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# TG/MS/FTIR STUDY OF THERMAL DECOMPOSITIONS OF SOME BABY TEATS

BY

**ANDREEA MIHĂILĂ[1], MĂDĂLINA MACOVEI[1], LĂCRĂMIOARA MAIECZKI[1], MARINA VODUŢ[1], NIŢĂ TUDORACHI[2] and GABRIELA LISĂ[1,*]**

[1]"Gheorghe Asachi" Technical University of Iaşi, Romania,
"Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection
[2]"Petru Poni" Institute of Macromolecular Chemistry, Iaşi, Romania

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**Abstract.** Our research consisted of the determination of the mass losses and degradation products in gaseous state obtained further to the analysis of teats used for the feeding of babies by means of the TG/MS/FTIR technique. The TG curve profiles are similar in the teats made of silicone rubber, the resulting residue amounting to 57%. The teat made of latex is almost fully degraded, the resulting amount of residue being only 0.5%. The analysis of the MS spectra obtained at 371°C temperature has provided information of the main ionic fragments resulting during the thermal decomposition onset stage. The findings were also confirmed by the FTIR spectra recorded for the same temperature. Our research also confirmed the presence of Bisphenol A in one of the two teats made of silicone rubber.

**Keywords:** thermal decompositions; TG/MS/FTIR; baby teats; Bisphenol A.

[*]Corresponding author; *e-mail*: gapreot@ch.tuiasi.ro

## 1. Introduction

Mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR) are two frequently used methods of analysis of degradation products in the gaseous state obtained by thermogravimetric analysis (TGA). The advantage is that they may provide simultaneous information about the degradation products and about the mass loss. In other words, they are used for the quantitative and qualitative analysis of gaseous mixture components (Duemichena *et al.*, 2014).

The TG/MS/FTIR technique used to analyze certain materials that different baby feeding utensils are made of is extremely important as it may reveal the presence of harmful substances, such as Bisphenol A (BPA). Unfortunately, researchers have proven that this chemical industrial toxin BPA is a form of synthetic estrogen which penetrates the skin and has harmful effects on human health (Kaddar *et al*., 2008). Some studies have shown that the structure of this compound is very similar to that of the estradiol hormone, as it is able to bind and activate the same estrogen receptor as the natural hormone. Bisphenol A is an organic agent obtained only through synthetic chemical means from acetone, further to condensation reactions. Since BPA is not the result of biosynthesis, there are no enzymes capable of degrading such compounds. Thus, once in the body, the structure of Bisphenol A remains unchanged, which increases its harmfulness.

Bisphenol A, as a substance present in different materials from which it may get into the body, was forbidden in a very small number of countries worldwide (Denmark, France), although the harmful action of this compound has been proven. The EU has taken action to forbid the use of BPA in feeding bottles, teats and pacifiers since early 2011. The toxicity of Bisphenol A for the human body has been proven both in the USA and in the EU. Only those plastic materials containing Bisphenol A which release harmful compounds one way or another are dangerous for humans and especially for children. Feeding bottles and pacifiers containing BPA are particularly dangerous since they are all the time in contact with saliva and release harmful toxins directly into the baby’s body.

As it has already been proven (Vandenberg *et al.*, 2013), Bisphenol A causes endocrine disorders (it disrupts the functioning of the thyroid gland and has an estrogenizing effect). This compound also affects the central nervous system, especially in children. Far-reaching studies (Taylor *et al.*, 2011; Zalko *et al.*, 2011) conducted over the years have shown that BPA supports the onset of obesity and adipose mass development. Nowadays it is common knowledge that Bisphenol A is carcinogenic (Acevedo *et al.*, 2013) and that it may cause sterility in both men and women. There are clinical studies that have shown that Bisphenol A supports the onset of type II diabetes mellitus.

As a continuation of the work carried out by our research team (Mihăilă *et al.*, 2017), this paper is aimed at analyzing the gaseous products resulting from the thermal decomposition in the air of three types of teats by means of the joint TG/MS/FTIR technique.

## 2. Experimental

*Materials*

The materials subjected to thermogravimetric analysis are 3 types of baby teats. The teat marked B3 is made of latex and is yellow-brownish. The teats B1 and B2 are made of silicon rubber and they are transparent.

*Methods*

In last years coupled techniques have become popular and have been successfully applied to obtain solutions of many analytical problems. Thermogravimetric analysis (TGA) coupled with Fourier transform infrared spectroscopy (FTIR) and with mass spectroscopy (MS) is a good practical example of this type.

TG/MS/FTIR technique is used to analyze thermal behavior but also to investigate the kinetics of thermal degradation. This method can be used for a lot of investigations including monitoring of evolving of volatile products in situ as a function of temperature. One of the major advantages is system ability to gather continuously and simultaneously quantitative and qualitative informations about the gases evolved in the technique. One disadvantage is the incapability to detect the presence of high molecular weight components of the studied sample.

This analyzes technique offer information about the decomposition mechanism of small molecules. Fourier transformed infrared spectroscopy (FTIR) and mass spectroscopy (MS) are two common detection methods used for TGA analyses for the rate of degradation of gaseous products.

The coupled technique consist in transfer the gases from the TGA instruments like a heated transfer line for avoiding the condensation. After the transfer, applying the FTIR technique adds specificity to entire method. For experimental work, the installation is formed by a thermogravimetric analyzer, a mass spectrometer and a FTIR spectrometer. FTIR analyze offer information that are not obtained after applying TG and MS techniques. TG, MS and FTIR techniques work well together to give a complete picture of the decomposition of studied sample.

In this analyzes usually pure argon is used as a purge and protective gas. Gaseous products are after conducted to the FTIR spectrometer and mass spectrometer throw two capillary lines which are connected with the thermobalance.

At this combined method exist advantages but also exist disadvantages. Is desired to optimize the sample size by using the coupled method TG-MS-FTIR.

*Instruments*

The joint TG/MS/FTIR technique was applied by means of equipment including an STA 449F1 Jupiter thermogravimetric analysis device (manufactured by Netzsch – Germany) coupled with an FTIR Vertex-70 spectrophotometer (manufactured by Bruker-Germany) and a QMS 403C Aëolos mass spectrometer (manufactured by Netzsch-Germany). The mass of the analyzed samples ranged between 4 and 6 mg and the heating rate was 10°C/min within the 25-620°C temperature range in 20 mL/min air flow atmosphere.

## 3. Results and Discussions

Fig. 1 shows a comparison between the TG curves recorded for samples B1, B2 and B3 in the air, within the 25-620°C temperature range, with a 10°C/min heating rate, whereas Fig. 2 shows the Gram Schmidt curves. The profile of the TG curves of samples B1 and B2 is similar, the amount of resulting residue being 57%. In sample B3 the degradation is almost complete, the resulting residue being 0.5%. The Gram Schmidt diagram reveals a complex decomposition mechanism the first decomposition stage of which occurs within the 300 - 400°C temperature range for all the researched teats. The first thermal decomposition peak in the three analyzed teats was recorded at about the same temperature value, which means that the analysis of the MS and FTIR spectra recorded for this temperature reveals information about the main ionic fragments resulting from their thermal decomposition onset stage.

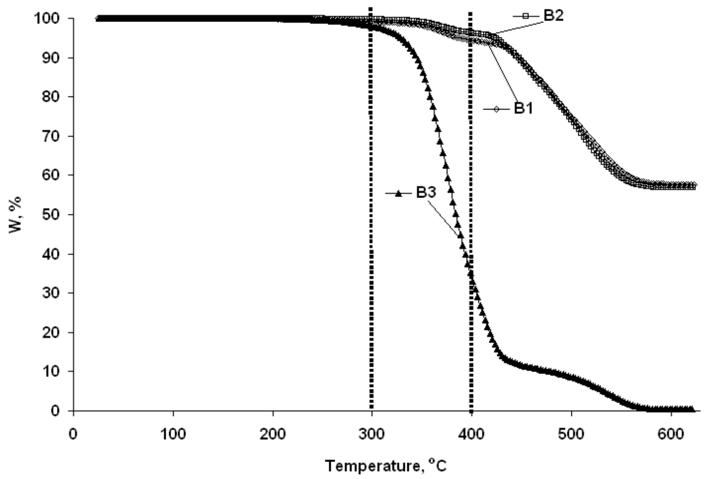


Fig. 1 − TG curves.

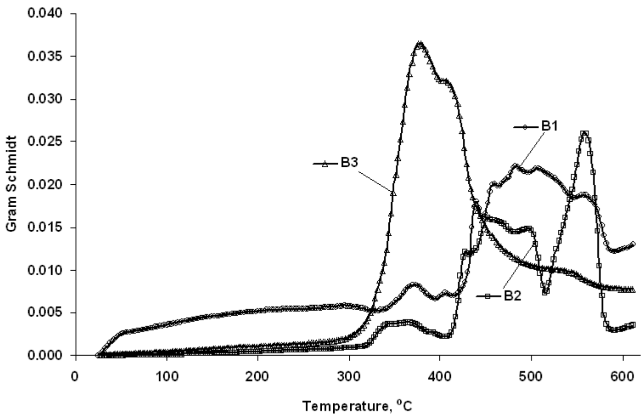


Fig. 2 − Gram Schmidt diagram.

Fig. 3 shows the MS spectra for the teat marked B1, which we assumed was made of silicone rubber, according to the DSC curves obtained from a previous study (Mihăilă *et al.*, 2017). The assumption was confirmed by the ionic fragments present in the MS spectra. Thus, m/z=73 may be associated with the $Si^{+}(CH_3)_3$ ionic fragment; m/z=75 with the $Si^{+}(CH_3)_2O$ ionic fragment, and m/z=208 with the $[Si^{+}(CH_3)_2O]_3$ $[M^{+}$-15] ionic fragment, which according to literature (Camino *et al.*, 2002; Mazhar *et al.*, 1990) occurs due to the formation of cyclic structures on polydimethylsiloxane degradation and has the highest ionic current intensity. We were surprised to find the m/z=96 ($C_{15}H_{12}^{++}$) ionic fragment, which indicates the presence of Bisphenol A (BPA). This ionic fragment was associated by Lisă G. *et al*. (Lisă *et al.*, 2015; Hamciuc *et al.*, 2018) with the onset of the thermal decomposition of the BPA, which was one of the components of aromatic polyethers.

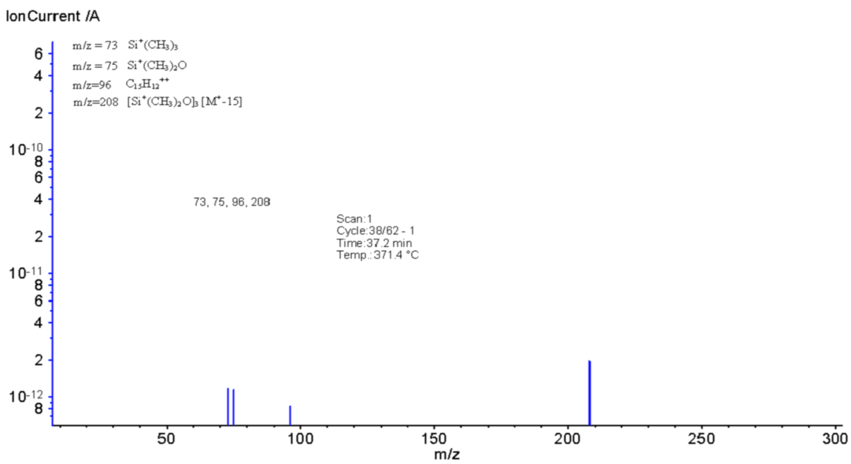


Fig. 3 − The MS spectra for the teat marked B1.

The MS spectra shown in Fig. 4 for the teat marked B2 reveals the presence of the following ionic fragments: m/z=18 ($H_2O^+$), m/z=30 ($HCHO^+$), m/z=44 ($CO_2^+$), m/z=50 ($C_4H_2^+$), m/z=75 $Si^+(CH_3)_2O$ and m/z=208 $[Si^+(CH_3)_2O]_3$ $[M^+-15]$, which confirm the presence of polydimethylsiloxane in this teat as well, as previously assumed from the analysis of the DSC curves (Mihăilă *et al.*, 2017). We found that this teat did not contain BPA, as specified on the product package.

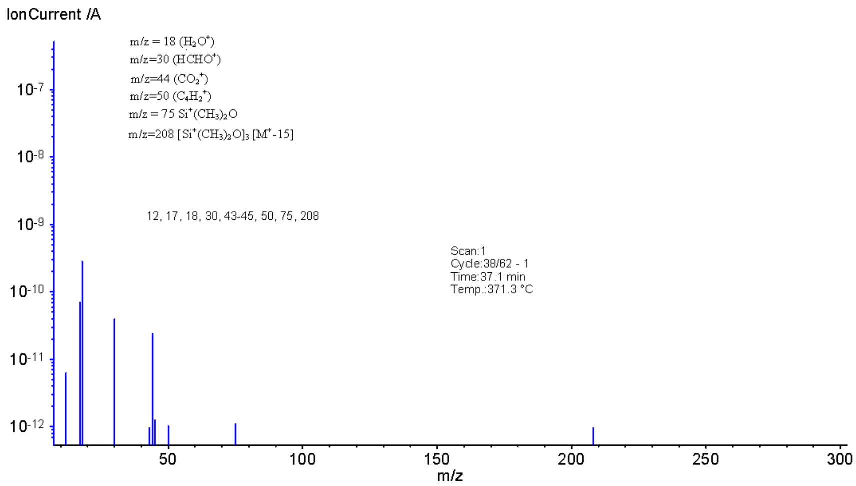


Fig. 4 − The MS spectra for the teat marked B2.

As expected, the mass spectra of sample B3 (Fig. 5) made of latex contains many more ionic fragments, among which we should mention: fragment m/z=104 ($C_8H_8^+$, specific to the styrene monomer), m/z=56 ($C_3H_4O^+$, acrylaldehyde), m/z=68 ($C_4H_8O^+$, butyl aldehyde), m/z=94 ($C_6H_6O^+$, phenol), m/z=107 ($C_6H_5CHO^+$, benzaldehyde), m/z=116 ($C_9H_8^+$, indene), m/z=120 ($C_8H_8O^+$, styrene oxide), m/z=128 ($C_{10}H_8^+$, naphthalene), m/z=39 ($C_3H_3^+$), m/z=51 ($C_4H_3^+$), m/z=63 ($C_5H_3^+$), m/z=78 ($C_6H_6^+$), m/z=91 ($C_7H_7^+$), m/z=118 ($C_9H_{10}^+$, $\alpha$-metylstyrene) and at the highest peak for m/z=28 ($CO^+$) (Sprânceană *et al.*, 2017). All the ionic fragments identified confirm for this sample as well our previous assumption based on DSC curve analysis (Lisă *et al.*, 2017), namely that this teat contains styrene-butadiene rubber.

The FTIR spectra recorded at 371°C temperature are shown comparatively in Fig. 6 for the three teats. The findings are in line with those obtained from MS spectra interpretation. Thus, the samples B1 and B2 made of silicone rubber in the 810 and 1260 $cm^{-1}$ area revealed four peaks which, according to literature (Tomer *et al.*, 2012; Yang *et al.*, 2011), are specific to polysiloxanes: the 1069 and 1030 $cm^{-1}$ bands correspond to the Si-O-Si bond vibration, the 1262 $cm^{-1}$ ones are specific to the $Si-CH_3$ bonds and the 813 $cm^{-1}$ ones are specific to Si-O-C bonds.

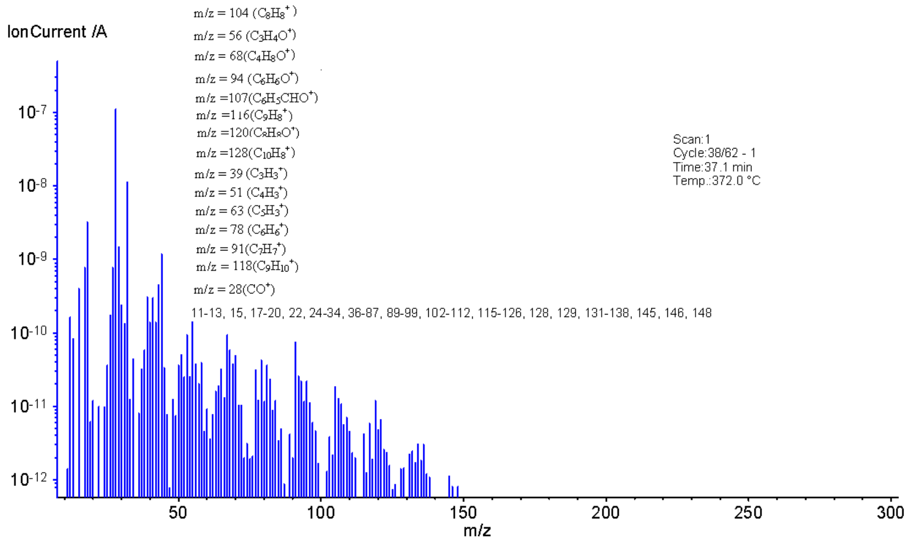


Fig. 5 – The MS spectra for the teat marked B3.

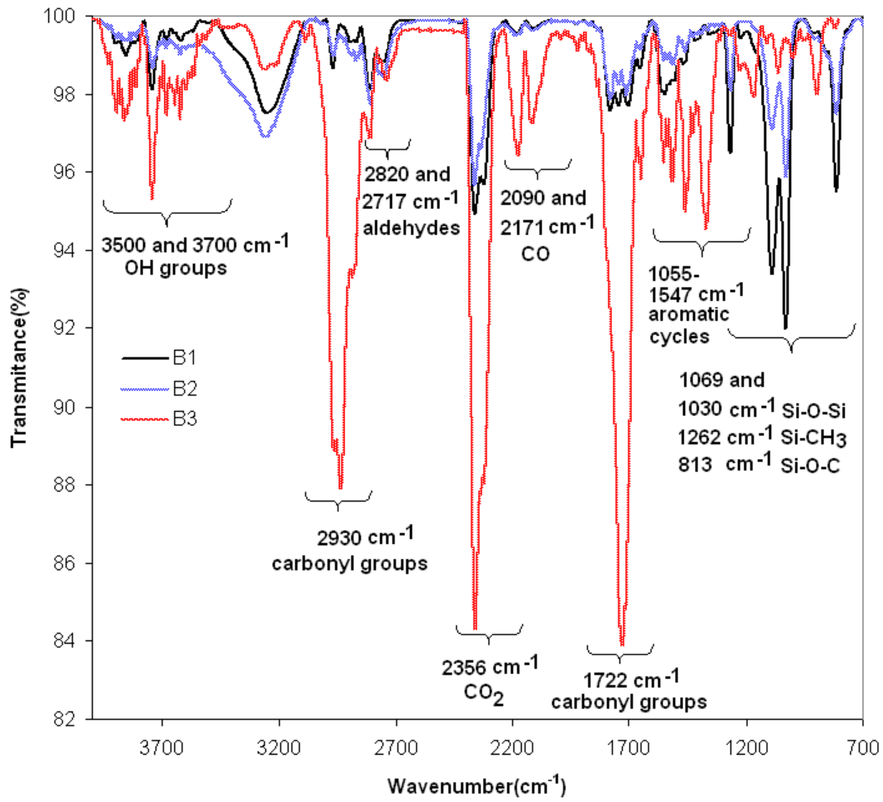


Fig. 6 – The FTIR spectra for the three teats: B1, B2 and B3.

As far as the B3 sample is concerned, the bands specific to CO were detected at 2090 and 2171cm$^{-1}$, those specific to $CO_2$ at 2356 cm$^{-1}$, those specific to –OH groups in the 3500 and 3700 cm$^{-1}$ area, and those specific to the carbonyl groups at 1722 cm$^{-1}$ and 2930 cm$^{-1}$, respectively. The 1055, 1160, 1365, 1459, 1516 and 1547 cm$^{-1}$ bands may be specific to aromatic cycles; and the presence of aldehydes is confirmed by the specific 2820 and 2717 cm$^{-1}$ bands (Rogulska *et al.*, 2013).

## 3. Conclusions

The TG/MS/FTIR technique applied to the three types of teats used for baby bottle feeding allowed us to analyze simultaneously the mass loss and degradation products in the gaseous state obtained through their thermal decomposition.

The MS spectra enabled us to identify the presence of Bisphenol A (BPA) in the sample marked B1. This teat is supplied in Romania by a company from Thailand. The analysis of the MS spectra at 371°C temperature also revealed information about the main ionic fragments resulting during the thermal decomposition onset stage. The following ionic fragments were detected in the teats made of silicon rubber: m/z=73 $Si^+(CH_3)_3$, m/z=75 $Si^+(CH_3)_2O$ and m/z=208 $[Si^+(CH_3)_2O]_3$ $[M^+$-15] specific to polydimethylsiloxane degradation. As for the teat made of latex, the highest intensity fragments that we identified were: m/z=28 associated with $CO^+$, m/z=104 ($C_8H_8^+$, specific to styrene monomer), m/z=120 ($C_8H_8O^+$, styrene oxide), m/z=78 ($C_6H_6^+$), m/z=91 ($C_7H_7^+$), m/z=118 ($C_9H_{10}^+$, $\alpha$-metylstyrene), etc. The FTIR specters recorded at 371°C temperature reveal for the teats made of silicone rubber a sequence of peak specific to polysiloxanes: the 1069 and 1030 cm$^{-1}$ bands correspond to the Si-O-Si bond vibration, the 1262 cm$^{-1}$ ones are specific to the Si-$CH_3$ bonds and the 813 cm$^{-1}$ ones are specific to Si-O-C bonds. In the sample made of latex we identified bands specific to CO at 2090 and 2171cm$^{-1}$, the 1055, 1160, 1365, 1459, 1516 and 1547 cm$^{-1}$ bands specific to aromatic cycles, etc.

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## STUDIUL TG/MS/FTIR PRIVIND DESCOMPUNEREA TERMICĂ A UNOR TETINE PENTRU BEBELUŞI

(Rezumat)

În acest studiu s-a analizat pierderea de masă şi produsele de degradare în stare gazoasă obţinute din analiza unor tetine utilizate pentru alimentarea bebeluşilor aplicând tehnica TG/MS/FTIR. Profilul curbelor TG este asemănător în cazul tetinelor confecţionate din cauciuc siliconic, cantitatea de reziduu rezultată fiind de 57%.

Degradarea tetinei confecţionate din latex este aproape completă rezultând o cantitate de reziduu de 0,5%. Analiza spectrelor MS obţinute la temperatura de 371°C au condus la obţinerea de informaţii cu privire la principalele fragmente ionice care rezultă în etapa de debut a descompunerii termice. Rezultatele au fost confirmate şi de spectrele FTIR înregistrate la aceeaşi temperatură. Studiul a confirmat de asemenea, prezenţa de bisfenol A pentru una dintre cele două tetine confecţionate din cauciuc siliconic.