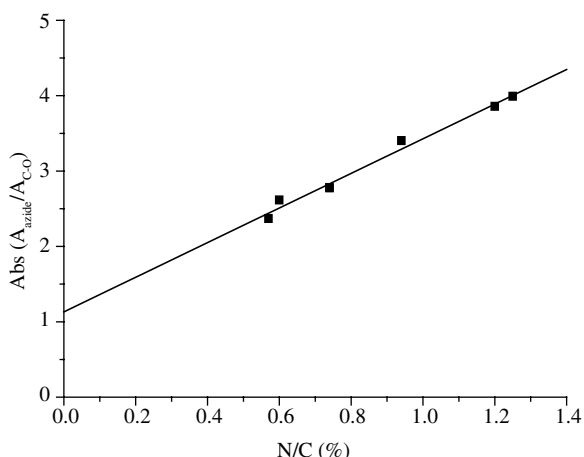


Figura 5. Values of absorbance ( $A_{2100}/A_{1100}$ ) vs. %N/C by elemental analysis.

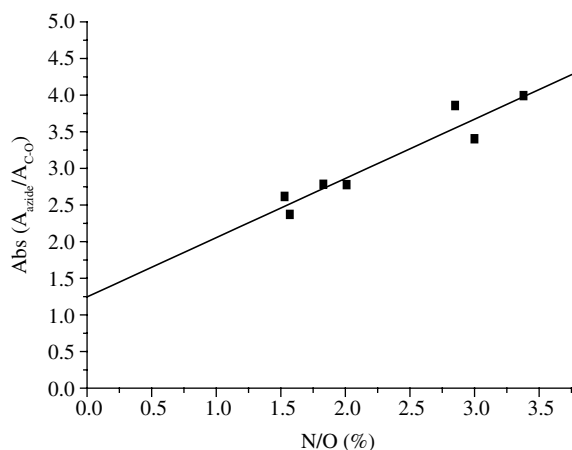


Figura 6. Values of absorbance ( $A_{2100}/A_{1100}$ ) vs. %N/O by elemental analysis.

#### Measurement of CHNO for sample AK 113 using MIR methodology

Sample AK 113 (Poly AMMO) was used as test sample for the method as it had an unknown CHNO content. It was used to verify the accuracy of the method.

The  $A_{2100}/A_{1100}$  measured value was 2.564 ( $\sigma_u = 0.015$  and relative deviation = 0.59%). The %C, %N and %O in the sample were measured using the three (Equations 5, 6 and 7) calibration curves. From the equations the following values were determined: %N = 29.08, %C = 46.60% O = 17.84 and %H = 6.48. These values are in a good agreement with the CHNO obtained from other similar samples of PolyAMMO as can be seen in Table 3.

Considering that CHN analysis has the same precision of IR, that IR is a technique available in the majority of analytical laboratories and the accuracy of the results obtained, the methodology developed can be a simple and quick alternative for the quality control of energetic binders.

## Conclusion

The use of IR spectroscopy in the MIR region for characterization and quantification of the amount of CHN in energetic binders, showed to be a good alternative to elemental analysis. The new method is simple, quick and precise enough to be used in the quality control of those compounds in industry.

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