

# Analysis of Degraded Natural Rubber Using Thermal Desorption and Pyrolysis / Direct Analysis in Real Time - Mass Spectrometry (TDP/DART-MS)

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## Introduction

Vulcanized natural rubber is widely used in the major industries. It is important to measure the degradation level for product design. Though many methods are used for detect of degradation e.g. Durometer, Extensometer and FT-IR, it is difficult to detect the differences between new and degraded in initial stage of degradation. DART-MS is one of the powerful methods for the rapid analysis for not only liquids but also solids [1]. However, this method is not suitable for polymer analysis since the polymer is hard to volatilize. We developed the thermal desorption and pyrolysis device for DART-MS system and applied for the polymer analysis [2].

The purpose of this work was to detect the differences between new and degraded in initial stage of degradation, rapidly and without any pretreatment.

## Method and Samples

### Sample

Natural Rubber bands  
130°C × 30min at atmospheric pressure.

### Analysis system (Fig. 1)

Q-ToF mass spectrometer : micrOTOF Q III(Bruker)  
Ion source : DART® ion source (IonSense LLC)  
Thermal desorption and pyrolysis (TDP) device, ionRocket (BioChromato, Inc.)

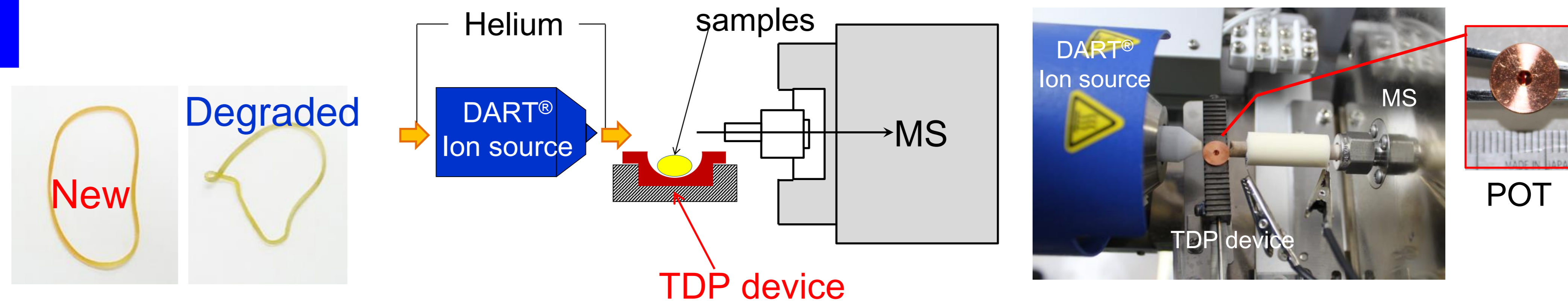


Fig. 1 TDP/DART-MS Analysis system

Small pieces (0.5 mm × 0.5 mm) of sample were put into the POT. Mass spectra were measured in positive-ion mode as the samples were heated from ambient temperature to 600°C at a rate of 100°C/min (Fig.2).

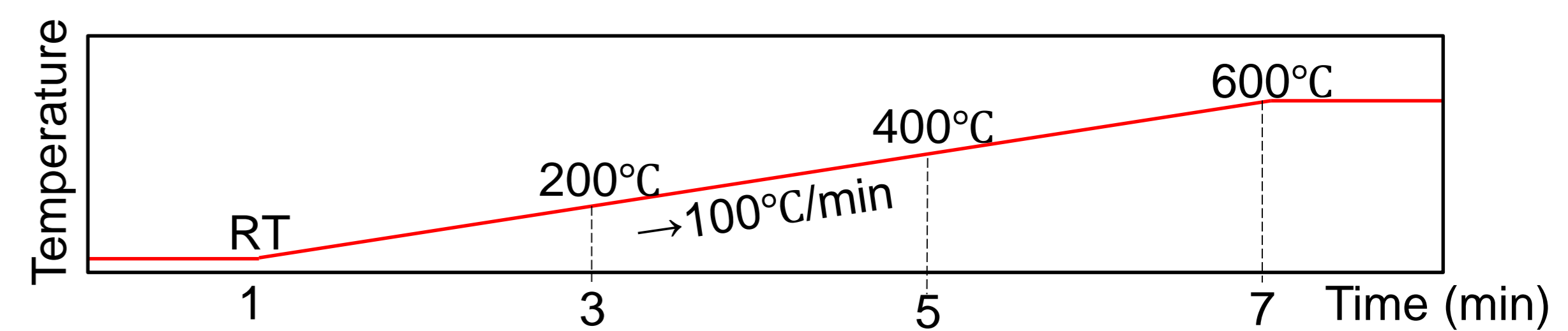


Fig.2 Example of heating condition of TDP device

## Results

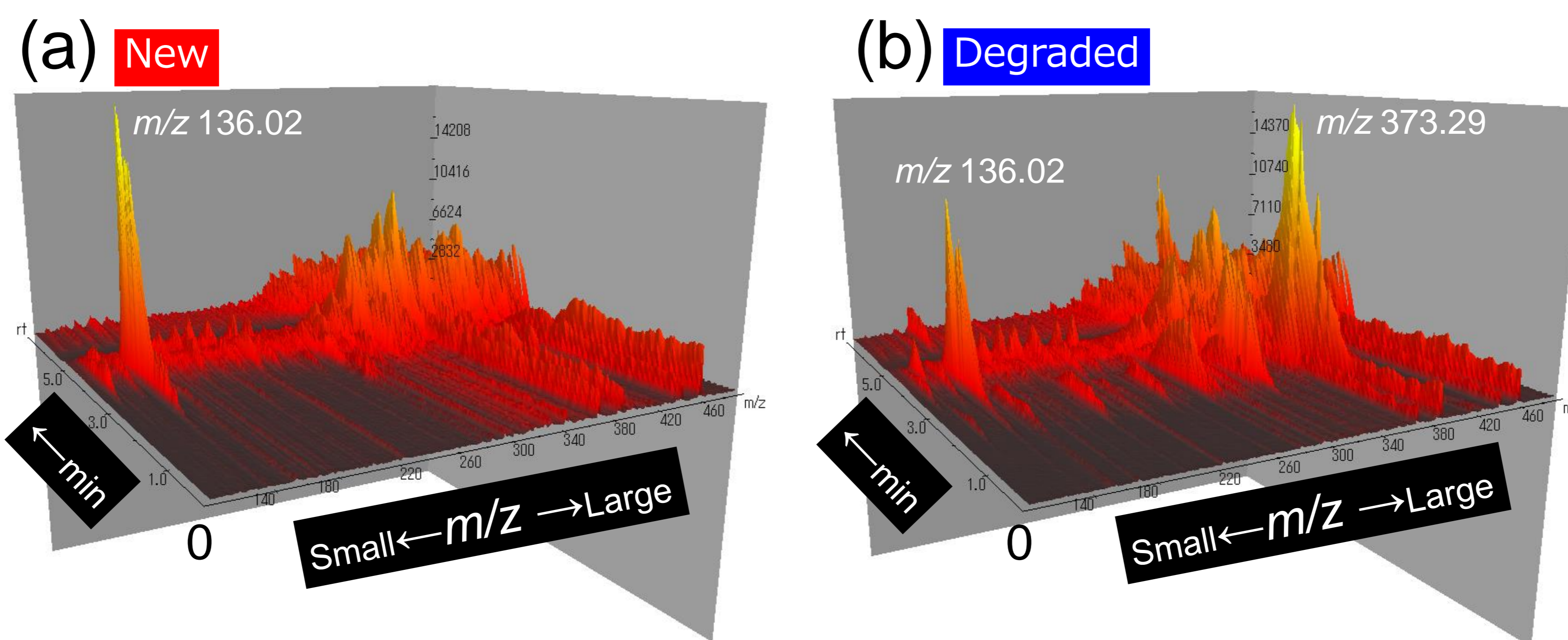


Fig.3 Three dimensional figures of TDP/DART-MS analysis; (a) New rubber band, (b) degraded rubber band  
Comparing the new and the degraded rubber bands,  $m/z$  136.02 has decreased after degradation test, otherwise,  $m/z$  373.29 has appeared after degradation test.

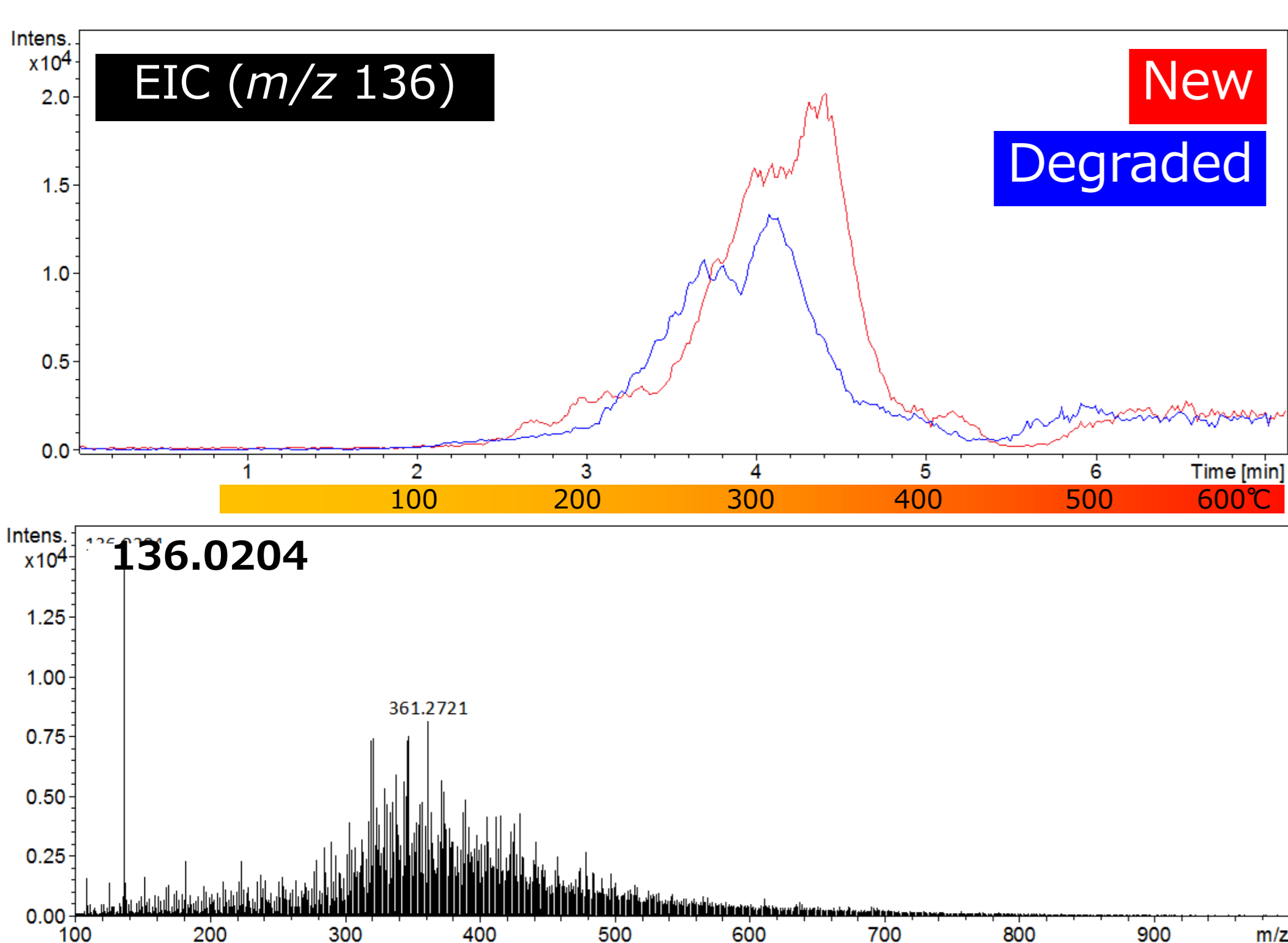


Fig.4 EIC(Extracted ion current gram) and corresponding MS spectrum of TDP/DART-MS. Compound ( $m/z$  136.02) has apparently decreased after degradation test

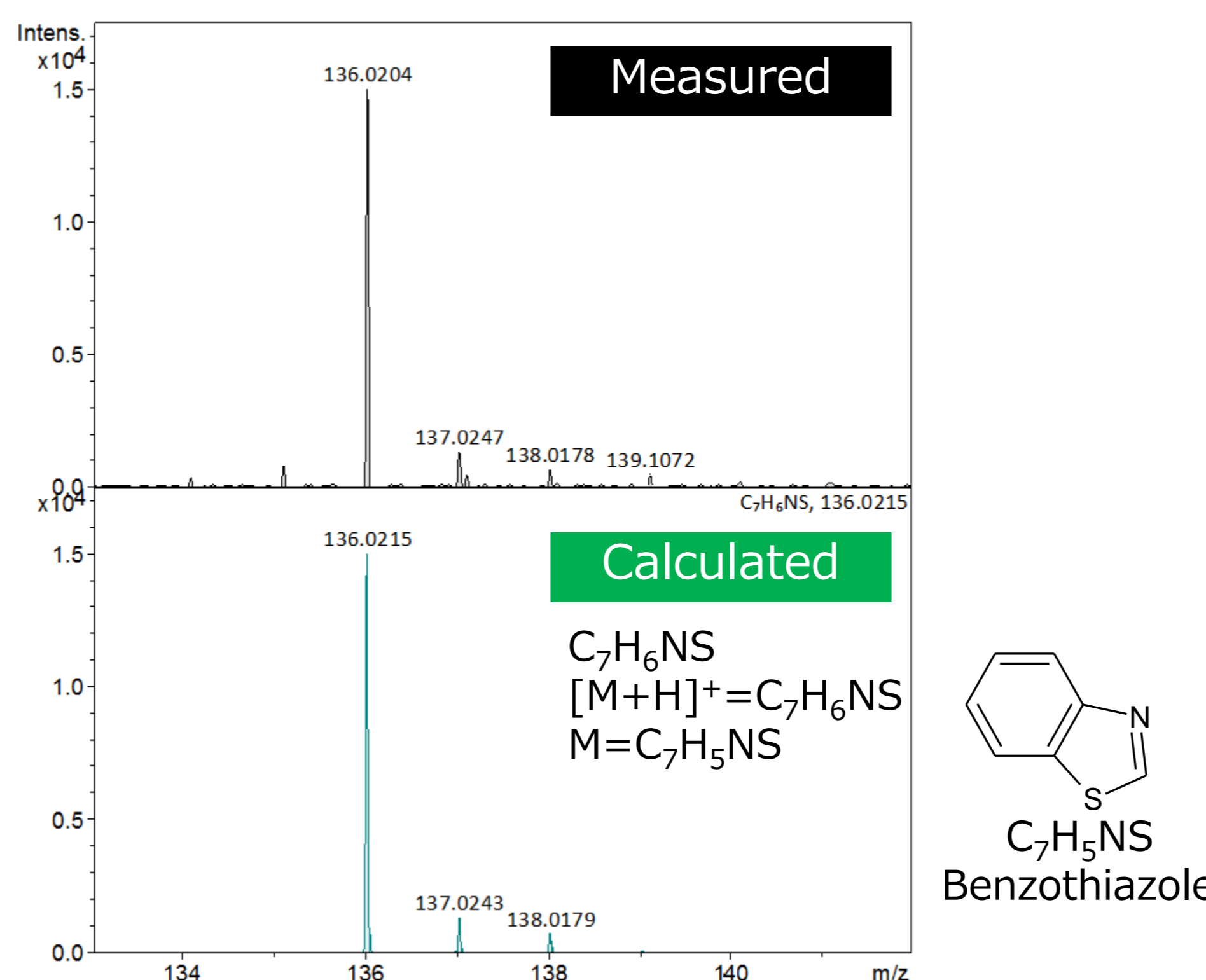


Fig.5 Results of chemical composition analysis  
It was estimated that  $m/z$  136.02 was by-product of vulcanization accelerator, benzothiazole.

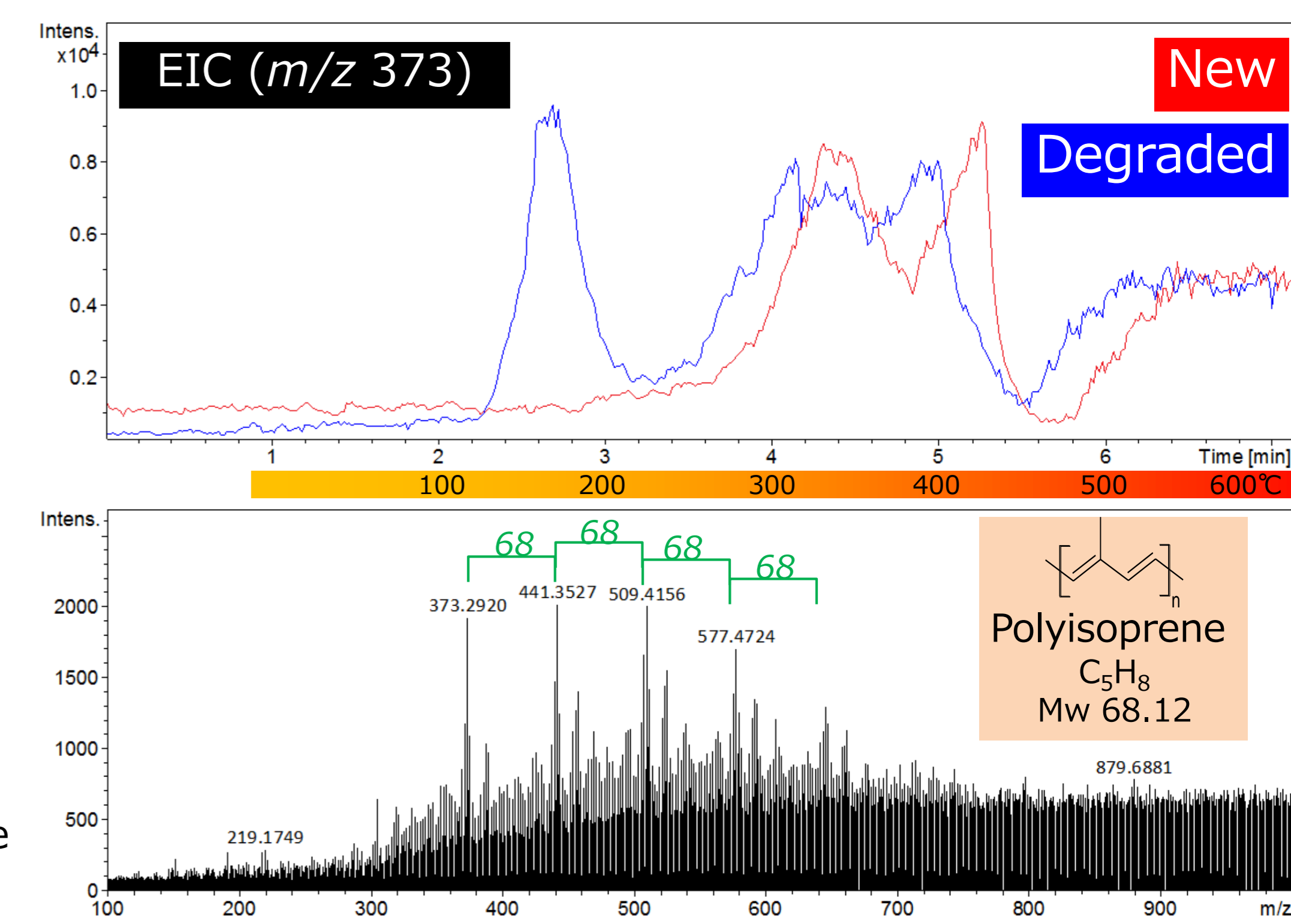


Fig.6 EIC and corresponding MS spectrum of TDP/DART-MS.  
Compound ( $m/z$  373.29) has apparently appeared after degradation test. And the peaks in 68 intervals were estimated it was low molecular of polymer matrix "the degraded products of polyisoprene".

## Conclusions

- In this work, we chose TDP/DART-MS in order to detect the differences between new and degraded rubbers, we detected both the decreasing of benzothiazole and the increasing of the degraded product of polyisoprene without any pretreatments.
- TDP/DART-MS is useful for insoluble materials, such as vulcanized rubber, thermosetting resin, organometallic complex and so on.

[1] R. B. Cody, J. A. Laramée & H. D. Durst, Anal. Chem., **77**, 2297-2302 (2005)

[2] H. Shimada, S. Kamikubo, T. Kawanishi, Y. Nakatani, Y. Noritake, R. Matsui, K. Kinoshita, Y. Shida, 60th ASMS Annual Conference, Abstract, ThP29 Poster655 (2012)