Examination of rocket fuel poisoning

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Modern rocket and space technology is based on developments of the 1970s

Environmental risks of rocket and space activities

Energy-intensive technologies.

Unique and small-scale production.

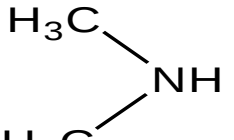
Global pollution of terrestrial and near-Earth space.

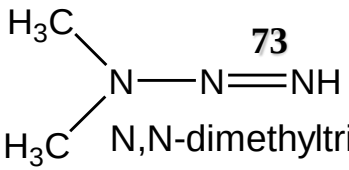
Ozone layer destruction.

Operation of hazardous production, use of toxic components.

“Heptil” - 1,1 - dimethyl hydrazine

Some of the well-known transformation products of UDMH


45
Dimethylamine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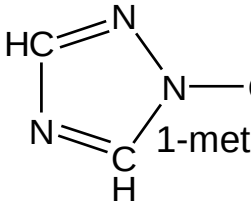
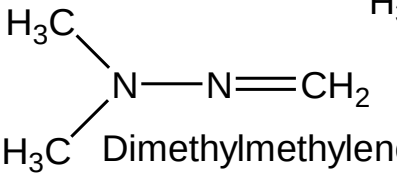
N,N-dimethyltriazene


83
1-methyl-1,2,4-triazole


74
Nitrozodimethylamine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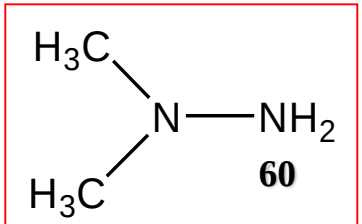
Dimethylmethylenehydrazine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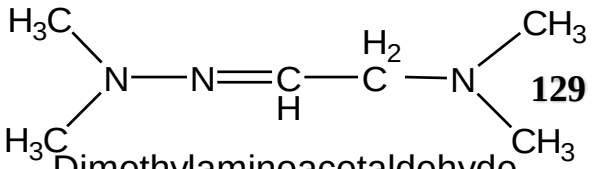
Unsymmetrical dimethylhydrazine (UDMH)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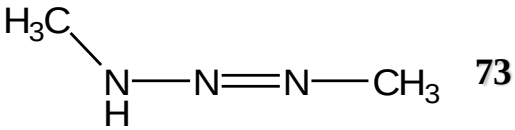
Dimethylaminoacetaldehyde dimethylhydrazone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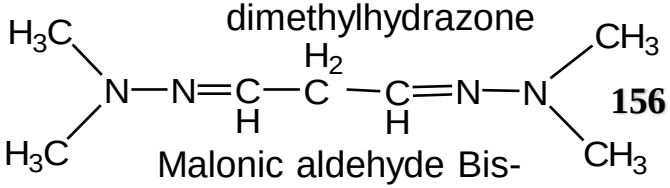
N1,N3-dimethyltriazene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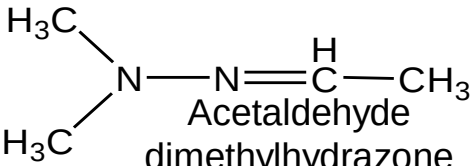
Malonic aldehyde Bis-dimethylhydrazone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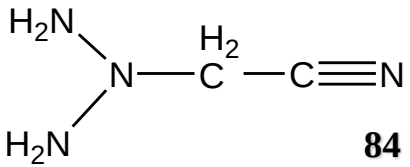
Acetaldehyde dimethylhydrazone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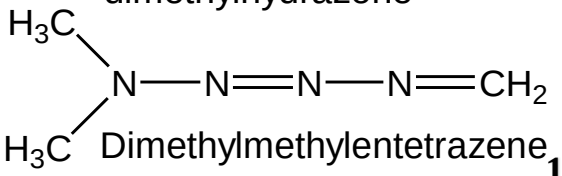
N,N-dimethylaminoacetonitrile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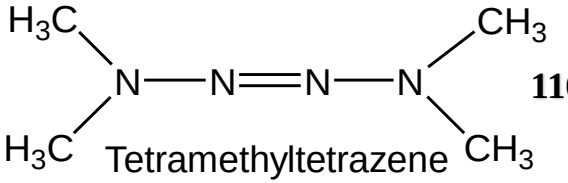
Dimethylmethylentetrazene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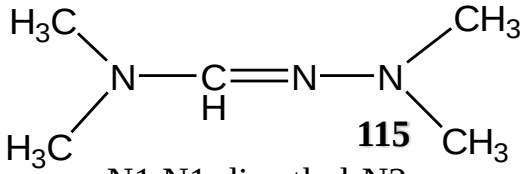
Tetramethyltetrazene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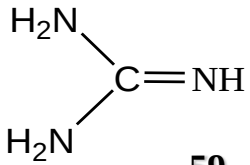
N1,N1-dimethyl-N2-(dimethylamino)formamidine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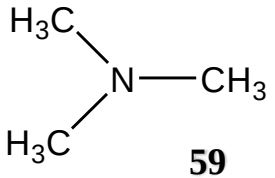
Guanidine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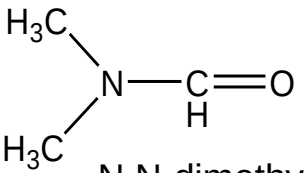
Trimethylamine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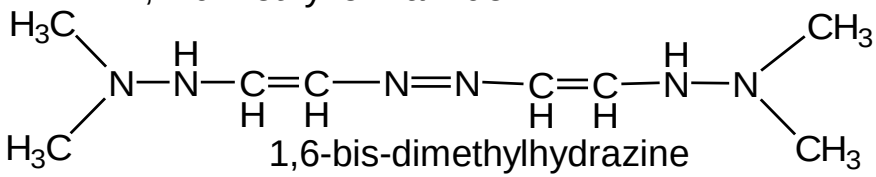
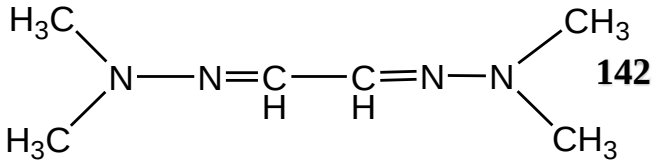
N,N-dimethylformamide


196
1,6-bis-dimethylhydrazine -3,4-diazohexatriene-1,3,5


142
Bis-dimethylhydrazoneglyoxal

Hygienic standards of UDMH and its transformation products

Substance	Maximum permissible concentration			
	Air working area, mg/m^3	Atmospheric air average daily, mg/m^3	Household water, mg/l	Soil, mg/kg
UDMH	0,1	0,001	0,02	0,1 *
Dimethylamine	1,0	0,005	0,1	-
Tetramethyltetrazene	3,0	0,005	0,1	-
Nitrozodimetilamine	0,001	0,001	0,01	-
N,N-dimethylformamide	10,0	-	-	-
Trimethylamine	5,0	0,16	0,05	
1-methyl-1,2,4-triazole	-	-	-	-
Dimethyl-1,2,4-triazole	-	-	-	-
Guanidine	-	-	0,1	-

* roughly safe exposure

The tasks of chromatography-mass spectrometry in the field of ecology of the rocket and space industry

Maintaining existing technologies

- Modernization based on in-depth studies of the mechanism of reactions
- Expansion of control and analytical procedures

Development of new technologies

- Cheap
- Reliable

Modern chromatographic-mass-spectrometric methods used in the rocket and space industry

ALL

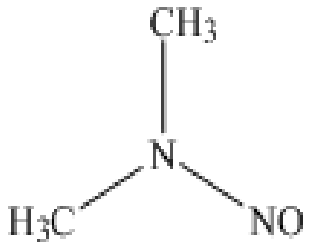
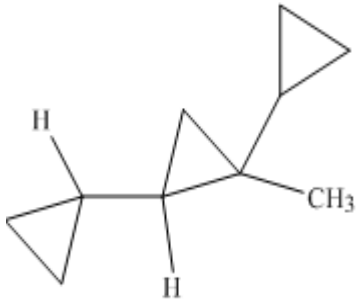
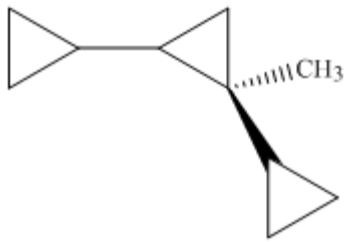
Variants of chromato-mass-spectrometry

- ON-LINE
  - GC-MS
  - LC-MS
    - IC-MS
    - CE-MS
- OFF-LINE
  - TLC-MS
  - LC-MS

GC-MS

- GC/GC – MS/MS
- Restriction of mass-spectrometry – no theory possessed to predict mass-spectra
- For gas chromatography molecular-statistical theory can calculate Henry constants (retention time) and empirical methods can calculate retention indexes

What does it mean "identify molecul"?

Levels of identification			
What atoms?	Atoms connection	Space distribution	Are optical isomers exist?
CxHy			

- Construct molecular structure
- Compare suspected structure and experimentally observed

Molecular structure

- Based on mathematic calculation of all possible structures of investigated class of isomers.

PCIB's	209
PCIBrB's	4078

- Theoretical (quantum-chemical or constructed based on structural chemistry lows.

Draw	Minutes
Calculate	Hours

Where we can find molecular structure?

Theoretical calculation	NMR
Gas-phase electron diffraction	IR-, UV-spectroscopy

- Roentgeno-structural analyses (X-ray studies)

Abilities of chromato-mass-spectrometry for isomers identification

Chromatography	Mass-spectrometry
Standards	Standards
Library search	Library search
Calculation of retention values	Calculation of mass-spectra
Correlations retention - structure	Regularities of fragmentation
Specific variants of analysis	Structure specific methods

- Combined libraries of retention indexes and mass-spectra
- Chromatographic filter for mass-spectral data

Abilities of chromato-mass-spectrometry for isomers identification

Chromatography	% of reliability	Mass-spectrometry	% of reliability
Standards	25	Standards	50
Two columns	50	MS/MS	75
Library search	10	Library search	30
Calculation of retention values: (mol-stat.)	25	Calculation of mass-spectra	0
indexes	10	Sequence de novo	10
Correlations retention - structure	10	Regularities of fragmentation	10
Specific variants of analysis	?	Structure specific methods	?

- We must collect 125 %, because precision +/- 25%

MOLECULAR STATISTICAL METHOD

Henry constant for adsorption of quasirigid molecules:

$$K_1 = \frac{1}{4\pi}\iint\left(\frac{2kT}{\Phi''_z}\right)^{\frac{1}{2}}\exp\left(-\frac{\Phi_0}{kT}\right)\sin\Theta d\Theta d\Psi \quad (1)$$

where Φ_0 and Φ_z'' - values of potential function of intermolecular interaction of adsorbate molecules with the adsorbent, and it second derivative by the distance z the mass center of the molecule from the surface of the adsorbent at the equilibrium distance z_0. The values of Φ_z'', Φ_0 and z_0 depends on the Euler angles Θ and ψ, defining the orientation of the molecules on the surface of the adsorbent.

Potential function Φ:

$$\Phi = \sum_{a}\sum_{c(ITC)}\varphi_{a\ldots c(ITC)} \quad (2)$$

For $\varphi_{a\ldots c(ГТС)}$ the potential in Buckingham-Korner form was chosen:

$$\varphi_{a\ldots c(ГТС)} = -C_1 r^{-6} - C_2 r^{-8} + B\cdot\exp(-qr)\,, \quad (3)$$

where C_1 and C_2, kJ · nm ·mol^{-1} - parameters of attraction forces, B, kJ · nm ·mole^{-1}, q, nm^{-1} - the parameters of repulsive forces. Parameter of repulsive forces q taken to be 35.7 nm^{-1}

Molar differential heat ($\Delta\bar{U}_1$) and entropy ($\Delta\overline{S_1}$) of adsorption :

$$\ln K_{1.C} = = (\Delta\overline{S_1} + R)/R - \Delta\bar{U}_1/(RT)\,, \quad (4)$$

где $\Delta\overline{S_1}$ - entropy, $\Delta\bar{U}_1$- heat of adsorption.

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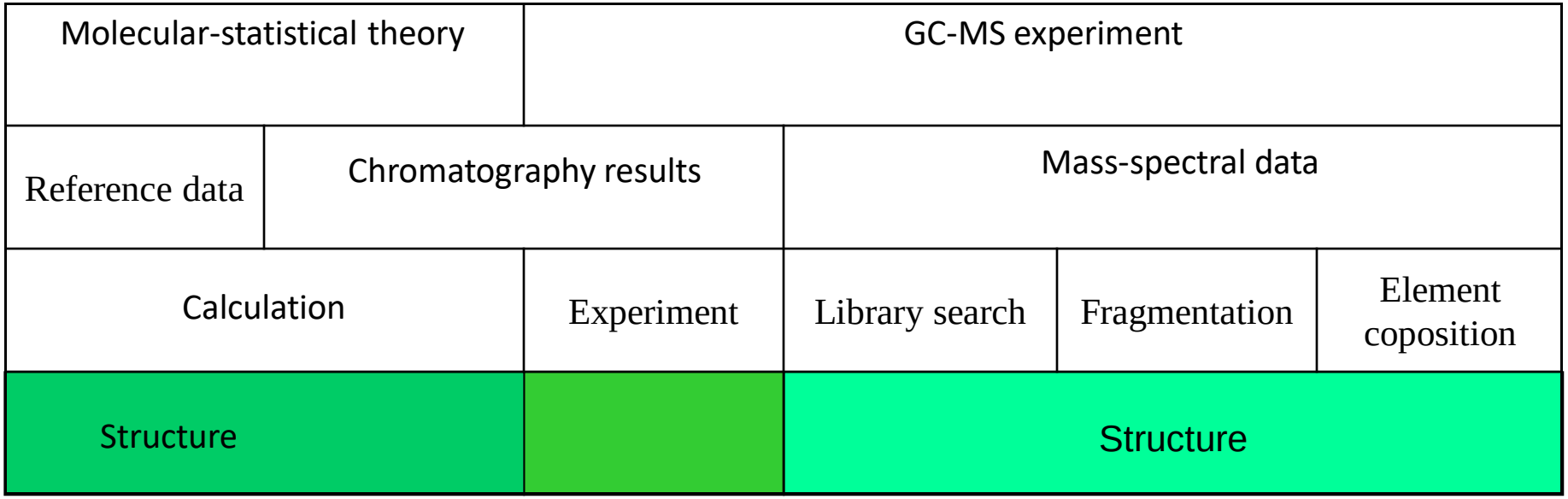
Combination of molecular-statistical calculations and GC-MS data



Molecula identification

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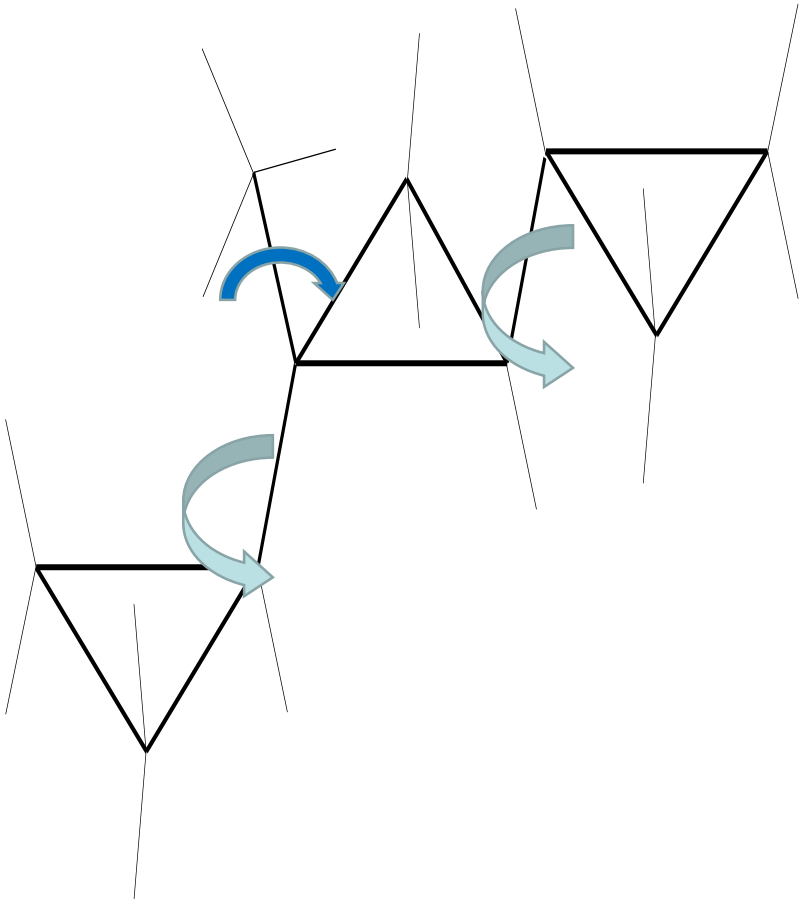
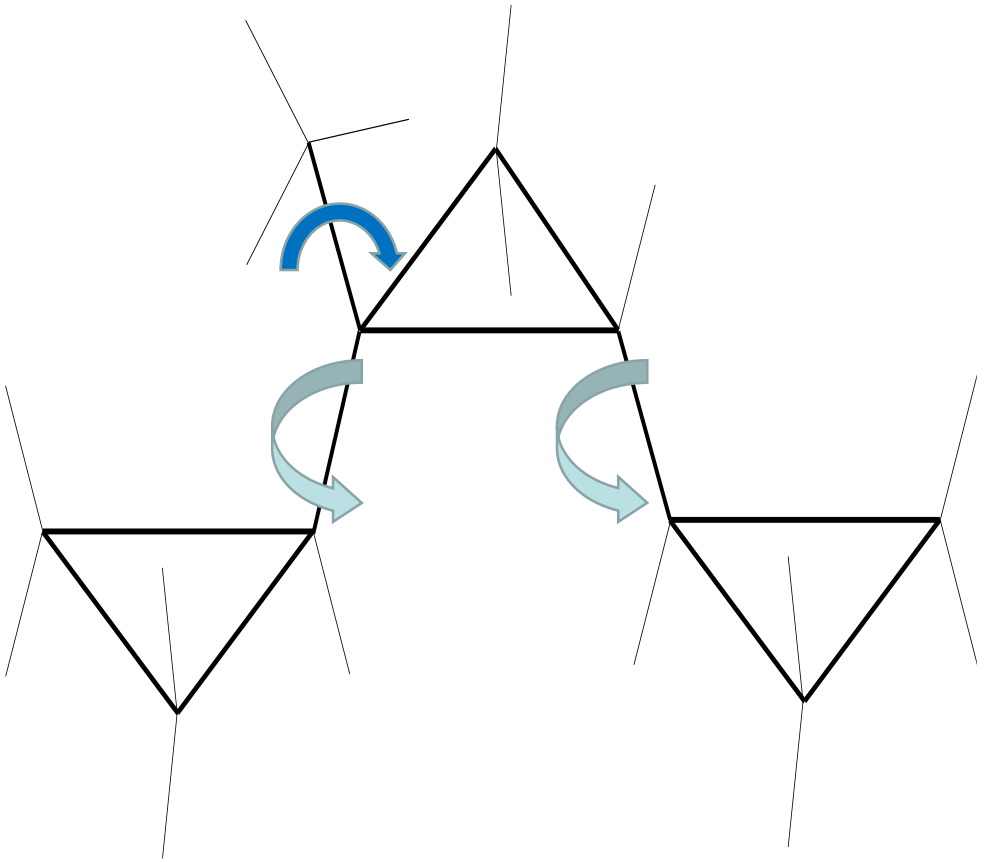
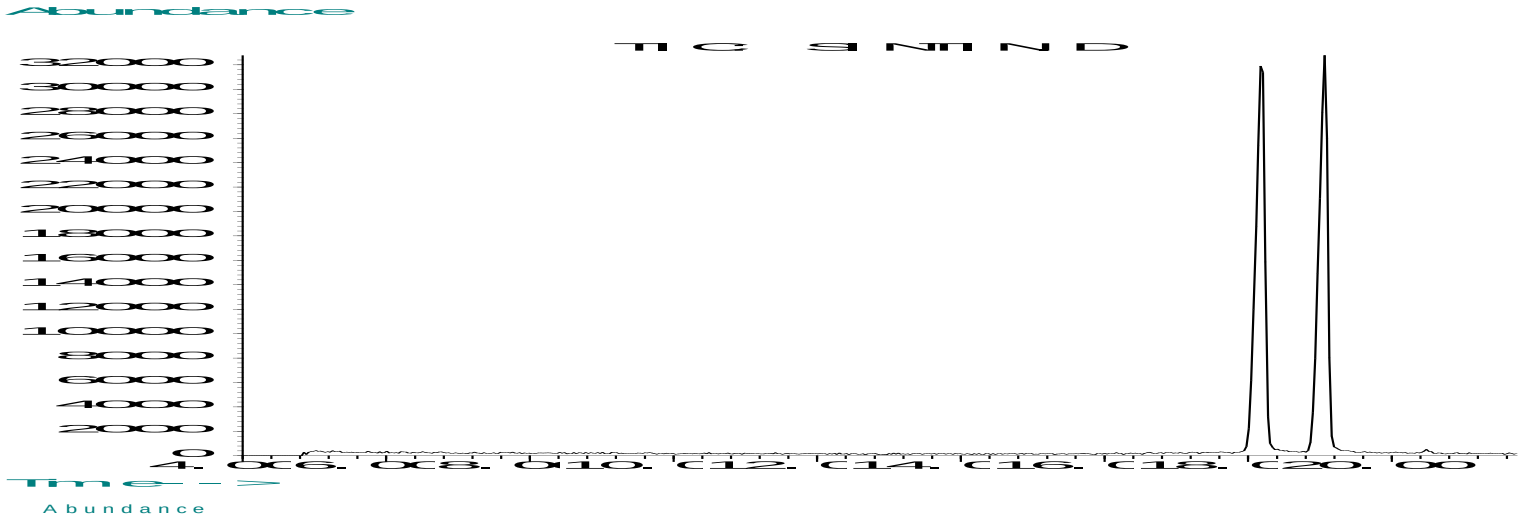
Structures of isomeric cis-, trans-methyl-dicyclopropyl- cyclopropanes

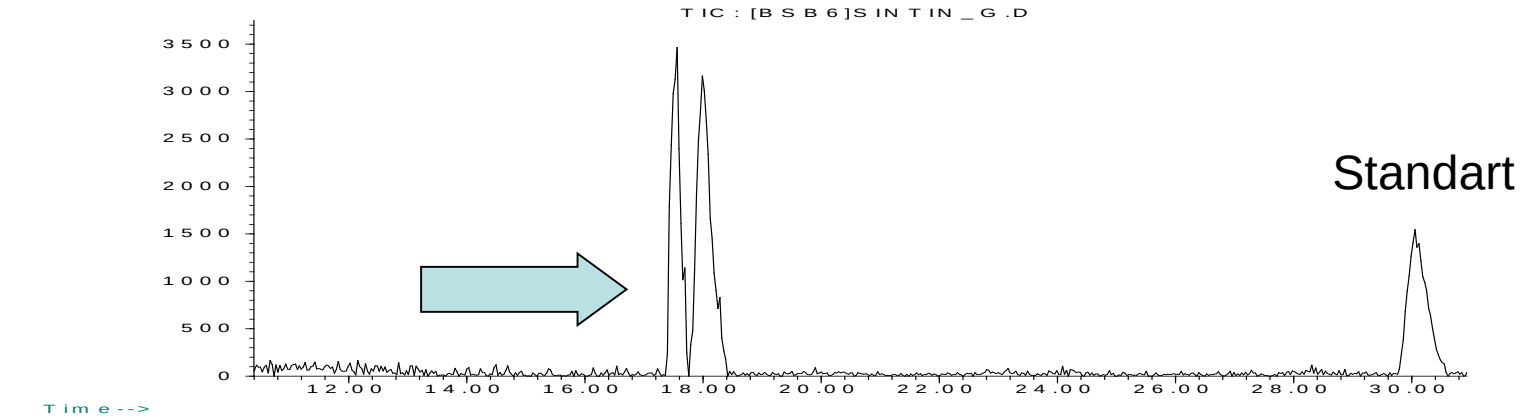




17

Chromatograms of isomeric cis-, trans-methyl-dicyclopropyl- cyclopropanes on DB-5 and micro packed column with GTCB.





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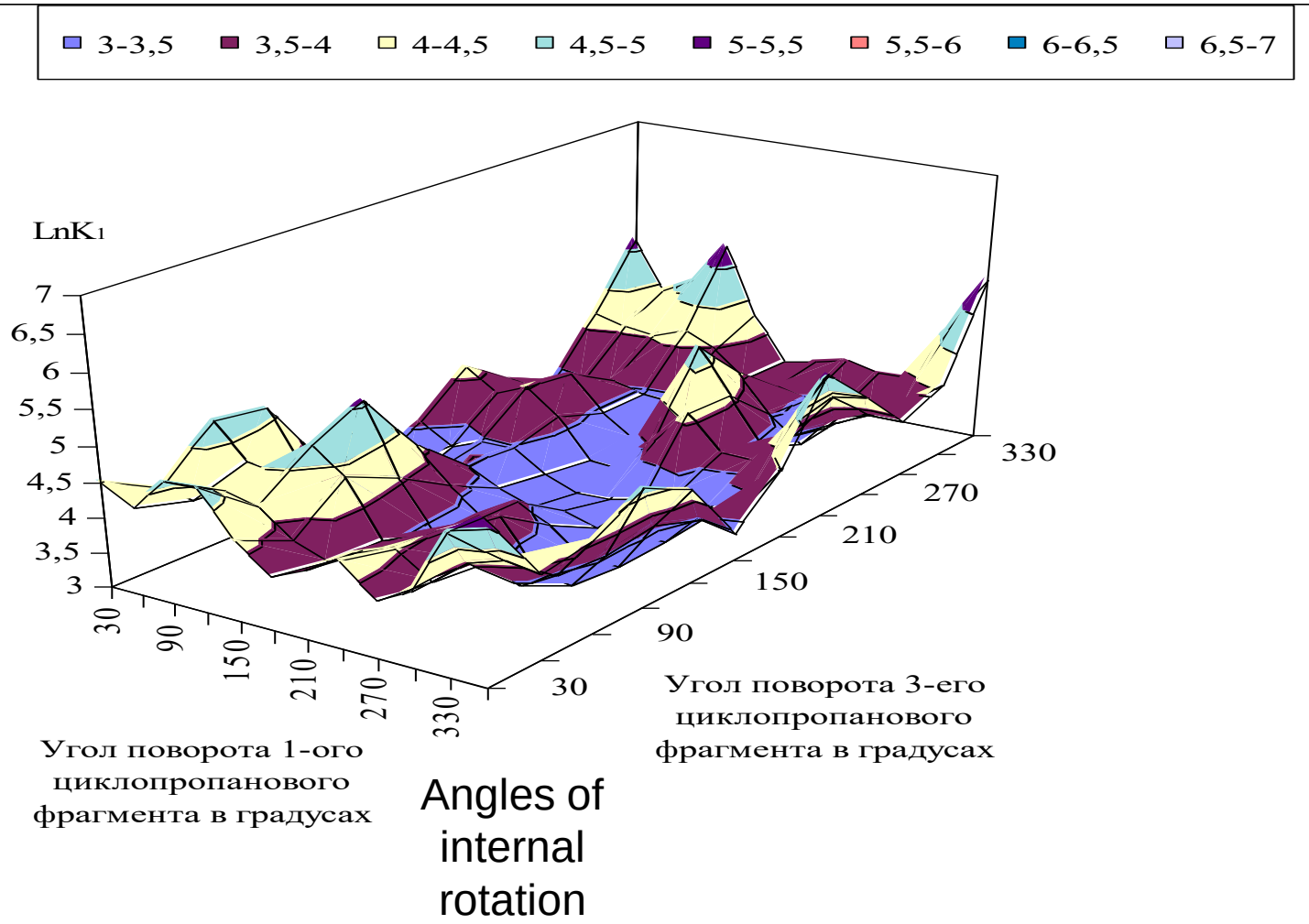
Three dimensional diagram



Angles of internal rotation

Differences between calculated Henry constants of isomeric cis-, trans-methyl-dicyclopropyl- cyclopropanes for different angles of internal rotation

		α_1					
		120	150	180	210	240	270
α_2	90	0,886	0,7340	0,4436	0,0811	0,0762	0,1813
	120	1,679	1,3483	0,786	0,1355	***-0,816***	***-0,7059***
	150	0,693	0,6968	0,4361	0,2076	***-0,532***	***-0,7968***
	180	0,016	***-0,056***	***-0,165***	***-0,119***	0,0206	0,0011
	210	***-0,142***	0,0218	***-0,148***	***-0,095***	0,4120	1,1031
	240	***-0,682***	***-0,386***	***-0,572***	***-0,363***	0,3134	***-0,0467***
	270	***-0,363***	***-0,486***	***-0,294***	0,3801	0,3751	***-0,8227***

Kovach Retention indexes

$$J_x = J_n + (J_{n+1} - J_n)\frac{(f(t_{R,x}) - f(t_{R,n}))}{(f(t_{R,n+1}) - f(t_{R,n}))}$$

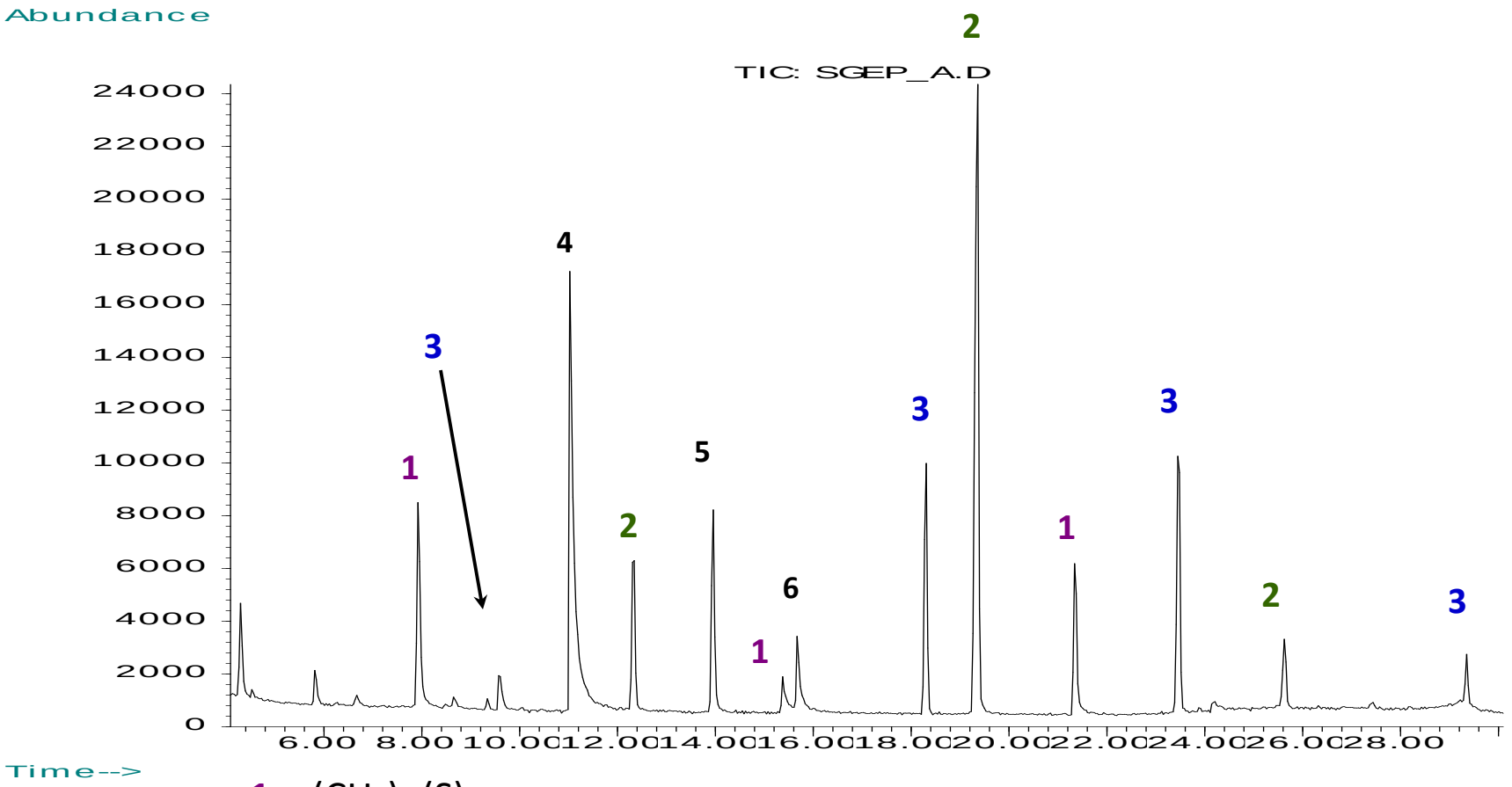
$$f(t_R) = t_R + q\lg(t_R - t_0)$$

Correlation "retention-property"

: any physical or chemical property of molecule($t_{boiling}$, van-der-Vaals volume, dipole moment, polarization, critical volume, pressure, temperature

: topology indexes

RIC of sulfur and non-symmetrical dimethylhydrazine interaction products



1 – $(CH_3)_2(S)_n$

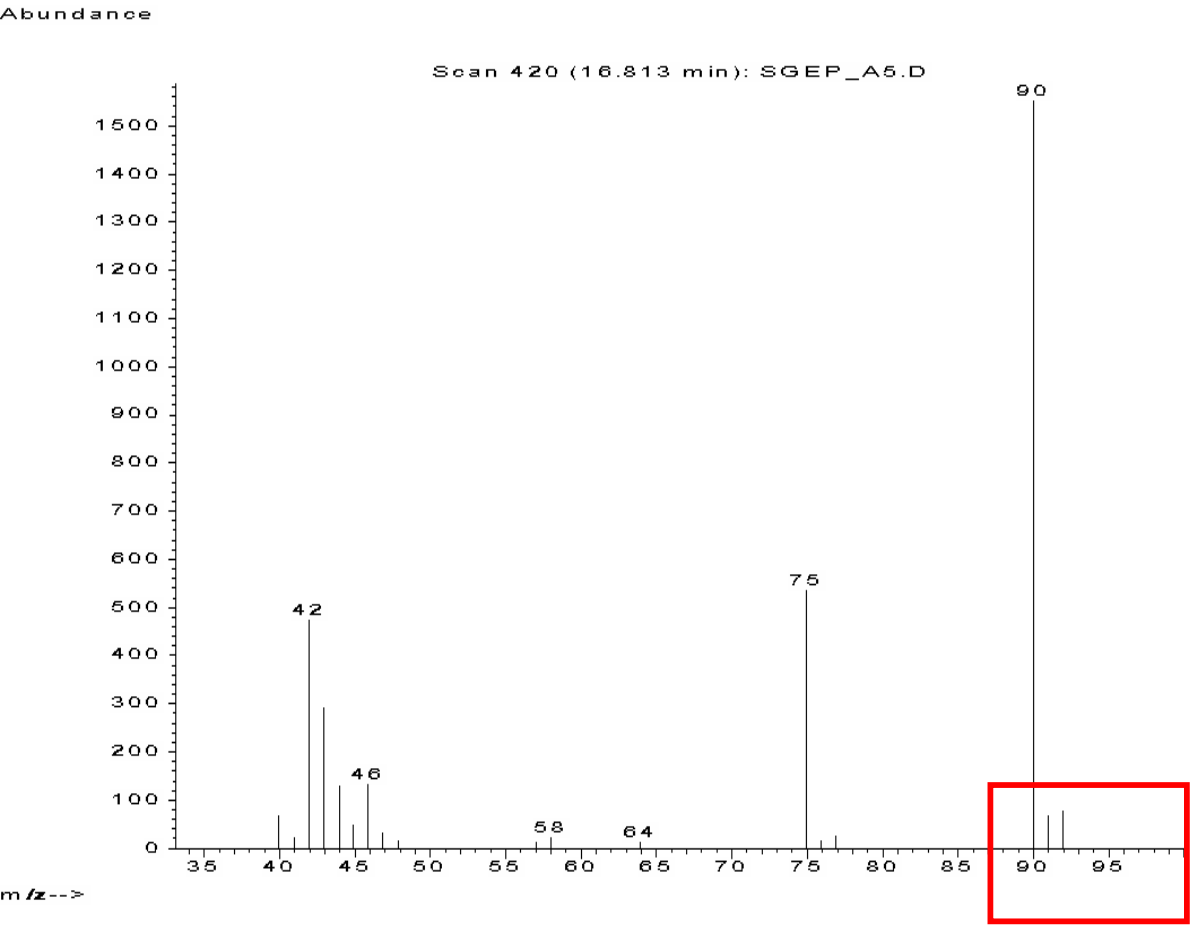
2 – $(CH_3)_2NCH_3S_n$,

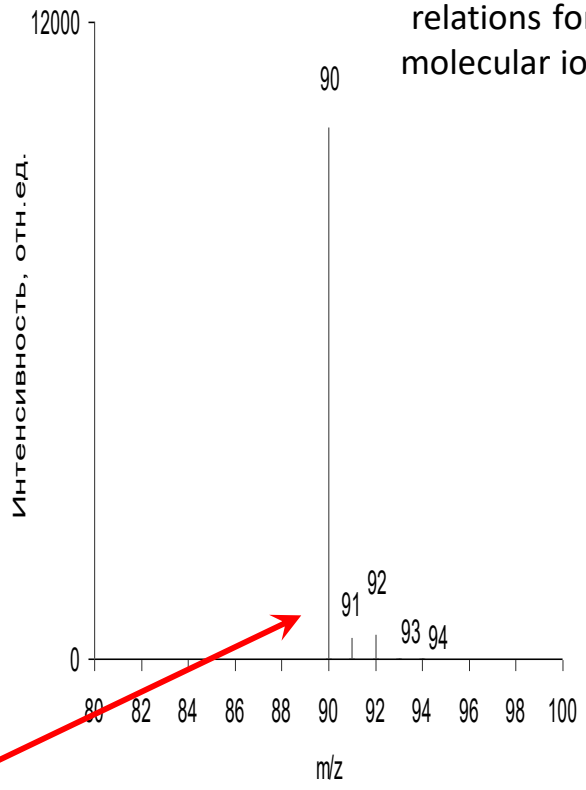
3 - $((CH_3)_2N)_2S_n$

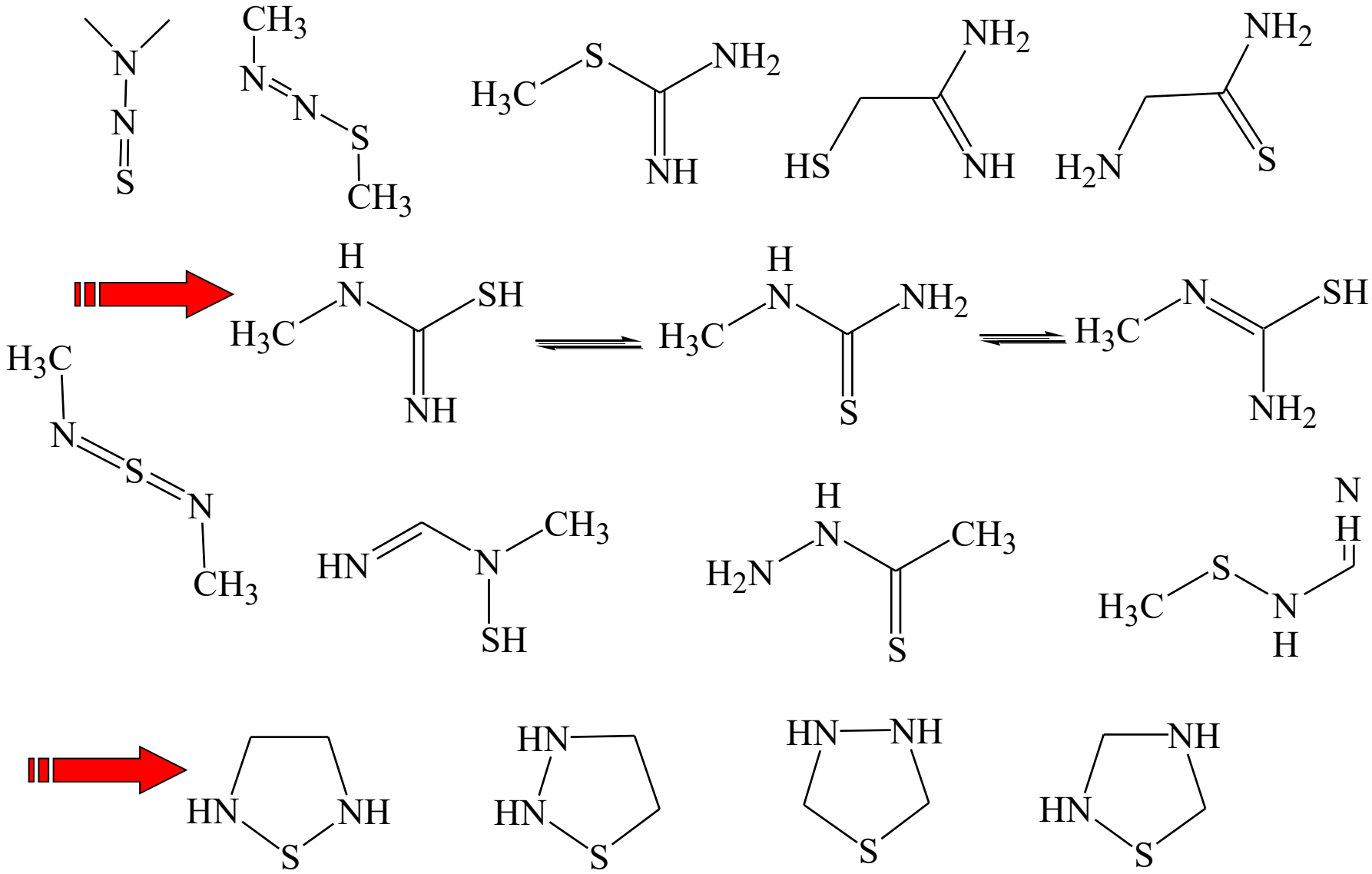
4, 5, 6 Unknown substances

Mass-spectrum of unknown molecul

Theoretically calculated isotopic relations for molecular ion





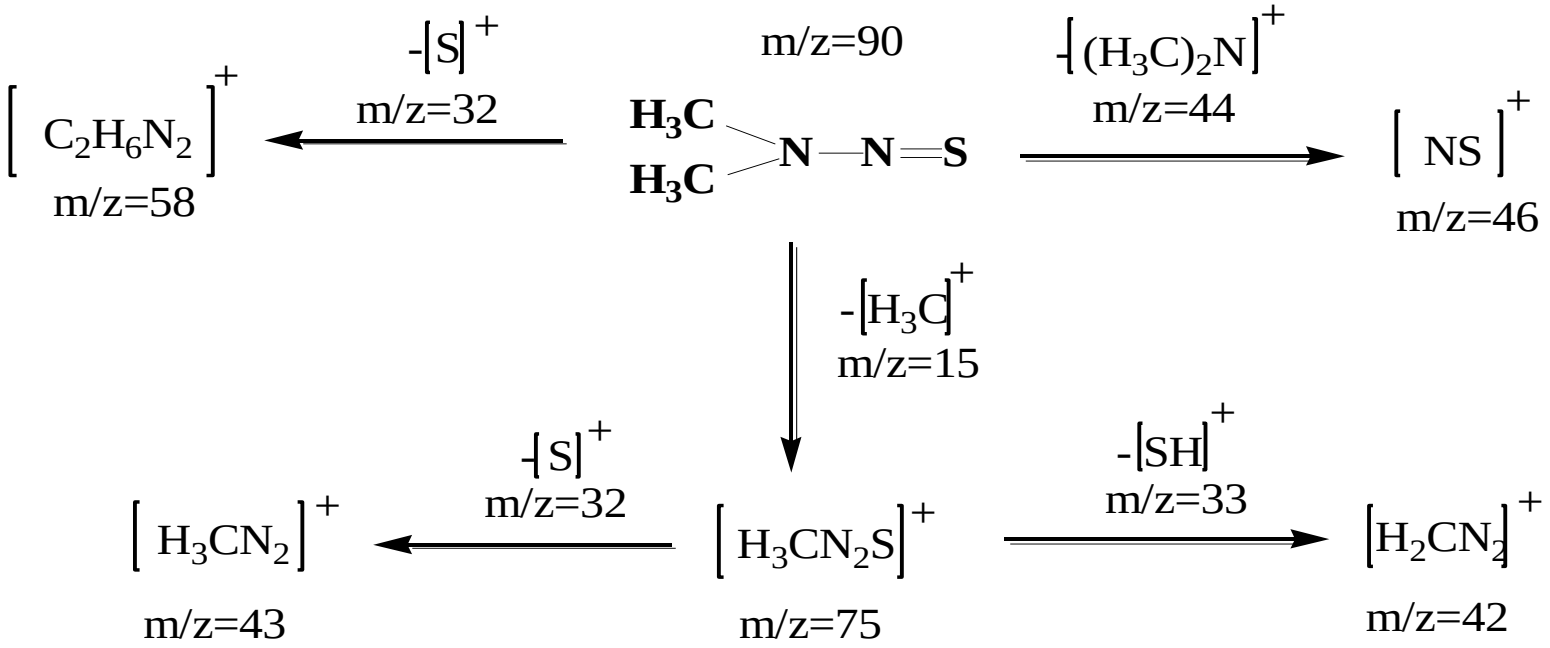


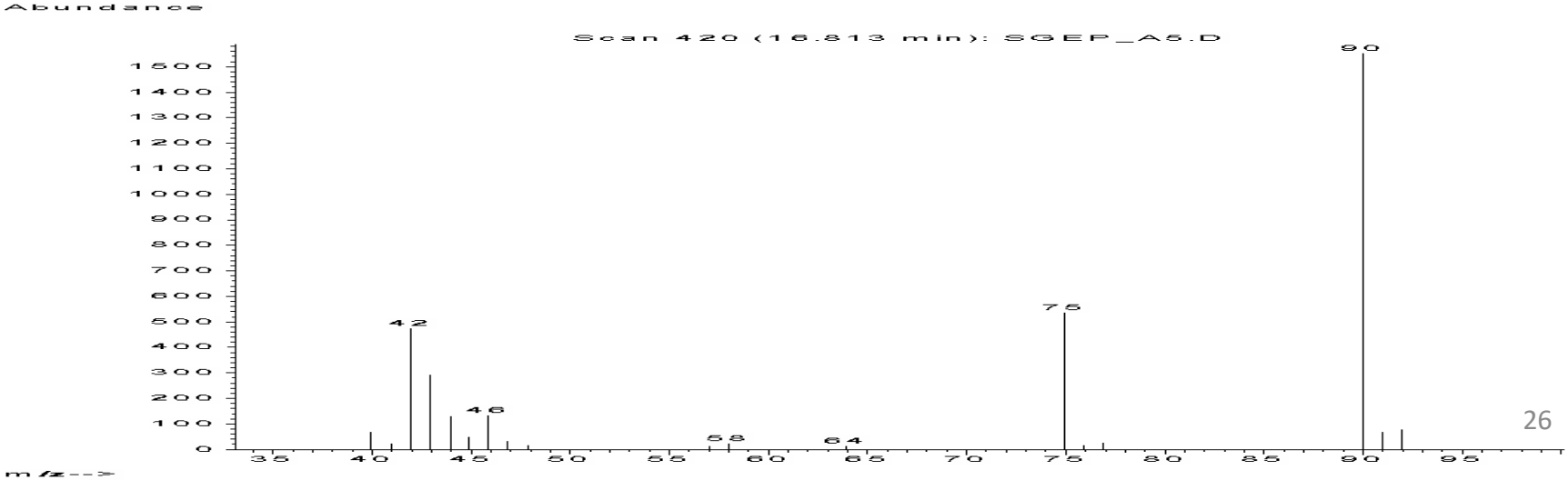
Retention indexes (RI)

t_r, min	Substance	RI	MW	$(m/z)^{10}_{0}$
5,9	**Dimethyldisulfide***	**730**	**94**	**94**
9,4	di-(N,N-dimethylaminosulfide	816	120	76
11,3	Dimethylhydrazonedimethylformamide	869	115	44
12,5	N,N-dimethylaminomethyldisulfide	904	123	76
14.1	**Dimethyltrisulfide ***	**952**	**126**	**126**
15,6	**Dimethylsulfonitrosoamine**	998	90	90
15,9	N,N-dimethylmetanosulfoamide	1008	89	89
18,6	di-(N,N-dimethylaminodisulfide	1093	152	44
19,6	N,N-dimethylaminomethyltrisulfide	1126	155	76
21,6	**Dimethyltetrasulfide ***	**1191**	**158**	**79**
23,7	di-(N,N-dimethylaminotrisulfide	1261	184	42
24,3	Unknown	1281	129	129
25,9	N,N-dimethylaminomethyltetrasulfide	1334	187	76

* compounds, choused as standards

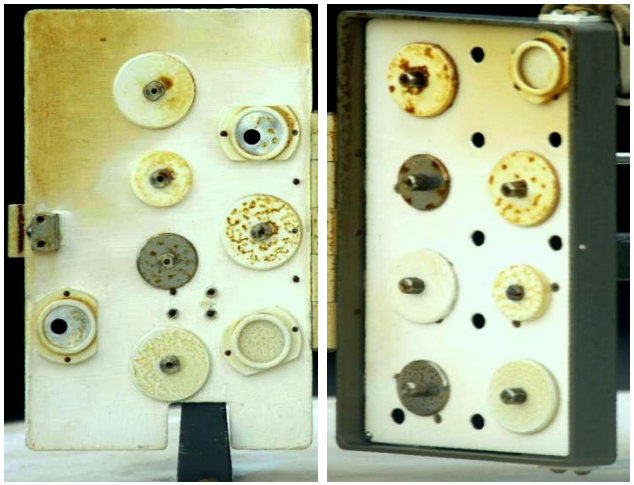
Suspected fragmentation scheme of dimethylsulfonitrosoamine

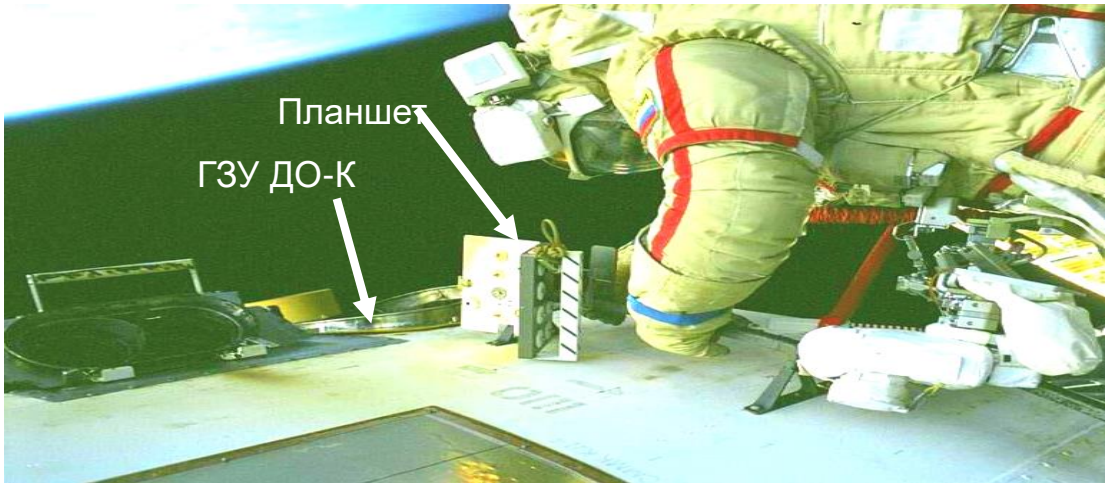


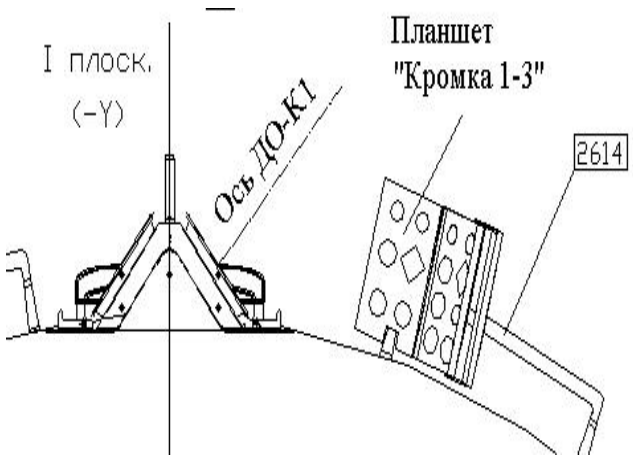


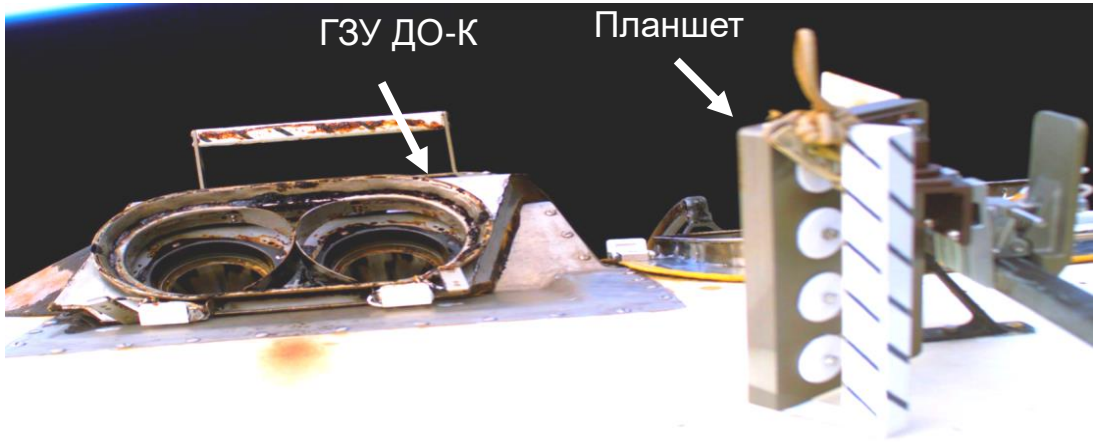
Space experiments

“Kromka 1-3” - ISS









Chemical composition of products of incomplete combustion of rocket fuel

Fresh precipitate

№	Substance		m/z	%
1	NO		30	8.97
2	CO_2		44	9.52
3	Ammonia		17	16.45
4	H_2O		18	30.58
5	Dimethylamine		44	1.75
6	Trimethylamine		58	0.50
7	Formaldehyde dimethylhydrazone		42	0.68
8	Derivative of Isocyanate		56	8.30
9	Dimethylhydrazine acetone		100	0.33
10	Nitrozodimethylamine		74	3.87
11	Dimethylaminoacetonitrile		83	3.10
12	N,N-dimethyldimethylformamide		73	1.06
13	4-dimethylaminomethyltetrasulfide		94	0.18
14	Dihydrazone dihydrazine		m/z	%
15	1-methyl-1H-1,2,4-triazole		83	5.65
16	4,5-dihydro-3,4,5-trimethyl-1H-pirazole		97	0.67
17	N,N-diethylacetamide		115	0.42
18	1H-3,5-diamino-1,2,4-triazole		99	1.14
19	heterocyclic nitrogen-containing compound		107	0.07
20	Imidazole		108	0.19
21	1H-1,2,4-trimethyltriazole		97	0.38
22	6-methyl-4,5-diaminopirimidine		124	0.37
23	N,N-dimethylurea		97	0.01
24	Derivative of N,N-dimethylurea		102	1.48
25	1H-4-nitropirazole		113	0.39
26	Derivative of UDMH		121	0.09
27	Derivative of UDMH		134	0.04

Dry precipitate

Substance
Nitrozodimethylamine
Dimethylaminoacetonitrile
N,N-dimethylformamide
Guanidine
1-methyl-1H-1,2,4-triazole
1H-1,2,4-trimethyltriazole

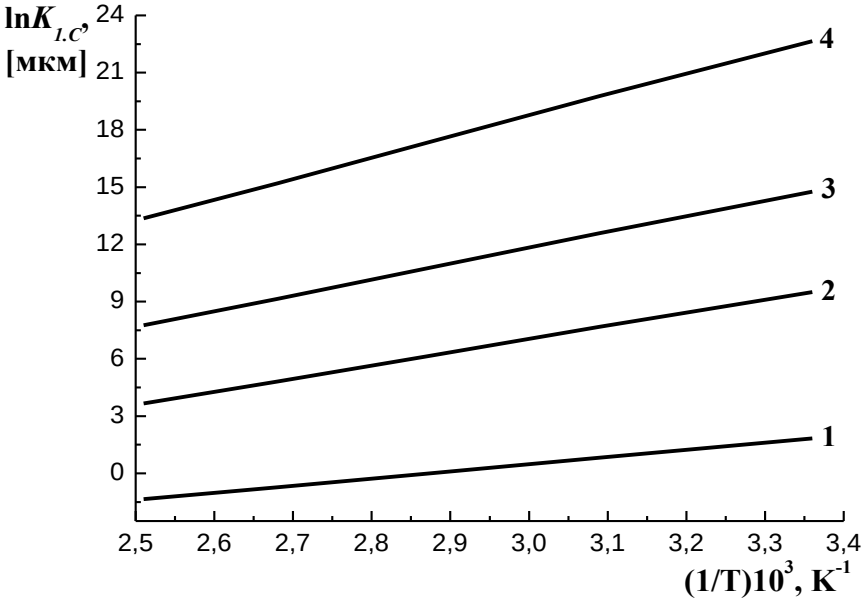
Complex salts with organic cations and inorganic anions NO_3^-, NO_2^-, CO_3^{2-} provide an abnormally high activity of contaminants even in a vacuum.

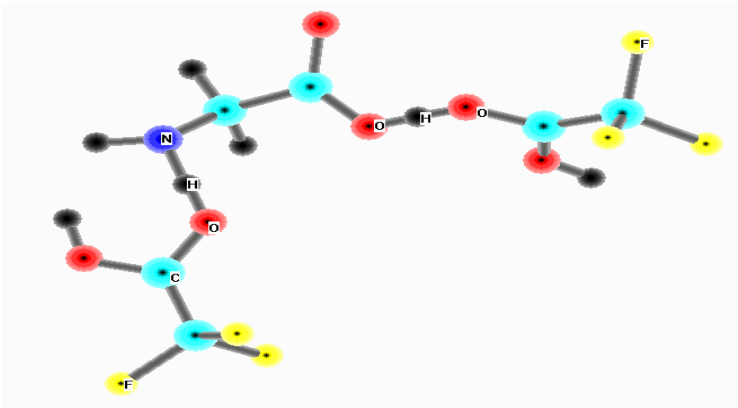
A lot of toxic products

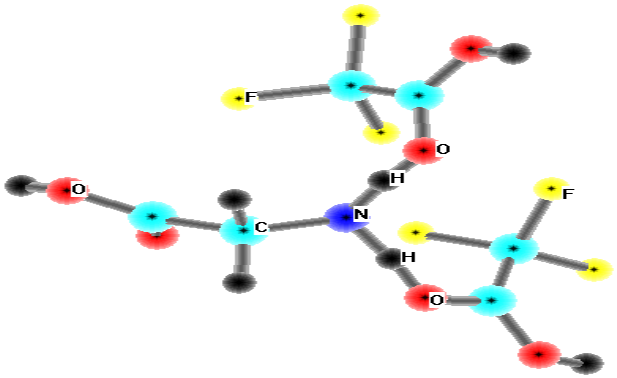
Abilities of HPLC-MS for molecules identification

HPLC	Mass-spectrometry
Standards	Standards
Library search	Library search
Calculation of retention values	Calculation of mass-spectra
Correlations retention - structure	Regularities of fragmentation
Specific variants of analysis	Structure specific methods

Adsorption of isomeric associates

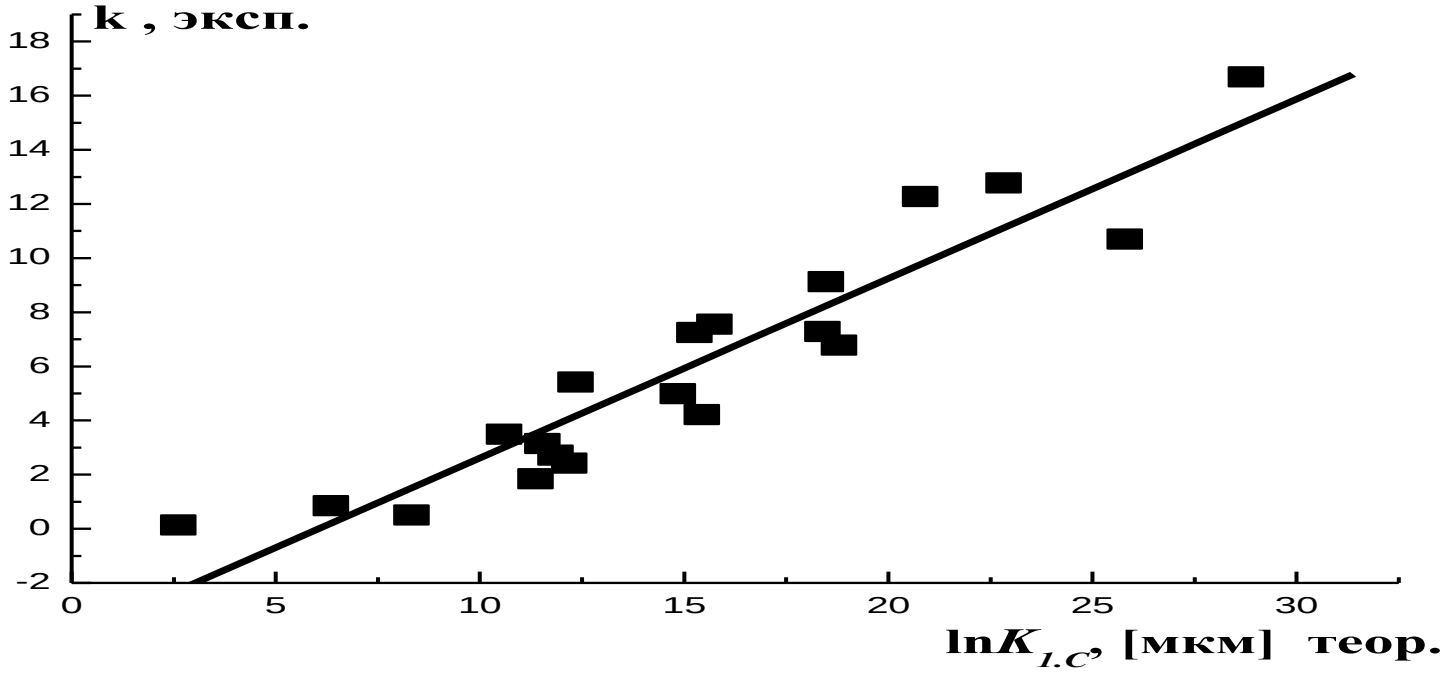






30

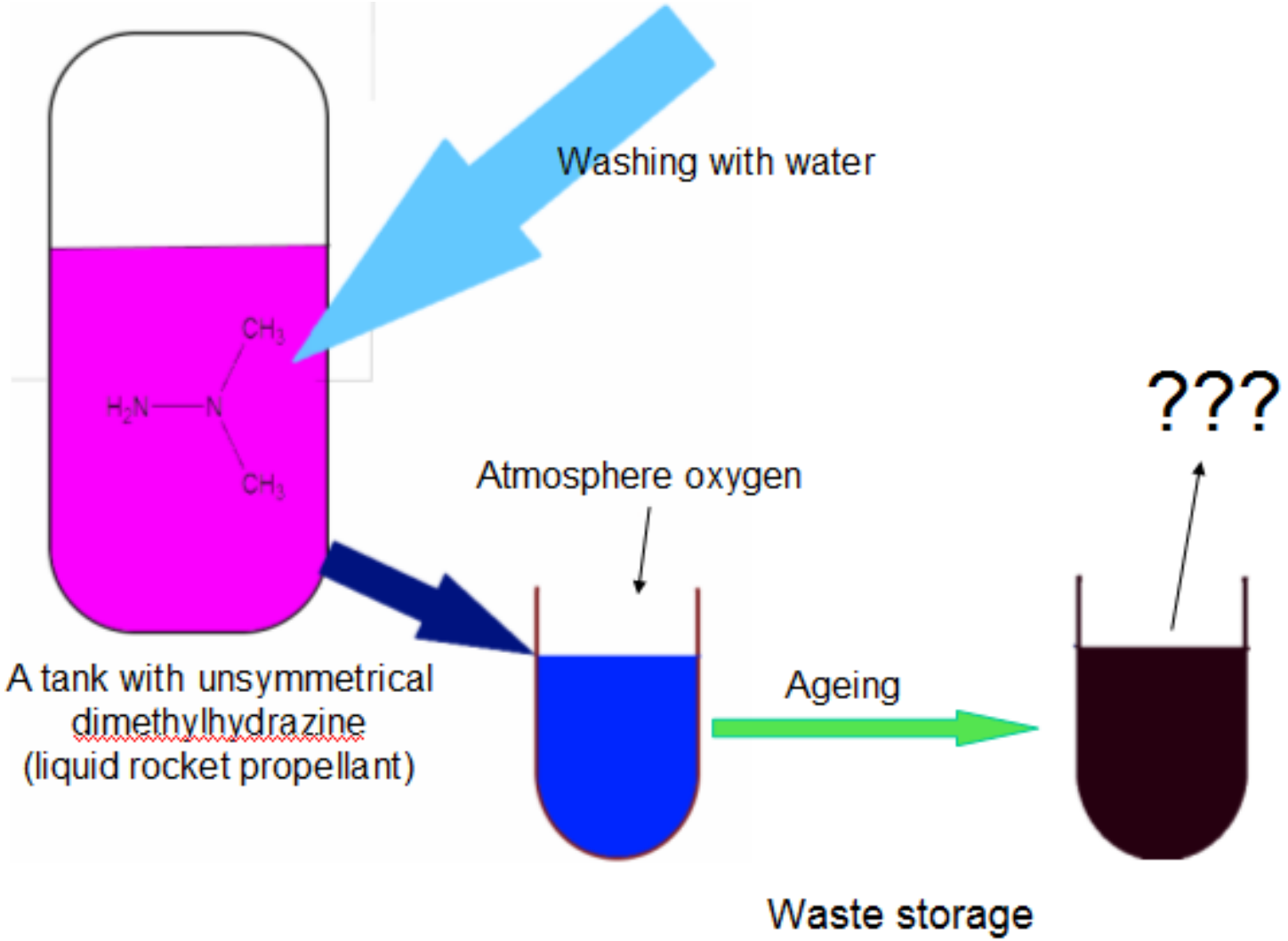
Correlation: molecular statistical calculation - experiment



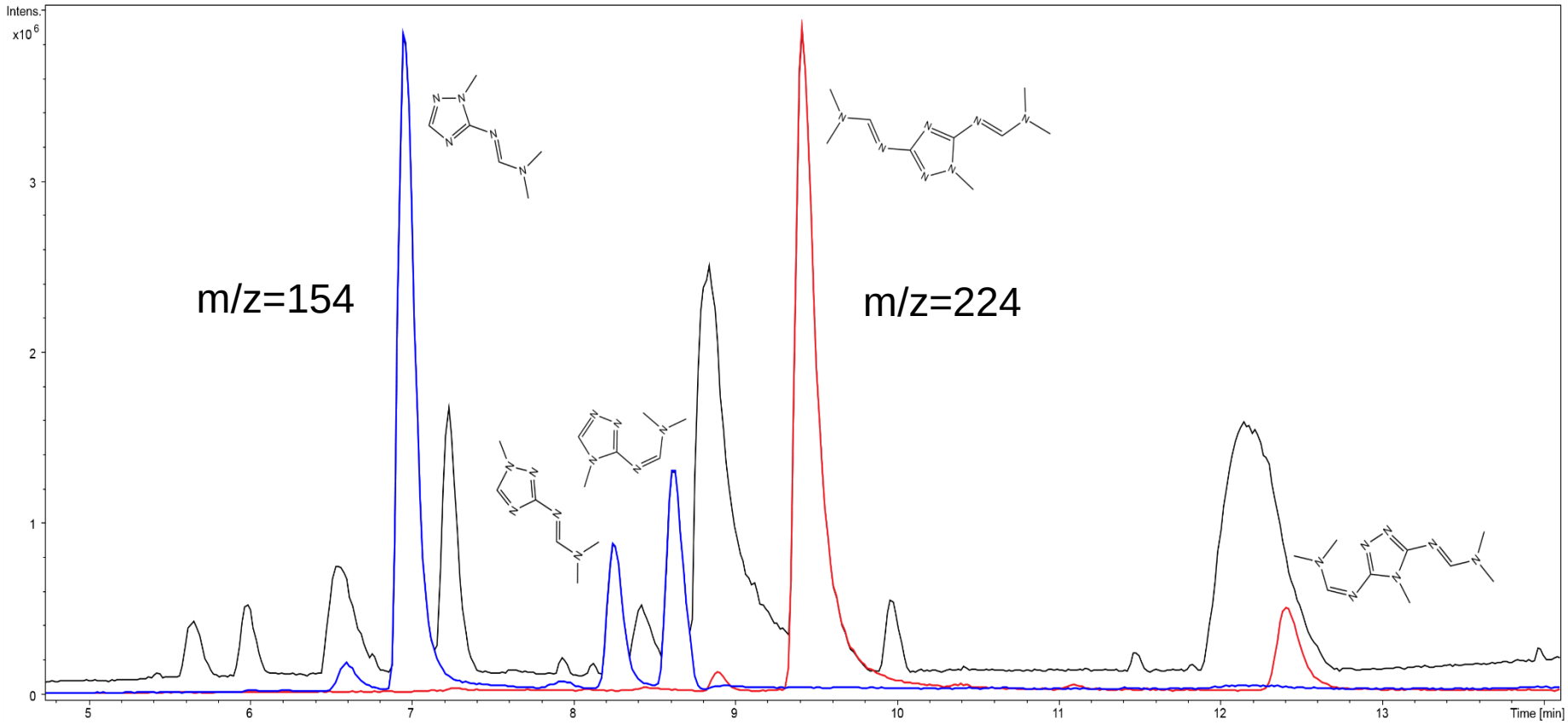
$R^2 = 0.976$

31

FORMATION OF THE PRODUCT OF OXIDATIVE TRANSFORMATION OF UDMH (BLACK OSMOL)

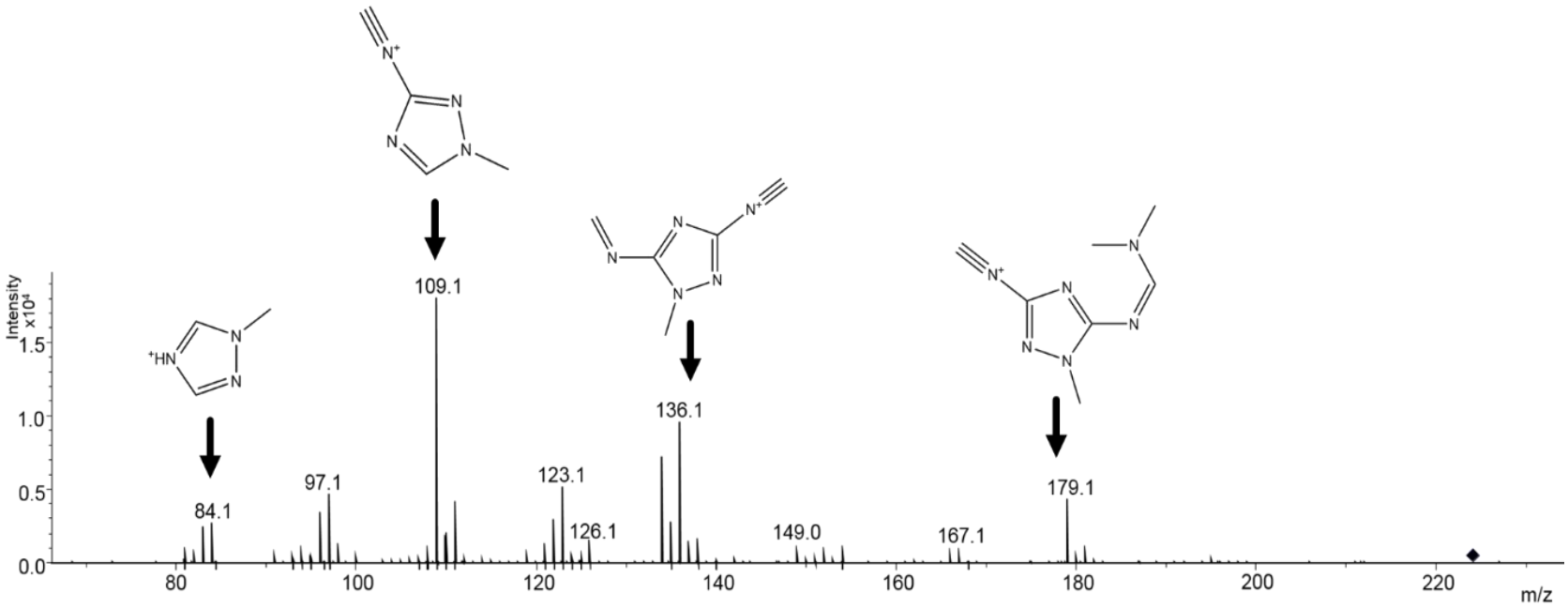


THE CHROMATOGRAM OF “BLACK OSMOL”

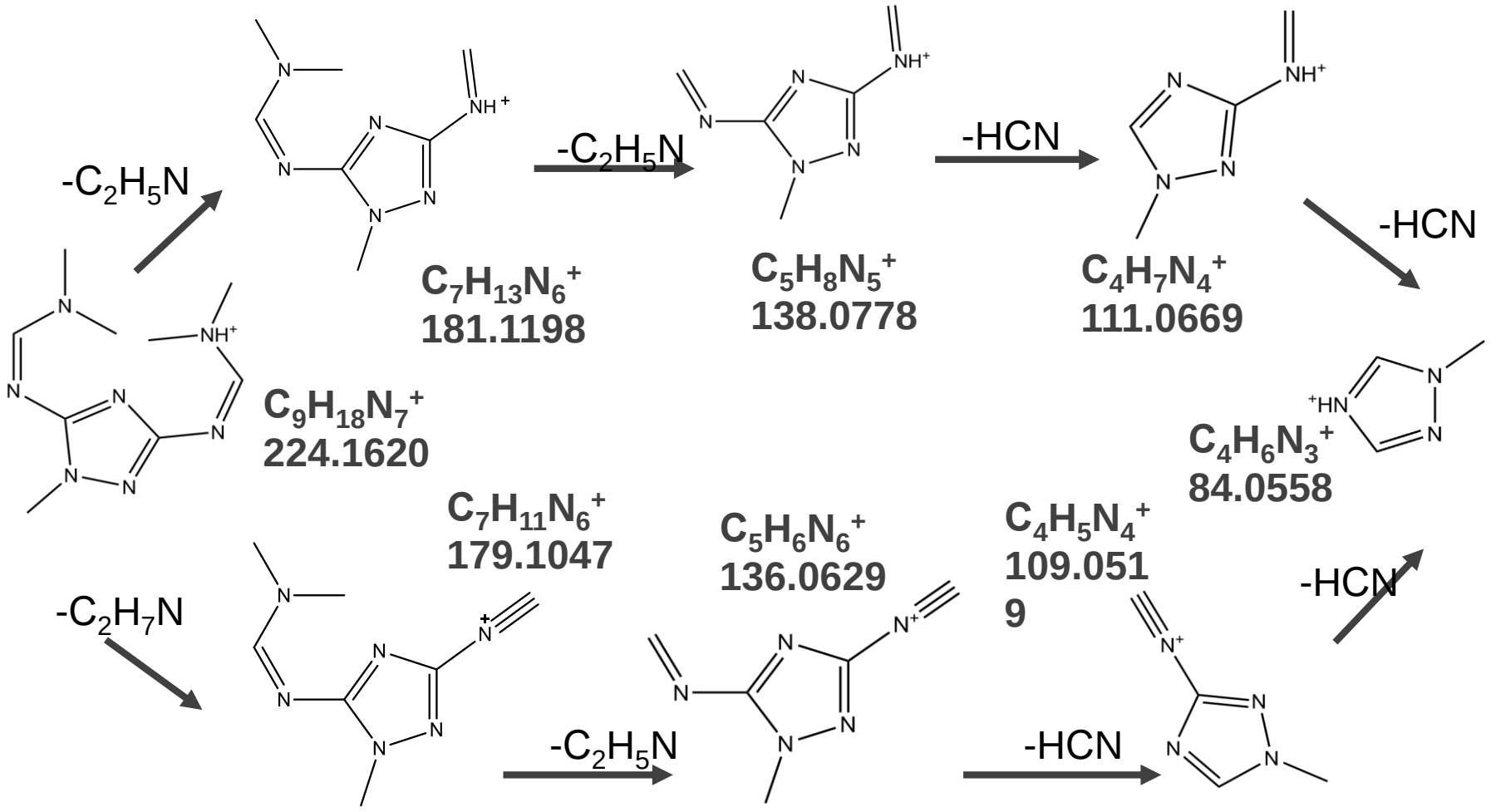


HPLC-ESI-ToF-MS (C18-column, extracted ion chromatogram)

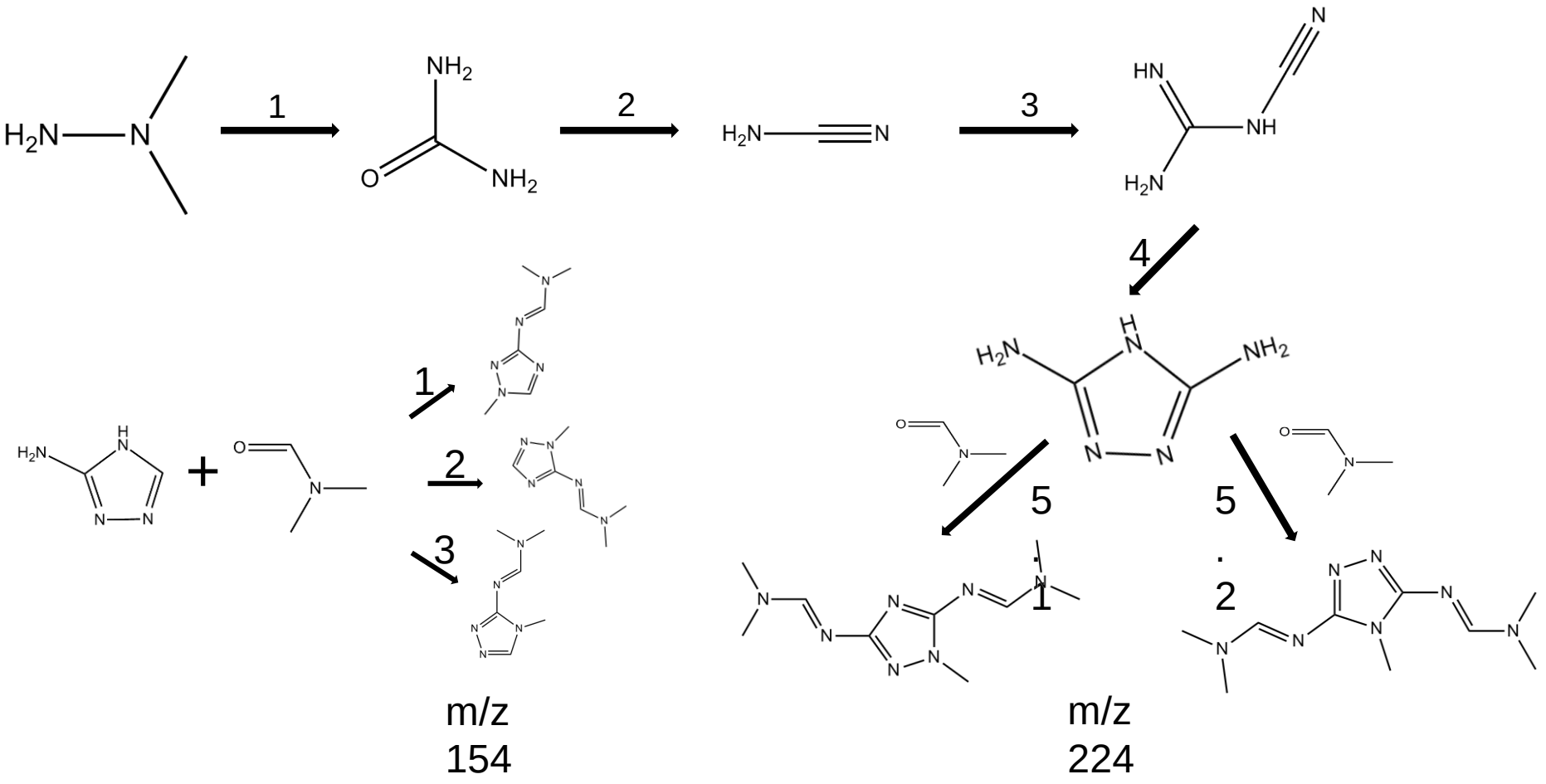
The tandem mass spectrum recorded for the ion with m / z 224 from the first peak with a retention time of 9.5 minutes



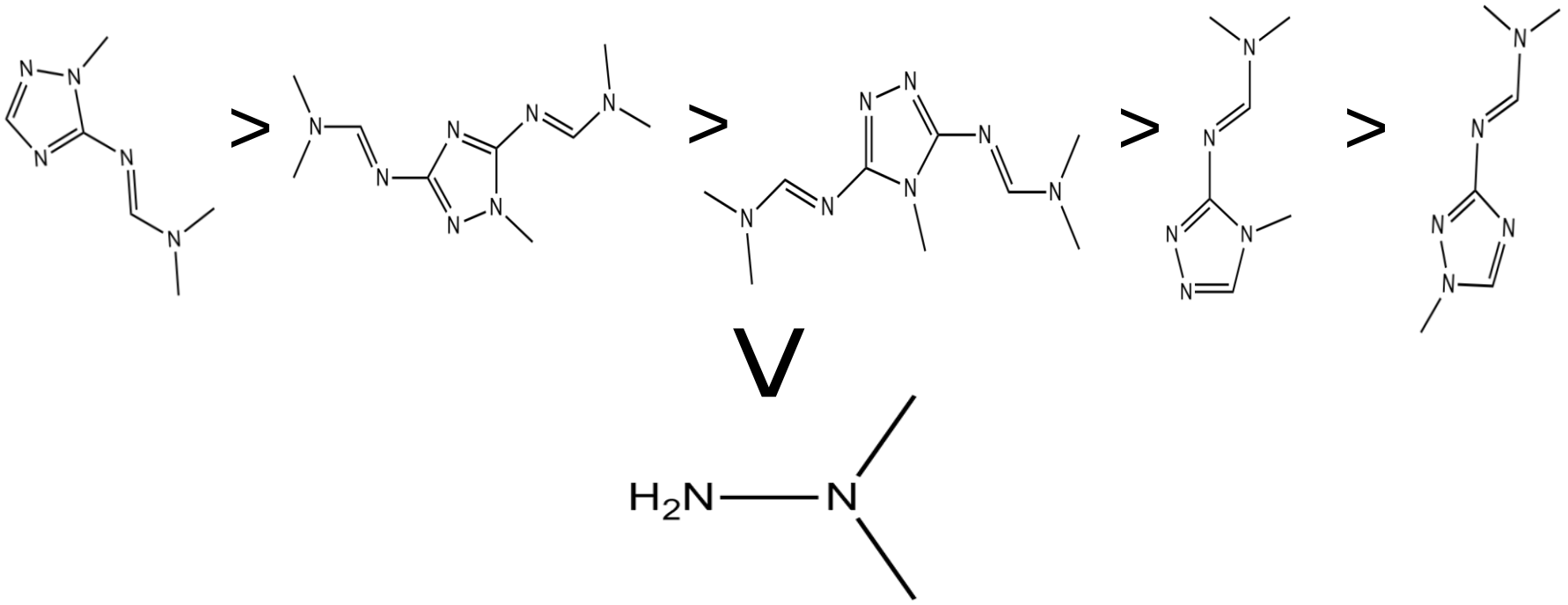
Scheme of fragmentation of ion 224



Possible directions of educationsubstances with m / z 154 and 224



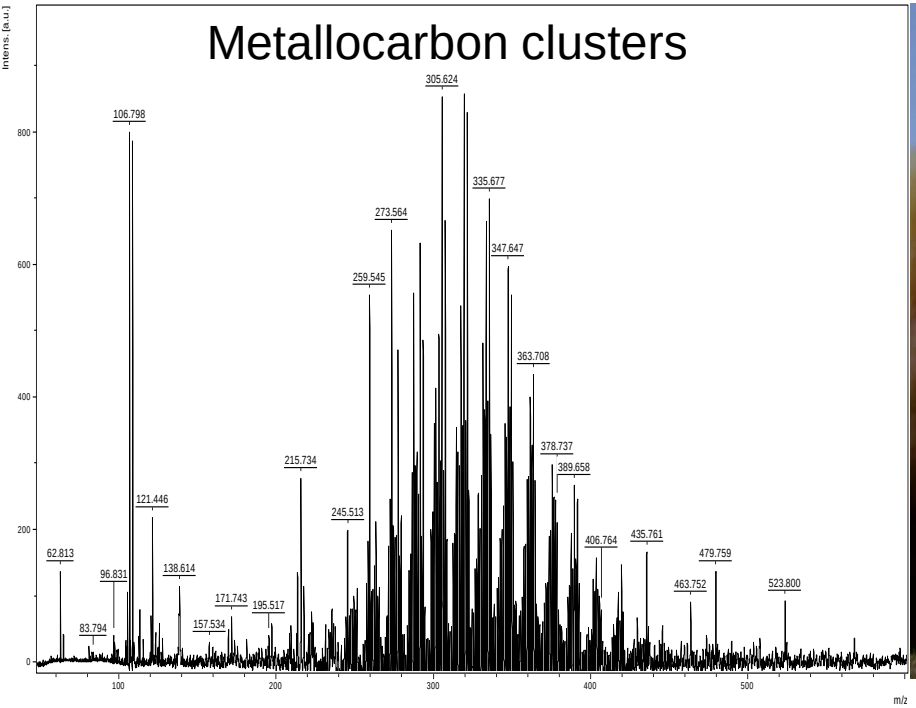
A number of sample toxicity in relation toof HELA cells in descending order



Conclusion

- When assessing the poisoning with rocket fuels, it is necessary to take into account the components of fuels and the products of their transformation.
- Establishing the structure of unknown products of transformation of rocket fuels is the most important stage in assessing their toxicity.
- Chromato-mass spectrometry, supplemented by calculations of retention values, is the main method for studying rocket fuel poisoning.

Thank you for the attention!



Mass spectrum SALDI of "zarubashechnogo" space.

The launch of the Proton launch vehicle