# "Single Step derivatization with $CF_3$ enone of Thiophene at Ambient temperature to determine Propellant Grade Hydrazines: A Study by GC & GC-MS"

**by**

***Selvakumar Subramanian*[ab], Somanathan Narayanasastri *[b] and Audisesha Reddy Kami Reddy[a]***

[a]*Chemical Testing Lab, Solid Propellant Space Booster Plant,*
*SDSC-SHAR Centre,*
*Indian Space Research Organization (ISRO),*
*Sriharikota 524124, Andhra Pradesh, India*
*Tel.: +91-8623-223013; fax: +91-8623-225154*
*E-mail: selvakumar.s@shar.gov.in , kumarreka@hotmail.com*

[b]*Polymer Division, Central Leather Research Institute (CLRI),*
*Council of Scientific and Industrial Research (CSIR),*
*Adyar, Chennai 600020, Tamil Nadu, India.*
*Tel.: +91-44-24437189; E-mail: nsomanathan@rediffmail.com*
.

* To whom correspondence should be addressed.

**GC Column Selection procedure for analysis:**

Scouting experiments were performed for the selection of column with several test conditions. GC packed columns tried were SE 30-10%-Dimethylpolysiloxane on Chromosorb-WHP-60/80, 25% Carbowax-20M on Chromosorb-WHP-70/80, 10% UCW-98 (Methylvinylpolysiloxane)-Chromosorb-WHP - 80/100, 30 % Theed on Chromosorb-WHP - 30/60, 25% PEG 400 on Anakrom AB -70/80. SE-30 column is found to be suitable for present study as it is superior in quality with good thermal stability. Isothermal and temperature programming methods were tried to resolve the peaks. Temperature programming was found to be better option for good resolution and quantification. Experimental conditions thus optimized and standardized are given in manuscript. System suitability check (reproducibility check) has been performed using SE30 column and it is found that relative standard deviation (RSD) for five injections of $CF_3$ enone is less than 1 %. Areas obtained from main peaks of derivatives of hydrazine, MMH and UH25 were also taken for reproducibility check and RSD for five determinations of each individual derivative peaks was found to be less than 1 %.

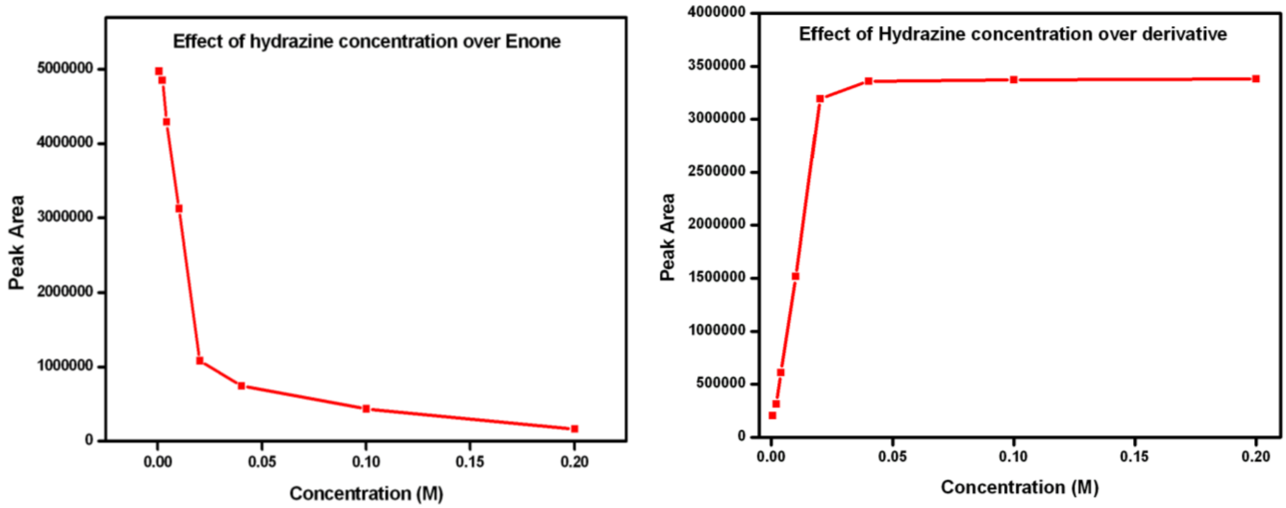



**Fig. S1.** Effect of hydrazine concentration over area of $CF_3$ enone (A) and its derivative (B)

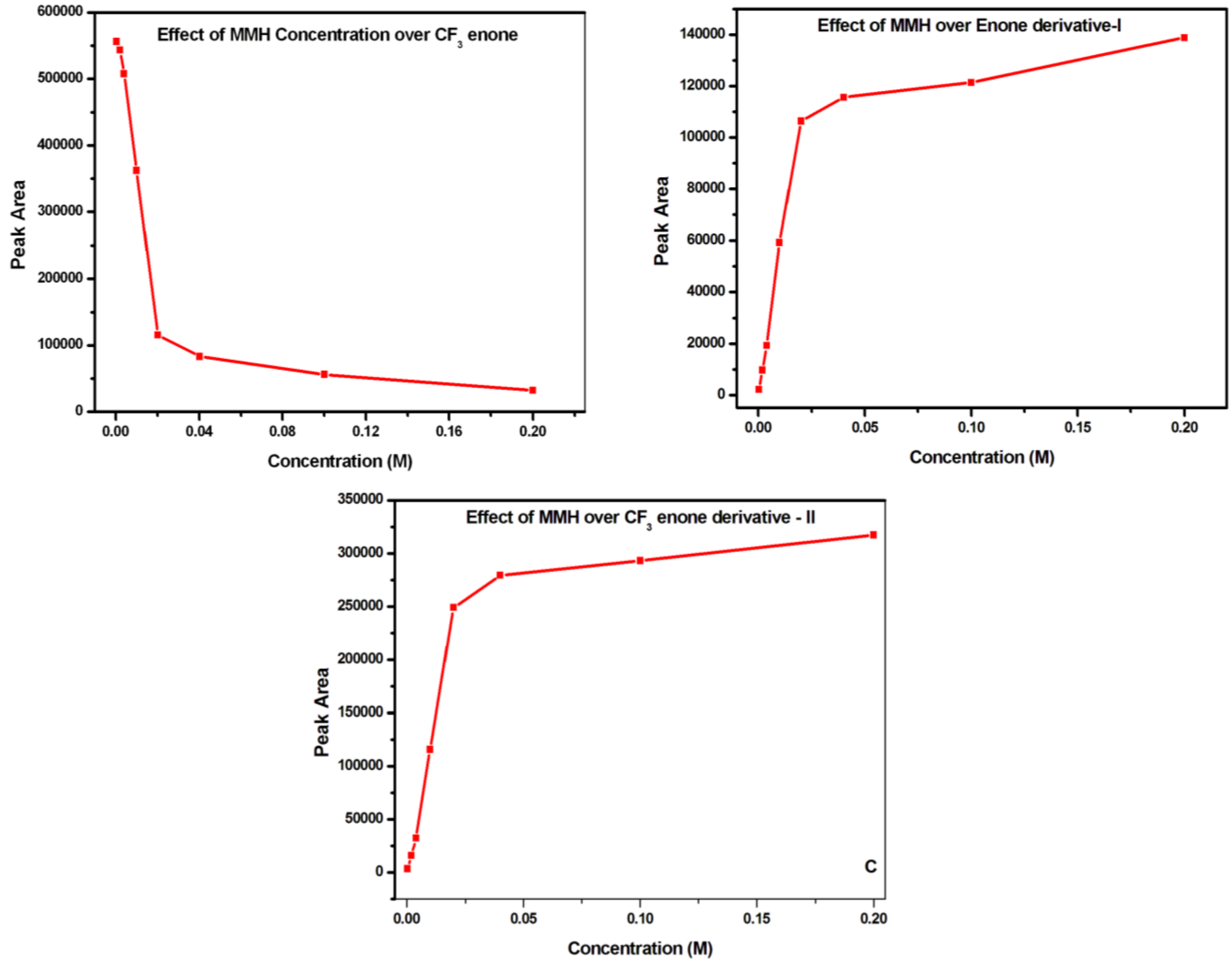



**Fig.S2** Effect of MMH concentration over peak area of $CF_3$ enone (A) and $CF_3$ enone derivative-I –Pyrazoline-I (B) $CF_3$ enone derivative-II –Pyrazoline-II (C)

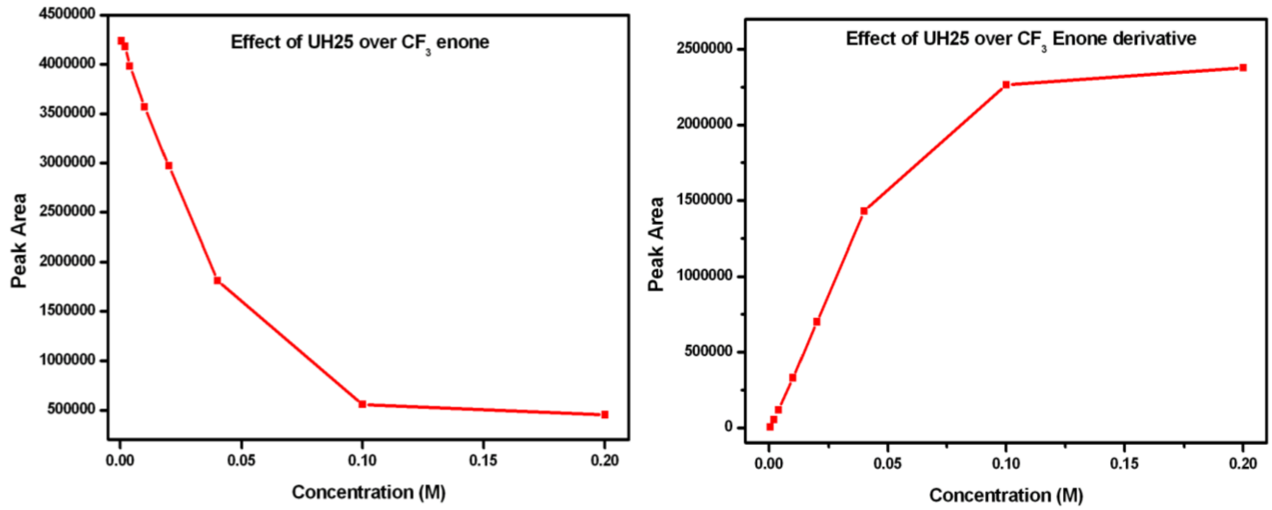



**Fig.S3** Effect of UH25 concentration over peak area of $CF_3$ enone (A) and UH25 derivative of $CF_3$ enone (B)

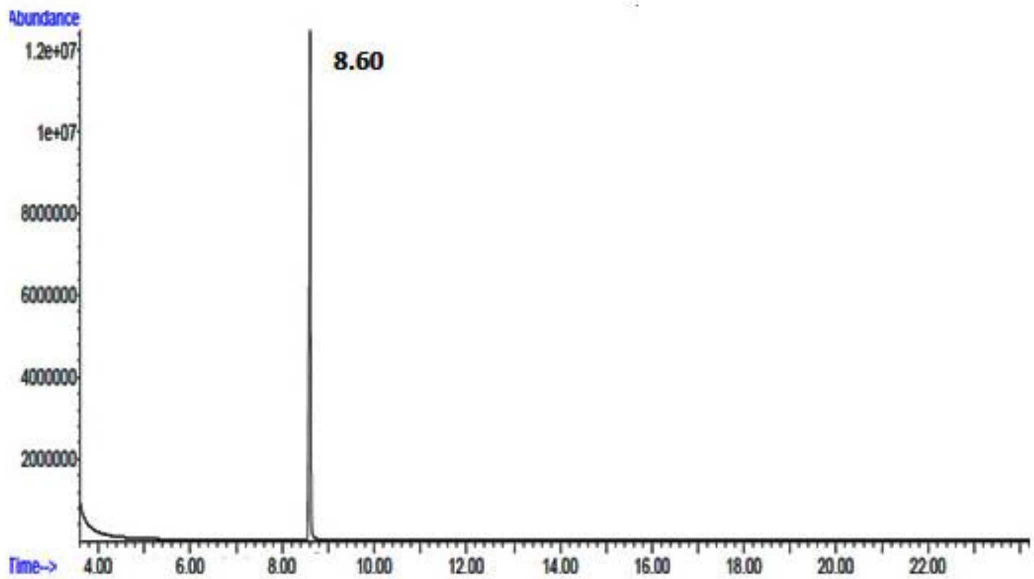



**Fig. S4** Chromatogram for $CF_3$ Enone

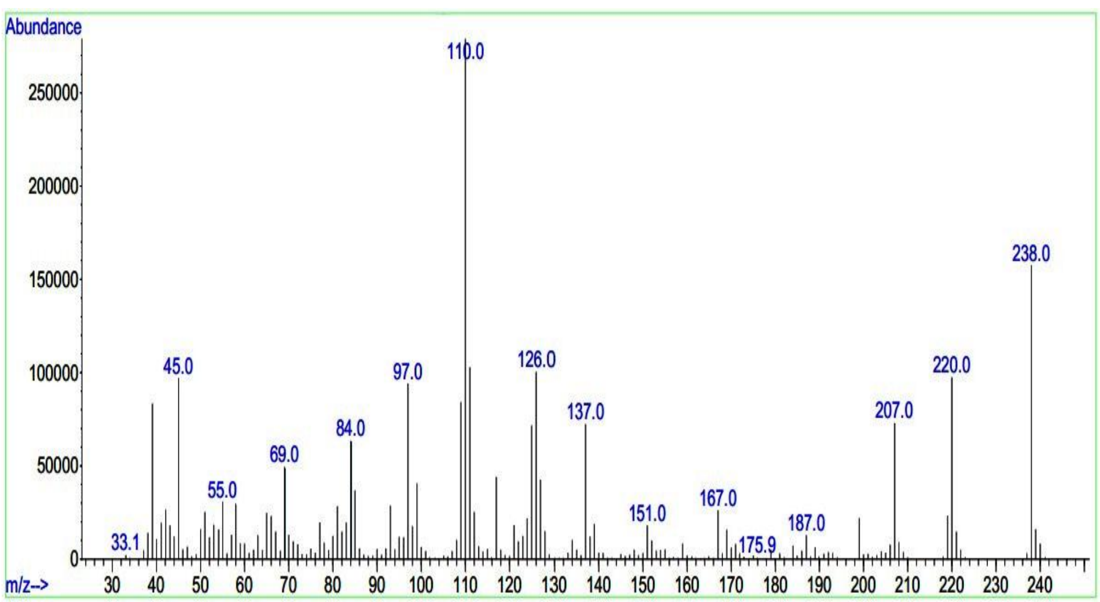



**Fig.S5** Mass Spectra for the peak eluted at 14.06 min. (Pyrazolidine)

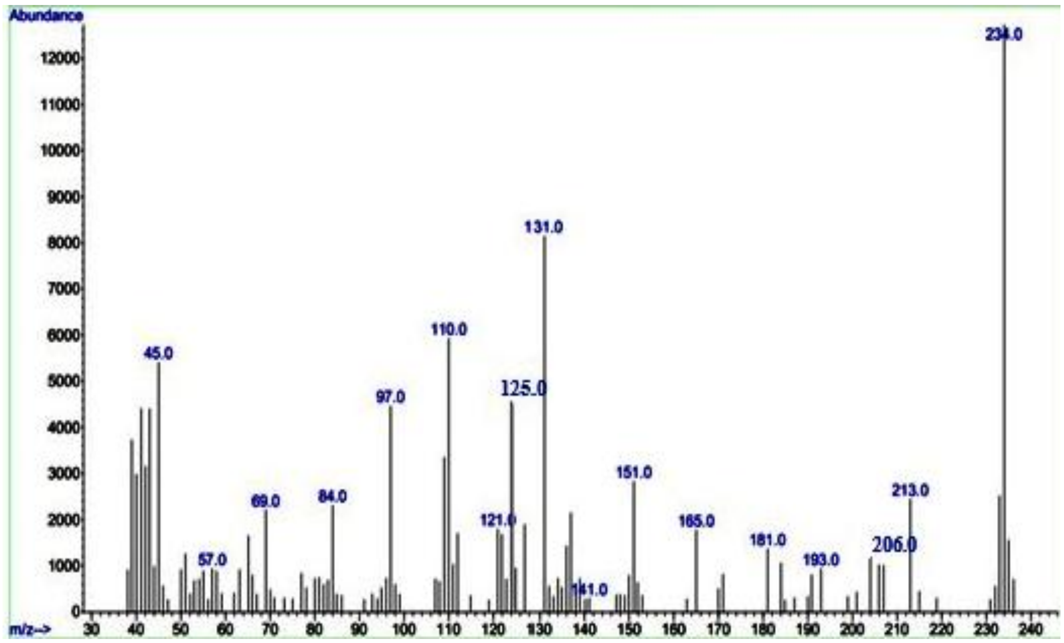



**Fig.S6** Mass Spectra for the peak eluted at 10.41 min. (Pyrazoline I – MMH Derivative-I)

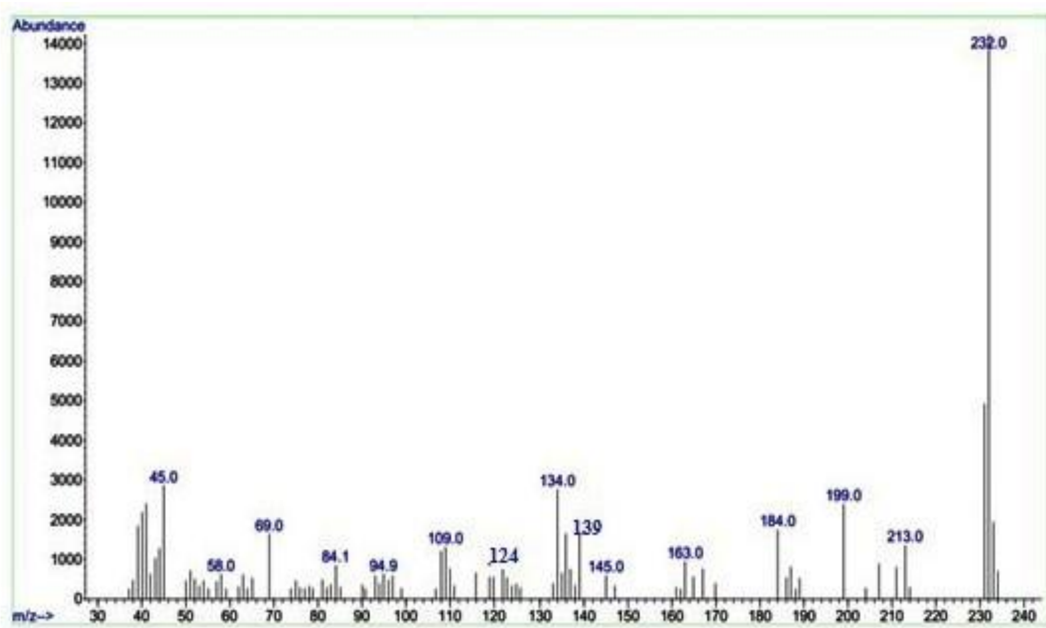



**Fig.S7** Mass Spectra for the peak eluted at 13.91 min. (Pyrazole- I – MMH Derivative-III )

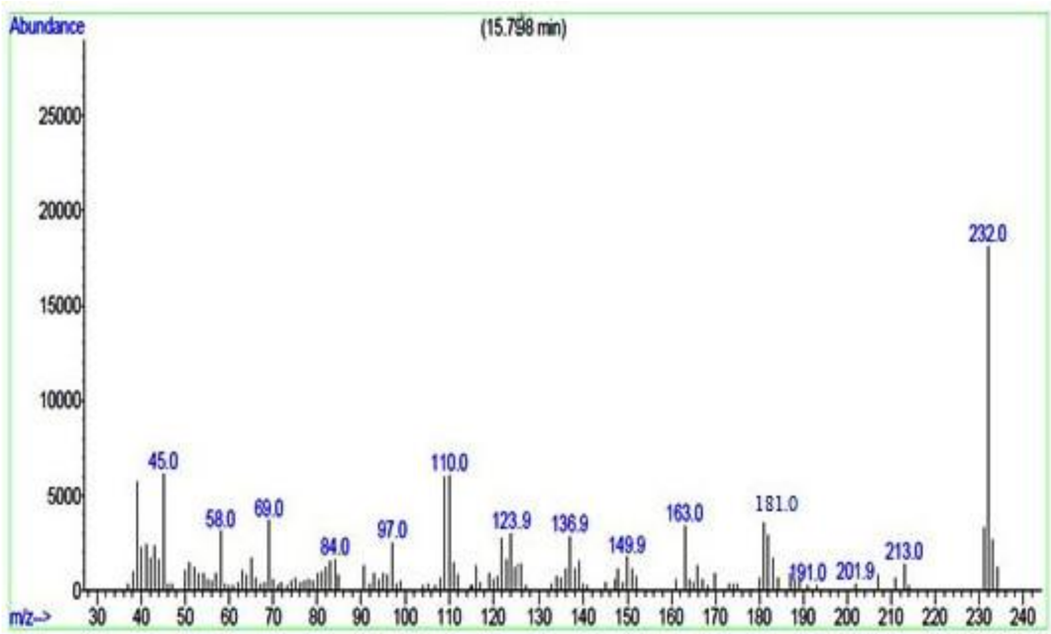



**Fig.S8** Mass Spectra for the peak eluted at 15.80 min. (Pyrazole- II - MMH Derivative-IV)

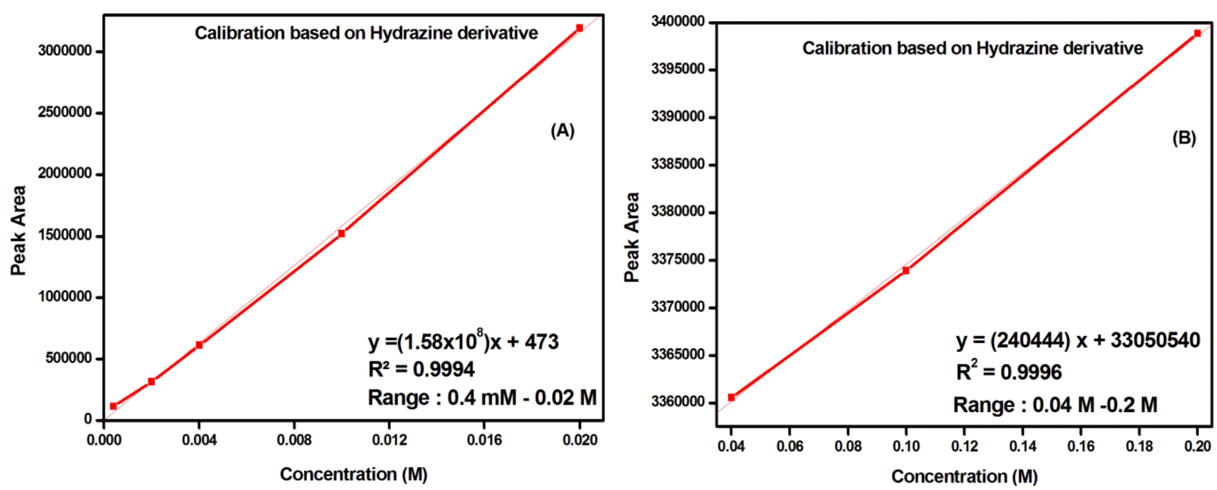



**Fig.S9.** Calibration graphs for the determination of hydrazine based on Pyrazolidine (hydrazine derivative) in the concentration range of 0.4 mM-0.02M (A) and 0.04 M – 0.2 M (B).

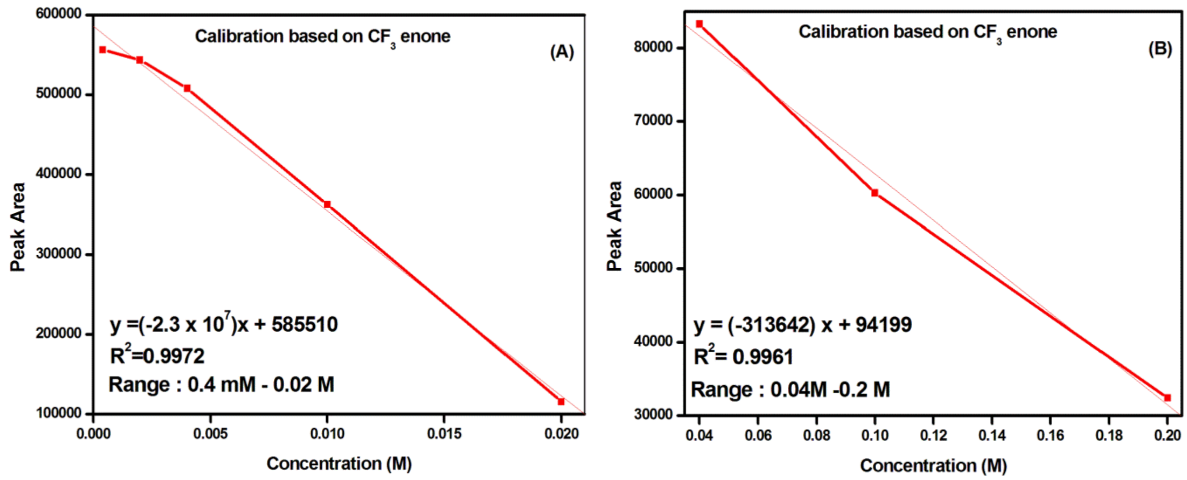



**Fig.S10.** Calibration graphs for the determination of MMH based on $CF_3$ enone in the concentration range of 0.4 mM-0.02M (A) and 0.04 M – 0.2 M (B).

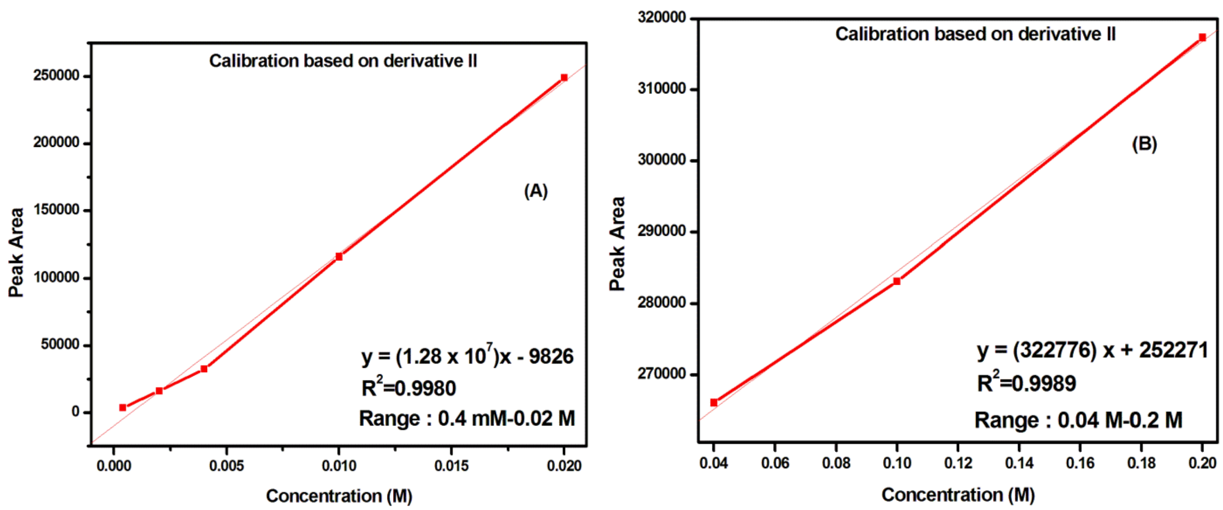



**Fig.S11.** Calibration graphs for the determination of MMH based on Pyrazoline-II (MMH derivative II) in the concentration range of 0.4 mM-0.02M (A) and 0.04 M – 0.2 M (B).

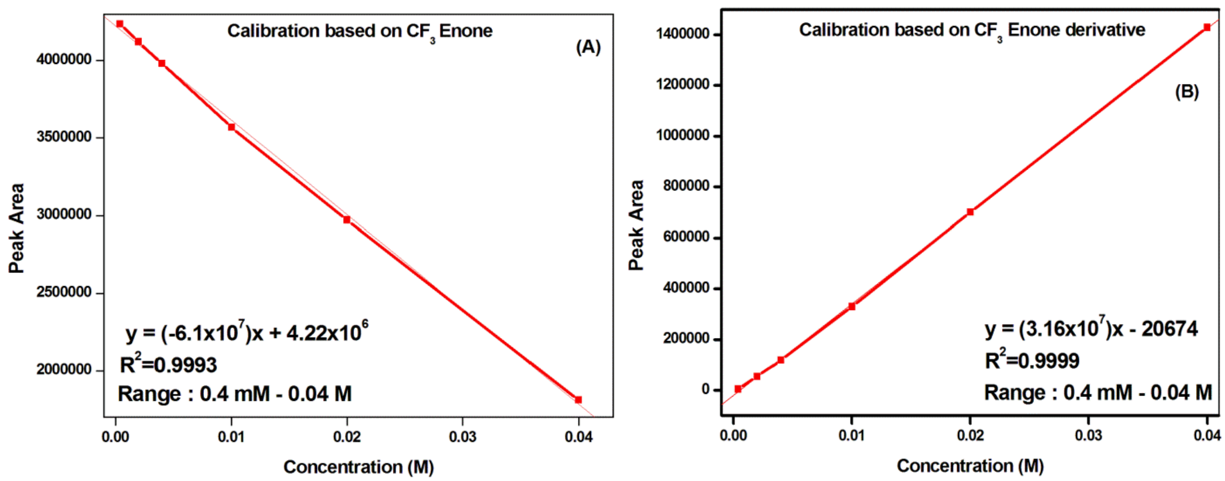
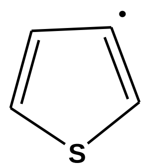



**Fig.S12.** Calibration graphs for the determination of hydrazine (in UH25) based on $CF_3$ enone (A) & UH25 derivative of $CF_3$ enone (B) in the concentration range of 0.4 mM-0.04 M.

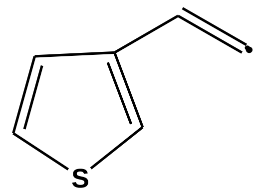
# FP-01

## Fragmentation pattern for $CF_3$ enone peak (R.T. - 8.6 min.)

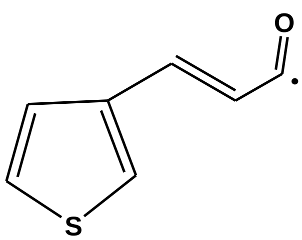
$CF_3^{\bullet+}$
68.99



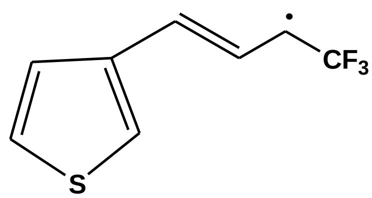
$C_4H_3S^{+\bullet}$
82.99



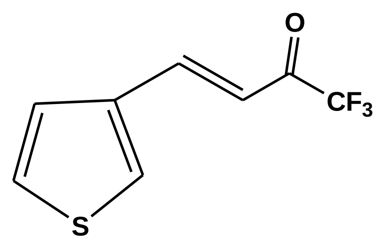
$C_6H_5S^{+\bullet}$
109.01




$C_7H_5OS^{+\bullet}$
137.01




$C_8H_6F_3S^{+\bullet}$
191.01




$C_8H_5F_3OS^{+\bullet}$
m/e : 206

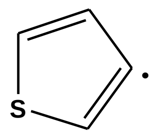
**$CF_3$ enone**

**FP-02**

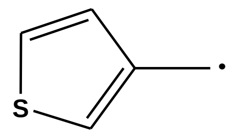
**Fragmentation pattern for the peak of hydrazine derivative I**

**(Pyrazoline - Retention time -11.87 min.)**

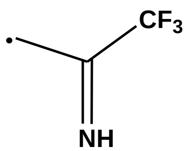
**$CF_3^{+\bullet}$**
**68.99**



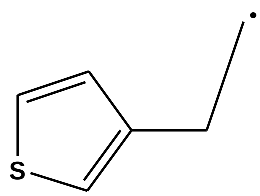
**$C_4H_3S^{+\bullet}$**
**82.99**



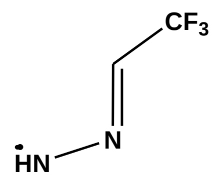
**$C_5H_5S^{+\bullet}$**
**97.01**



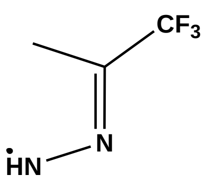
**$C_3H_3F_3N^{+\bullet}$**
**110.02**



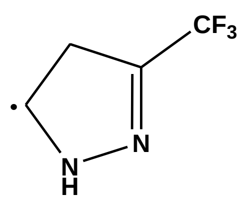
**$C_6H_7S^{+\bullet}$**
**111.03**



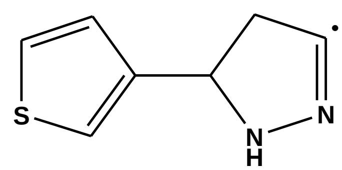
**$C_2H_2F_3N_2^{+\bullet}$**
**111.02**



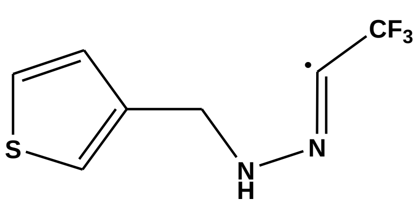
**$C_3H_4F_3N_2^{+\bullet}$**
**125.03**



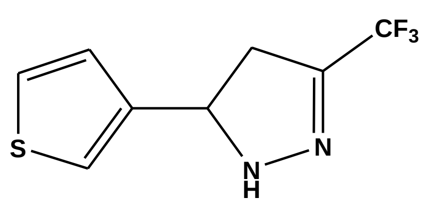
**$C_4H_4F_3N_2^{+\bullet}$**
**137.03**



**$C_7H_7N_2S^{+\bullet}$**
**151.03**



**$C_7H_6F_3N_2S^{+\bullet}$**
**207.02**

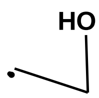


**$C_8H_7F_3N_2S^{+\bullet}$**
**m/e: 220.03**

**FP-03**

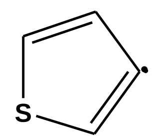
**Fragmentation pattern for the peak of hydrazine derivative II**

**Pyrazolidine - (Retention time -14.06 min.)**

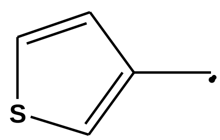



**$C_2H_5O^{+\bullet}$**
**45.03**

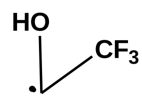
**$CF_3^{+\bullet}$**
**68.99**



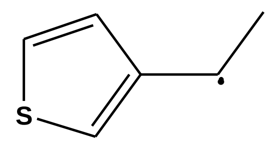

**$C_4H_3S^{+\bullet}$**
**82.99**



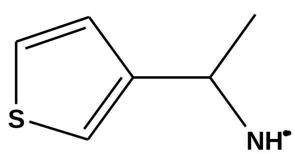

**$C_5H_5S^{+\bullet}$**
**97.01**



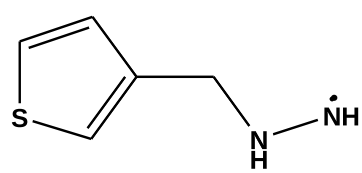

**$C_2H_2F_3O^{+\bullet}$**
**99.01**



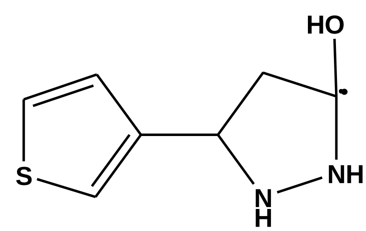

**$C_6H_7S^{+\bullet}$**
**111.03**



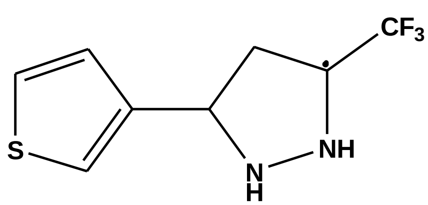

**$C_6H_8NS^{+\bullet}$**
**126.04**



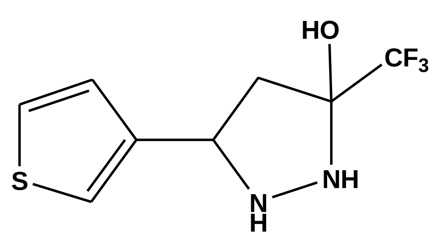

**$C_5H_7N_2S^{+\bullet}$**
**127.03**




**$C_7H_9N_2OS^{+\bullet}$**
**169.04**




**$C_8H_8F_3N_2S^{+\bullet}$**
**220.04**



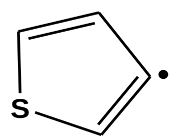

**$C_8H_9F_3N_2OS^{+\bullet}$**
**m/e: 238.04**

**FP-04**

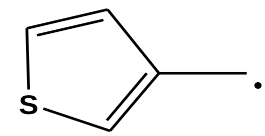
**Fragmentation pattern for the peak of derivative I of MMH**

**Pyrazoline-1 Retention time :10.41 min.**

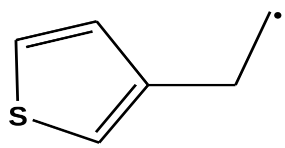
**$CF_3^{+\bullet}$**
**68.99**



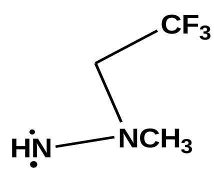
**$C_4H_3S^{+\bullet}$**
**82.99**



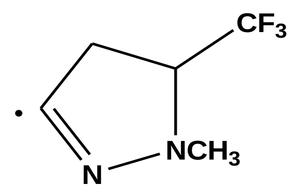
**$C_5H_5S^{+\bullet}$**
**97.01**



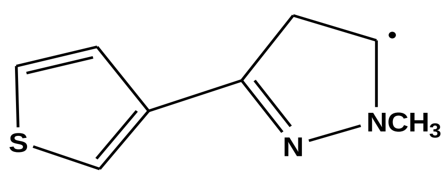
**$C_6H_7S^{+\bullet}$**
**111.03**



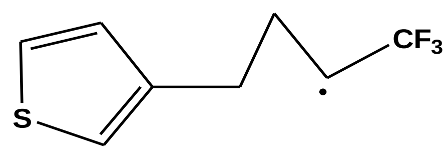
**$C_3H_6F_3N_2^{+\bullet}$**
**127.05**



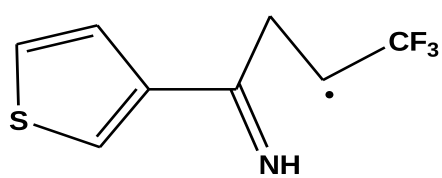
**$C_5H_6F_3N_2^{+\bullet}$**
**151.05**



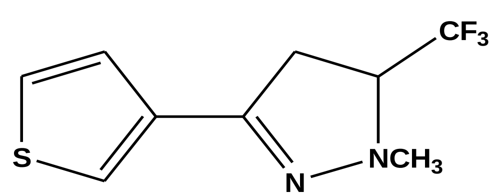
**$C_8H_9N_2S^{+\bullet}$**
**165.05**



**$C_8H_8F_3S^{+\bullet}$**
**193.03**



**$C_8H_7F_3NS^{+\bullet}$**
**206.03**



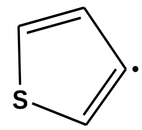
**$C_9H_9F_3N_2S^{+\bullet}$**
**234.04**

**FP-05**

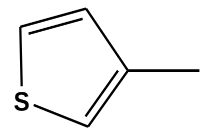
**Fragmentation pattern for the peak of derivative II of MMH**

**Pyrazoline-II Retention time :12.74 min.**

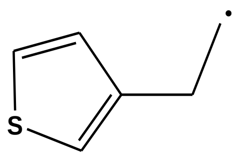
**$CF_3^{+\bullet}$**
**68.99**



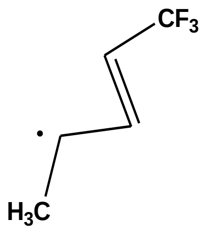

**$C_4H_3S^{+\bullet}$**
**82.99**



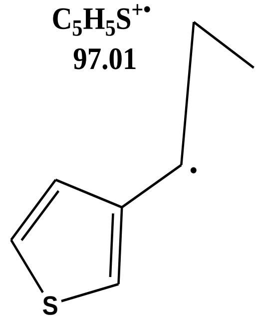

**$C_5H_5S^{+\bullet}$**
**97.01**



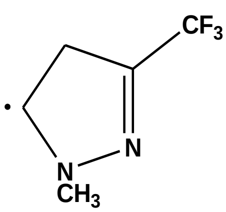

**$C_6H_7S^{+\bullet}$**
**111.03**



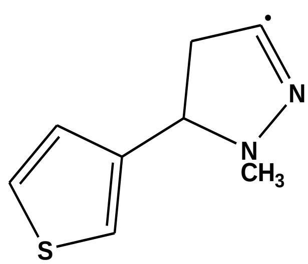

**$C_3H_4F_3N_2^{+\bullet}$**
**125.03**



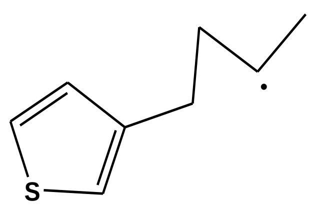

**$C_7H_9S^{+\bullet}$**
**125.04**



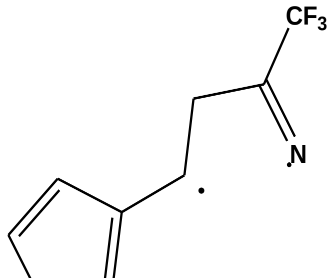

**$C_5H_6F_3N_2^{+\bullet}$**
**151.05**



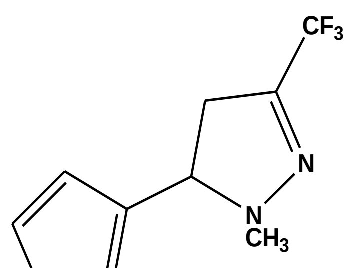

**$C_8H_9N_2S^{+\bullet}$**
**165.05**




**$C_8H_8F_3S^{+\bullet}$**
**193.03**




**$C_8H_7F_3NS^{+\bullet}$**
**206.03**



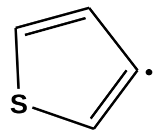

**$C_9H_9F_3N_2S^{+\bullet}$**
**m/e : 234.04**

## FP-06

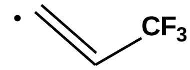
## Fragmentation pattern for the peak of MMH derivative III

## Pyrazole-I-Retention time : 13.91 min

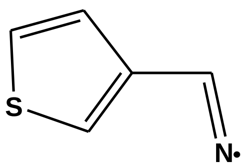
$CF_3^{+\bullet}$
68.99



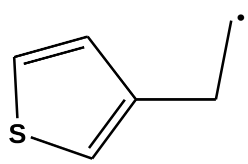

$C_4H_3S^{+\bullet}$
82.99



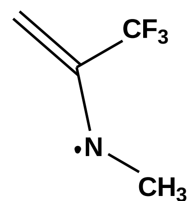

$C_3H_2F_3^{+\bullet}$
95.01



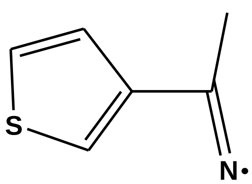

$C_5H_4NS^{+\bullet}$
110.01



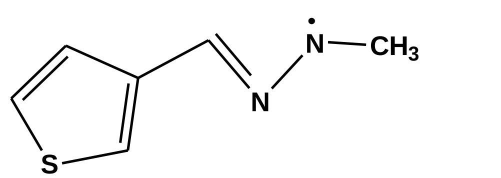

$C_6H_7S^{+\bullet}$
111.03



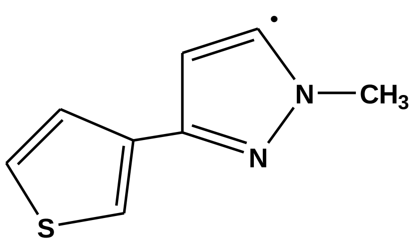

$C_4H_5F_3N^{+\bullet}$
124.04



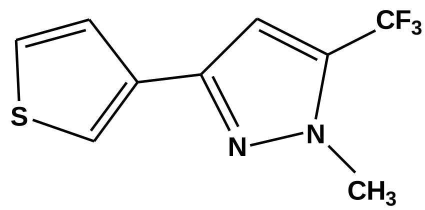

$C_6H_6NS^{+\bullet}$
124.02




$C_6H_7N_2S^{+\bullet}$
139.03




$C_8H_7N_2S^{+\bullet}$
163.03

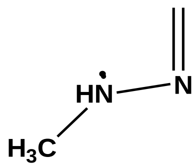



$C_9H_7F_3N_2S^{+\bullet}$
232.03

**FP-07**

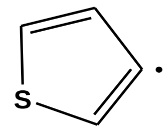
**Fragmentation pattern for the peak of MMH derivative IV**

**(Pyrazole-II- Retention time - 15.80 min)**

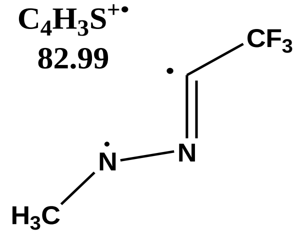


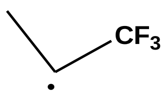
**$C_2H_5N_2^{+\bullet}$**
**57.05**

**$CF_3^{+\bullet}$**
**68.99**

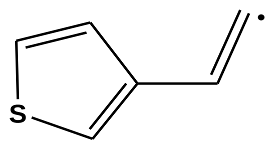


**$C_4H_3S^{+\bullet}$**
**82.99**



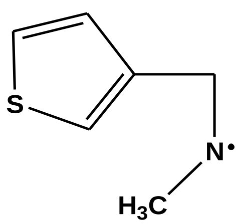


**$C_3H_4F_3^{+\bullet}$**
**97.03**

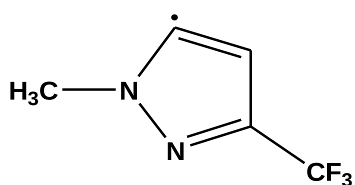


**$C_6H_5S^{+\bullet}$**
**109.01**

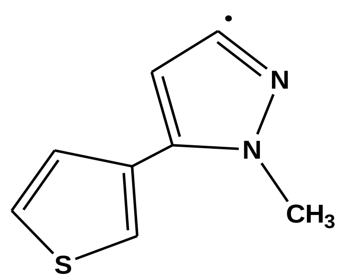
**$C_3H_3F_3N_2^{+\bullet}$**
**125.02**



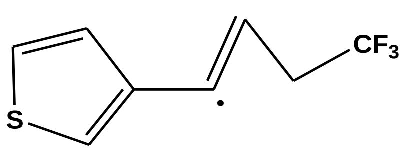
**$C_6H_8NS^{+\bullet}$**
**126.04**



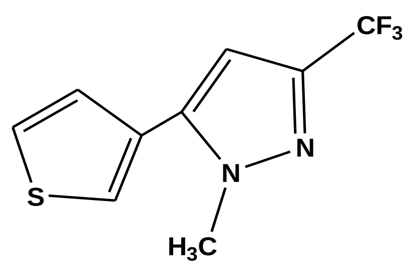
**$C_5H_4F_3N_2^{+\bullet}$**
**149.03**



**$C_8H_7N_2S^{+\bullet}$**
**163.03**



**$C_8H_6F_3S^{+\bullet}$**
**181.01**



**$C_9H_7F_3N_2S^{+\bullet}$**
**232.03**