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Chromatography – mass spectrometry in aerospace industry

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Abstract. The applications of chromatography – mass spectrometry in aerospace industry are considered. The primary attention is devoted to the development of physicochemical grounds of the use of various chromatography – mass spectrometry procedures to solve topical problems of this industry. Various methods for investigation of the composition of rocket fuels, surfaces of structural materials and environmental media affected by aerospace activities are compared. The application of chromatography – mass spectrometry for the development and evaluation of processes for decontaminations of equipment, industrial wastes and soils from rocket fuel components is substantiated. The bibliography includes 135 references.

I. Introduction

The chromatography – mass spectrometry (CMS) technique appeared in the 1960s as a combination of gas chromatography and mass spectrometry (GC – MS).[1] A liquid chromatograph was coupled with a mass spectrometer somewhat later, in the 1980s; however, currently the liquid chromatography – mass spectrometry (LC – MS) technique is being rapidly developed.[2] Other combinations are used less frequently but theoretically any chromatographic method can be coupled with any type of mass spectrometry. The key difference is in the type of coupling. Direct (on-line) and indirect (off-line) types of coupling are possible. Examples of the first type are GC – MS, high performance liquid chromatography – mass spectrometry (HPLC – MS), ion chromatography – inductively coupled plasma mass spectrometry (IC – ICP MS)[3] and electrophoresis – mass spectrometry;[4] the second type is exemplified by thin layer chromatography – fast atom bombardment and laser ionization mass spectrometry. In the latter case, the sample is manually transferred from the chromatographic system to the mass-spectrometric system; however, with the advent of automated injection systems, the differences between the versions become less pronounced. It is natural that CMS relies on the achievement of chromatography and mass spectrometry; although coupling of various methods brings about some limitations, most chromatographic procedures successfully operate with mass spectrometric detectors. An important feature of CMS is the possibility of using both chromatographic and mass spectrometric data for identification.[5] Today CMS techniques are widely used in analytical and organic chemistry, biology, medicine, clinical chemistry and other fields of science and technology.

Gradually, CMS is being introduced in the aerospace industry. The development of CMS is objectively restricted by the relatively high cost of instruments or the necessity of training professionals for skilled interpretation of experimental data.

The difficulties of introducing new methods of analysis (especially those based on chromatography coupled with mass spectrometry), which are usual for the aerospace industry, are caused by the enormous responsibility associated with every spacecraft launch.

High performance and reliable methods of analysis such as chromatography and mass spectrometry were used in the aerospace industry back in its early days.[6] Some chromatographic and mass-spectrometric procedures developed in the period from 1960 to 1980 are still used for quality control of rocket fuel components, analysis of orbital station atmosphere, solution of environmental problems related to pollution of environmental media.[7]

However, as the Russian space industry has entered the world market, it turned out that the procedures and instruments used in Russia are inconsistent with those used by the US National Aeronautics and Space Administration (NASA) and the European Space Agency (ESA). Many methods are obsolete and need to be transferred to modern

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equipment and to new principles of analysis. The need to use CMS is also caused by the change in the raw material base for the production of rocket fuel components.

One more reason requiring the use of CMS is the ever increasing public interest in the environmental consequences of the development of both military and civil space industries.[8] Examples of pollution of some areas that have aroused huge public attention are known.[9, 10] The complexity and ambiguity of the results of environmental studies and the difficulty of predicting the environmental consequences lead to the situation where industrial and military corporations can influence the choice of research areas, results and their evaluation.[8] Therefore, ecological research should be performed using the most reliable and informative methods and the results should be obtained in the form accessible for independent examination. Gas chromatography–mass spectrometry holds the top position among such methods.

Presumably, the key areas of the use of CMS in the aerospace industry will be as follows:

— the use of gas, liquid and ion chromatography coupled with mass spectrometric detection for analysis of rocket fuel components at all stages of production and service;

— the use of GC–MS and LC–MS for evaluation of environmental consequences of the space-related activity;

— the use of CMS to analyze surfaces of materials and to evaluate industrial processes employed in the aerospace industry.

The review covers works of Russian and foreign researchers published mainly during the last 15 years dealing with solution of the above-noted problems.

II. The use of gas, liquid and ion chromatography with mass-spectrometric detection for analysis of rocket fuel components

1. Analysis of propellants

a. Hydrocarbon propellants

Analysis of hydrocarbon propellants (petrols, kerosenes, diesel fuels), including rocket propellants, and determination of impurities in them are traditionally performed according to Russian State Standards (GOSTs) and/or ASTM (American Society for Testing and Materials) standards. By using capillary chromatography, it is possible to carry out structural-group analysis of hydrocarbon fuels. The advantage of the chromatographic procedure, for example, over X-ray fluorescence is the possibility to determine the type of compounds. This is necessary because fuels contain some compounds with valuable properties (oxygen-containing additives, benzene, aromatic hydrocarbons). Mass-spectrometric detection used in these procedures is suitable for detecting trace impurities. Gradual merging of chromatographic and classical methods of analysis takes place.[11] Gas chromatography is used to analyze particular fractions isolated by distillation, while mass spectrometry is used to determine groups of compounds (for example, the ASTMD 2789 method is suitable for dividing hydrocarbons into groups — paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes, indans and tetralins).

In extensive studies of the composition and properties of fuels, CMS is used in combination with selective detectors, IR spectroscopy and corrosion activity tests for each fraction collected upon distillation.[12] An important achievement is the use of chromatography for determining the final boiling point of a propellant, so-called simulated distillation procedure. In view of the inter-governmental agreements about the mutual recognition of regulatory documents, this procedure can be recommended for extensive practical use in Russia. If mass-spectrometric detection is used, much more information can be retrieved, and several types of analyses are actually covered. In rocket kerosenes, 150 to 200 components are usually detected; ~80% of these components can be identified by GC–MS. To construct correlations with the results of traditional methods of analysis, the identified compounds are usually split into groups according to chemical structure; most often, 3 to 8 groups are used.

The potential of such analyses is demonstrated below in relation to rocket propellant (kerosene) produced under the brand Naftil.[13] Total ion current chromatogram of the Naftil propellant is shown in Fig. 1. The qualitative composition of the sample was determined relying on the mass spectra and retention indices. Data on the quantitative composition were obtained using reference samples or assuming that ionization cross-sections of the reference samples and test compounds with similar structures are the same. The group composition of the test sample is presented in Table 1. Using these results, it is possible to identify the type of propellant from its group composition.

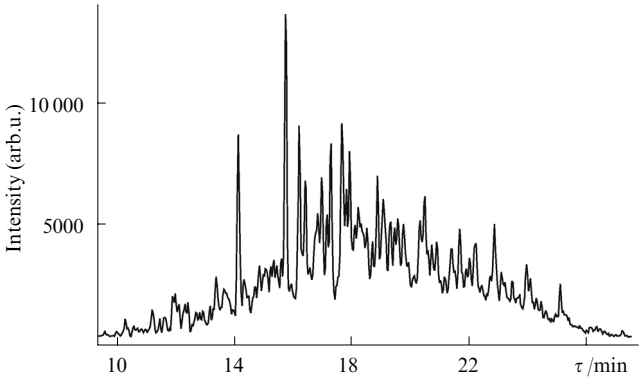


Figure 1. Total ion current chromatogram of a Naftil propellant sample.[13]
A 30 m × 0.53 mm ZB-5 capillary column was used;[13] τ is the retention time.

Table 1. Group composition (%) of the studied samples of the Naftil propellant.[15]

Compounds	No. 1	No. 2	No. 3	See [a]
Alkanes	38.40	28.89	26.65	25–40
Monocyclic hydrocarbons (cyclopentanes, cyclohexanes)	13.40	6.81	0.00	0–15
Naphthenes (alkyl-substituted decahydronaphthalenes, indenes)	46.70	62.96	69.17	45–70

Note. Samples No 1–3 were obtained from different storages.
[a] Data from Ref. 14.

This approach to analysis of the fuel quality was implemented in the 'Procedure of Determination of the Group Composition of the Naftil Propellant';[15] characteristics of the procedure indicate that by means of GC – MS, it is possible to determine the contents of the compounds over a broad range (five orders of magnitude).

Compounds	Contents (mass %)
Alkanes (normal and iso)	36 – 41
Naphthenes (substituted decahydronaphthalenes, substituted cyclic hydrocarbons)	58 – 64
Aromatic hydrocarbons	0.05 – 0.20
Unsaturated hydrocarbons	0.02 – 2.0

Classification of hydrocarbon fuels and identification of fuel components is a complicated task even when CMS is used because of the enormous number of compounds involved. One of the methods is construction of expert systems for interpretation of experimental data. Such a system was actually created.[16] The system is based on chromatographic retention times and ion mobility spectrometry data. Using the constructed expert system, 12 jet and rocket fuels were classified.

The progress of CMS also implies an increase in the efficiency of separation of compounds and ions. Chromatographic systems with two columns containing liquid stationary phases of different polarity were designed. They produce three-dimensional diagrams that show retention times in the columns and intensities of the peaks of components to be separated. These diagrams can be used for fuel identification and classification by the 'fingerprint' method. The identification becomes much more reliable if a mass spectrometer serves as the detector. Existing procedures of multidimensional mass spectrometry are used to record mass spectra of secondary and subsequent ions; however (due to sensitivity limitations), two-dimensional spectra are used most often. Two-dimensional chromatography and multidimensional mass spectrometry techniques can be coupled and supplemented by various computational algorithms. These aggregates are suitable for solving both general[17,18] and specific[19] tasks of separation of complex mixtures, for example, for fast determination of aromatic isomers.

The investigation of rocket fuels (unlike jet fuels) is often subject to special requirements: it is necessary to determine not only impurities and trace components but also the isomeric composition of the components. Isomers, which often have similar mass spectra and retention characteristics, can be identified by combinations of molecular-statistical, mass-spectrometric and chromatographic methods.[20]

The quantitative ratios of isomers and the composition of trace impurities are important criteria for assessment of the quality of a fuel; the presence of trace impurities attests to violation of storage, transportation and application conditions.

The possibilities of CMS were demonstrated in extensive studies of the synthetic hydrocarbon propellants Syntin and Decilin.[13] By varying the sorbent, it is possible to change the order of isomer elution and identify compounds relying on molecular-statistical calculations or retention indices. Chromatograms of the Syntin propellant measured on a capillary column and a micropacked column with graphitized thermal carbon black were compared. Although the separation efficiency was much higher on a capillary column, owing to high selectivity of graphitized thermal carbon black with respect to structural isomers, an acceptable separation was also attained on a micropacked column. When this column is used, compounds can be identified based on molecular-statistical calculations.

The qualitative composition and quantitative characteristics of trace impurities in a Syntin sample are as follows:

Compound	*1*	*2*	*3*	*4*	*5*
m/z	93	55	67	95	67
c /mg litre^{-1}	4.72	4.52	11.10	7.10	3.91

Here: *1* is pinene, *2* is a non-identified compound, *3* is indene derivative, *4* is octahydro-4,7-methano-1*H*-indene, *5* is indene derivative.

When CMS is utilized for identification, semiempirical molecular-statistical calculations can be performed for rigid molecules and molecules with several internal rotation angles. These calculations were carried out, in particular, for two internal rotation angles of cyclopropane isomer molecules in the Syntin propellant. Considering the van der Waals overlap of atoms during internal rotation, some of the conformations can be excluded from calculations. The results of calculations of the differences between the Henry constants for cyclopropane isomers present in the Syntin propellant are summarized in Table 2. The internal rotation angles can be corrected using a reference (naphthalene); for identification without a reference, the relative arrangement of isomer peaks in the chromatogram was used.

Table 2. Differences between the Henry constants (cm^3 m^{-2}) for isomeric components of the Syntin propellant at different internal rotation angles.[21]

α_1 /deg	α_2 /deg					
	120	150	180	210	240	270
90	0.8860	0.7340	0.4436	0.0811	0.0762	0.1813
120	1.6791	1.3483	0.7862	0.1355	−0.8163	−0.7059
150	0.6933	0.6968	0.4361	0.2076	−0.5315	−0.7968
180	0.0169	−0.0569	−0.1648	−0.1192	0.0206	0.0011
210	−0.1425	0.0218	−0.1477	−0.0950	0.4120	1.1031
240	−0.6824	−0.3862	−0.5718	−0.3639	0.3134	−0.0467
270	−0.3637	−0.4859	−0.2941	0.3801	0.3751	−0.8227

Note. The grey colour marks conformations that are impossible due to overlap of the van der Waals radii of atoms.

During investigation of a sample of the Decilin propellant, total ion current chromatograms were recorded. The composition of the sample (mass %) is given below:

Compound	*1*	*2*	*3*	*4*	*5*
c /mg litre^{-1}	0.52	71.43	0.29	27.78	0.08

Here: *1* is decahydronaphthalene, *2* is the *exo*-isomer of Decilin, *3* is adamantane, *4* is the *endo*-isomer of Decilin, *5* is methyldecahydronaphthalene.

By varying the conditions of chromatographic analysis, first of all, the sorbent or the liquid stationary phase, it is possible to change the order of elution of the test com-

pounds from the chromatographic column. The order of elution is often changed to verify the contents of particular impurities and trace impurities.

The identification of isomers is necessary to estimate an important characteristics of a propellant called 'storageability'. Complex isomer mixtures are identified using two methods — gas chromatography and mass spectrometry, as identical mass spectra and limited structural information available for the calculation of retention values do not allow this analysis to be done by a single method.[5, 20]

The difficulties that are faced during identification of compounds can be judged by analyzing mass chromatograms obtained for characteristic ions.[13]

An example of a mass chromatogram of characteristic ions of particular classes of compounds present in the Naftil propellant is given in Fig. 2. Alkanes give rise to the characteristic ion at m/z 57, perhydronaphthalene and its methyl and dimethyl derivatives are responsible for ions at m/z 138, 152 and 166, respectively, and anthracene and its methyl derivatives produce peaks at m/z 178 and 192, respectively.

Peaks of ions with equal masses corresponding to both molecular and fragment ions and isomers in concentrations differing by orders of magnitude were detected.

Chromatography–mass spectrometry is the only method suitable for fast and reliable monitoring of the propellant composition during long-term storage. Chromatograms were used to calculate the change in the total amounts of particular groups of compounds in a sample of Naftil over one year of storage. The amounts were determined relative to the total content of n-alkanes, which are the most stable compounds in the propellant. Using methyl-substituted perhydronaphthalenes as examples, it was found that the ratios of isomers and homologues change during storage. The amounts of mono- and dimethylperhydronaphthalenes changed most appreciably. The CMS data

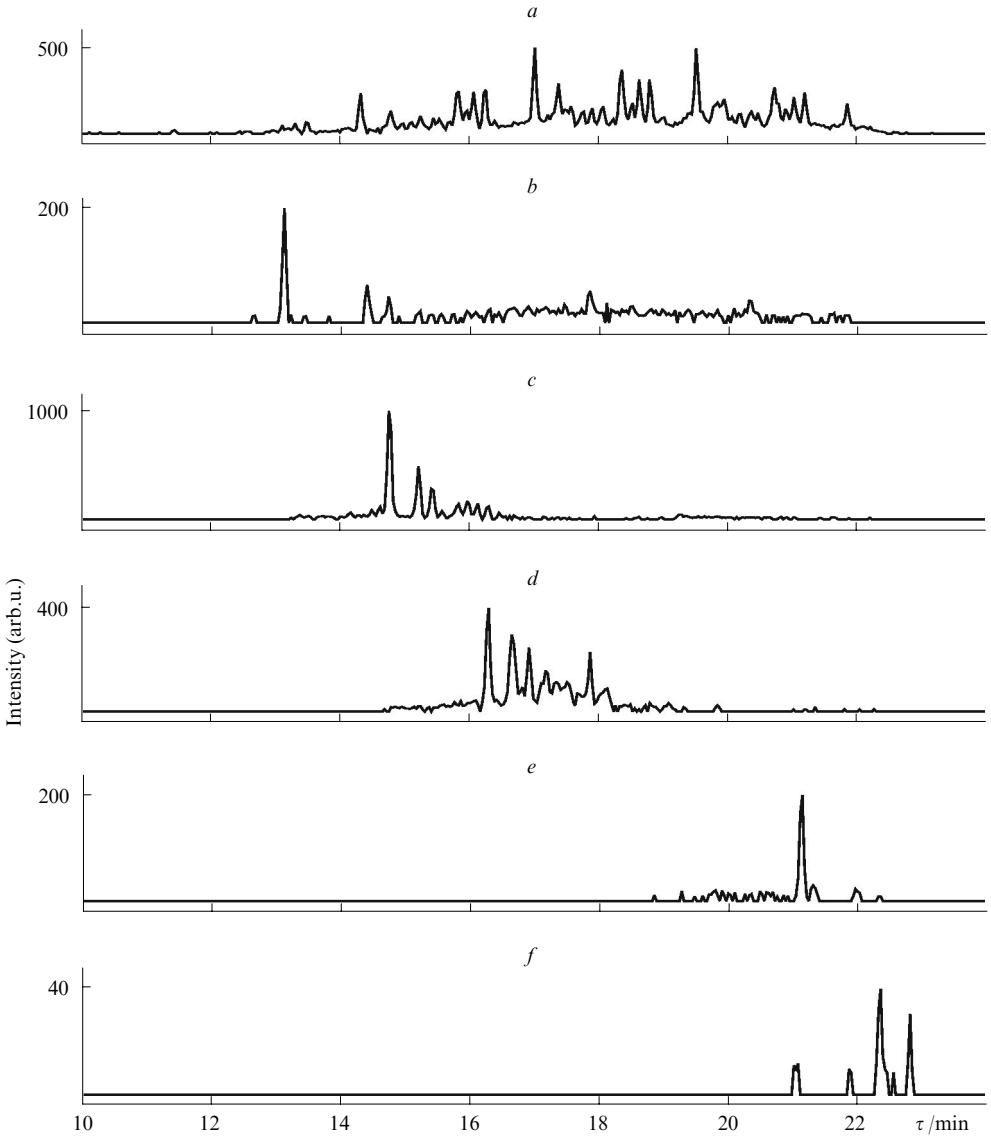


Figure 2. Mass chromatograms of characteristic ions for compounds of various classes constituting the Naftil propellant.[13] m/z = 57 (*a*), 138 (*b*), 125 (*c*), 166 (*d*) 178 (*e*), 192 (*f*).

and mathematical models of various types can serve as the basis for constructing an expert system for predicting the service life of fuels.

Gas chromatography–mass spectrometry and factorial analysis were used [22] to estimate the effect of microbiological contamination of fuels. For fuels of different types, the possibility of identification of the microbiological contamination was demonstrated under conditions where the classical identification based on libraries of mass spectra is impossible due to the insufficient sensitivity and high level of noise.

In the synthesis of new fuels, chromatography and CMS techniques are used in all stages: to analyze raw materials, optimize the industrial processes and to check the quality of the final product. One example is the catalytic synthesis of high-density hydrocarbon fuels based on selective dimerization of pinenes.[23] This work arouses particular interest, as a renewable feedstock, wood, was used to prepare the initial compound (pinene). By means of GC–MS, all isomeric dimers were reliably identified, which is needed to calculate the caloric value and, hence, to evaluate the potential value of the fuel.

The composition of fuels is studied not only for quality control but also to predict their properties. Having determined the chemical composition of a fuel by GC–MS, Liu *et al.*[24] established the relationship between its composition and properties such as flash point, boiling range, density, freeze point, aniline point and caloric value determined according to ASTM D93, ASTM D86, ASTM D1298, ASTM D2386, ASTM D611 and ASTM D2382, respectively. To construct correlations, the chemical compounds constituting the fuel were divided into eight groups, and correlations for these groups were constructed using different types of neural networks. For eighty fuels, correlation equations were proposed, the results thus obtained being comparable with the results obtained by ASTM methods, none of the methods being chromatographic or mass spectrometric. Thus, the above-mentioned properties of fuels predicted from CMS data are in good agreement (to within the errors) with the results of these methods.

A traditional application of GC–MS is analysis of the fuel combustion products. In this field, GC–MS is used both for analysis of the environmental consequences of fuel combustion and for optimization of combustion processes and design of the fuel composition. This method was utilized [25] to analyze light combustion products and products of hydrocarbon transformation using several chromatographic columns and additional chromatographic detectors. Model mixtures and real fuels were studied. Accumulation of various hydrocarbons was assessed and the general scheme of naphthalene formation was presented.

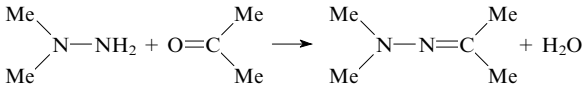
The above examples demonstrate that both Russian and foreign scientists engaged in the aerospace research use the GC–MS method more and more widely to analyze hydrocarbon fuels. However, the number of certified procedures is still limited, which is due to the complexity of the research targets.

b. Hydrazine propellants

US National Aeronautics and Space Administration uses mainly monomethylhydrazine and a mixture of hydrazine with monomethylhydrazine and unsymmetrical dimethylhydrazine (UDMH) as rocket propellants,[26] while European Space Agency employs all types of propellants.[27] The procedures used to analyze fuels are mainly based on chromatography and traditional chemical procedures.[28]

Unsymmetrical dimethylhydrazine is used most often as a rocket propellant in Russia and in China.[6, 7, 27] Analysis according to GOST stipulates the use of chromatography as an alternative to titrimetric determination of impurities and major components. The procedure used is based on the direct determination of UDMH by gas-liquid chromatography. Since UDMH is highly reactive (even when pure propellant samples are stored in tightly sealed vessels, transformation products are still accumulated), preferable is the procedure [29] that implies preliminary conversion of the compound to stable derivatives, for example, acetone dimethylhydrazone

Scheme 1



Using this procedure, the major compound and the trace impurities in UDMH are determined. Figure 3 shows the total ion current chromatogram of a UDMH sample, which shows the absence of impurities with relatively high molec-

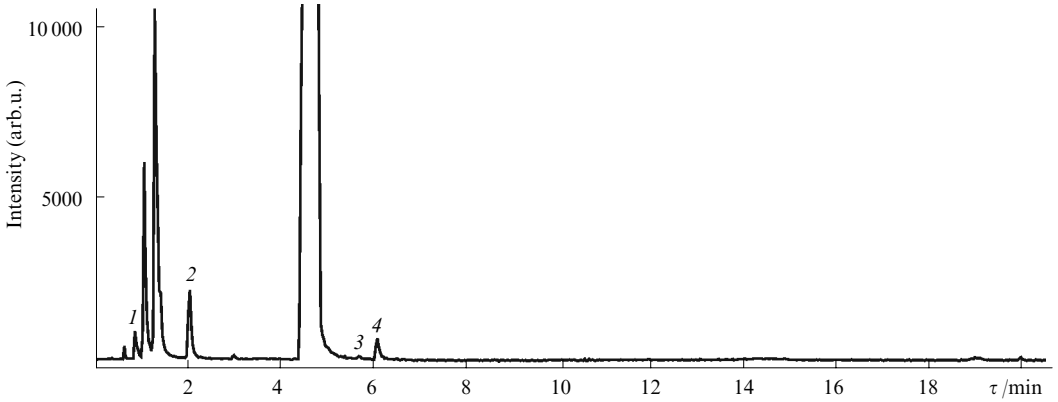


Figure 3. Total ion current chromatogram of a UDMH sample measured for quantification of impurities at a level of 0.05%–0.001%.[29] (*1*) Dimethylamine, (*2*) formaldehyde dimethylhydrazone, (*3*) nitrosodimethylamine, (*4*) acetone monomethylhydrazone.

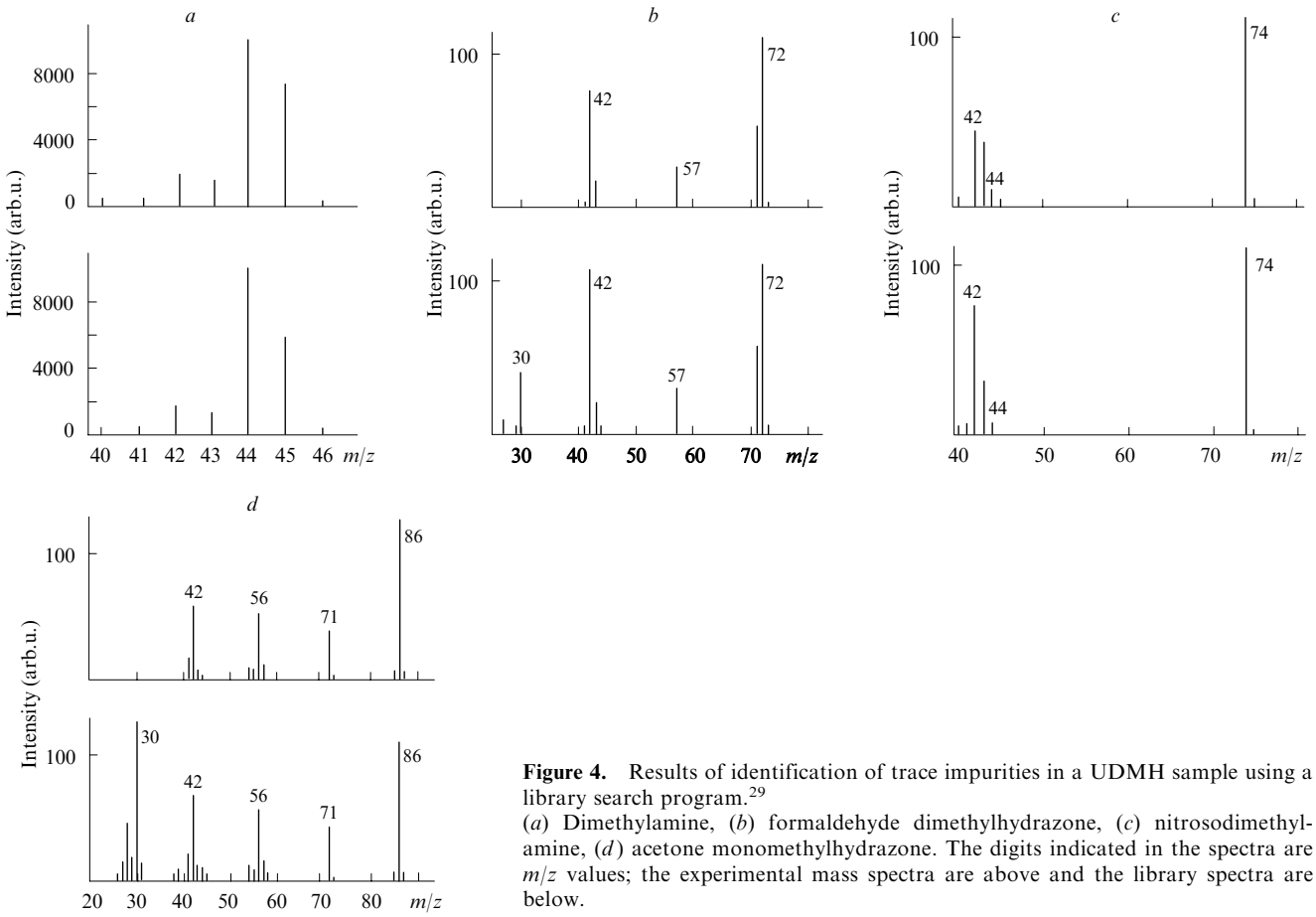


Figure 4. Results of identification of trace impurities in a UDMH sample using a library search program.[29]
(*a*) Dimethylamine, (*b*) formaldehyde dimethylhydrazone, (*c*) nitrosodimethylamine, (*d*) acetone monomethylhydrazone. The digits indicated in the spectra are m/z values; the experimental mass spectra are above and the library spectra are below.

ular masses (300–500 Da), which are usually unsaturated compounds and compounds that form 'tarry deposits' hampering fuel pumping and engine cooling. The results of identification of the detected trace impurities are presented in Fig. 4. The figure reflects the key difficulties that are faced in the identification of organic compounds by means of experimental and library mass spectra.

An example of good agreement between the library and experimental mass spectra (identity ratio 0.98) is shown in Fig. 4 *a*. This was achieved owing to the use of extensive libraries containing a huge array of experimental data — up to half a million electron ionization mass spectra;[30] this mode provides the most reproducible spectra. It is noteworthy that the libraries are constantly updated; even for known substances, the available mass spectra are replaced by newer and more reliable ones. For the spectra shown in Fig. 4 *b*, the identity ratio is 0.87, which is due to the different peak intensity ratios for the molecular and fragment ions at m/z 72 and 42, respectively. This difference is caused by various instrumental factors, for example, the geometry and the temperature of the ion source or the sample injection conditions.

The effect on the spectrum of an impurity caused by inadequate chromatographic separation from the component eluted earlier (acetone dimethylhydrazone) is demonstrated by Fig. 4 *c*. The ion at m/z 43 gives a contribution to a previous chromatographic peak having high intensity; in combination with the much higher amount of UDMH hydrazone of acetone and a lower content of nitrosodimethylamine, this leads to distortion of the spectrum and decreases the identity ratio to 0.79. Modern software for resolution (deconvolution) of chromatographic peaks is capable of eliminating these distortions.

For acetone monomethylhydrazone (see Fig. 4 *d*), the difference between the library and experimental spectra is caused only by different mass ranges chosen for identification. In the experiment, mass numbers were recorded starting at m/z 40, while the library spectrum also includes smaller masses in the range of 10–40 Da. This difference accounts for the decrease in the identity ratio from 1 (the ideal identity ratio) to 0.82 but this is sufficient for correct identification of the compound. However, these differences can be easily eliminated by changing the range of mass numbers for the experimental spectrum or by correcting the library spectrum. Most compounds that are present as trace impurities are known and can be obtained in a pure state; if necessary, they can be used as reference standards in the quantitative analysis.

It was noted above that if a propellant contains isomeric molecules with similar mass spectra, the order of elution of compounds from the chromatographic column may serve as an additional verification of the reliability of their identification. The chromatogram of a UDMH sample containing acetaldehyde and monomethylhydrazine as impurities obtained on a column with a low-polarity liquid stationary phase DB-5 is shown in Fig. 5. In this column, the retention time of the more polar hydrazone (acetone monomethylhydrazone) is longer than that of the isomeric acetaldehyde

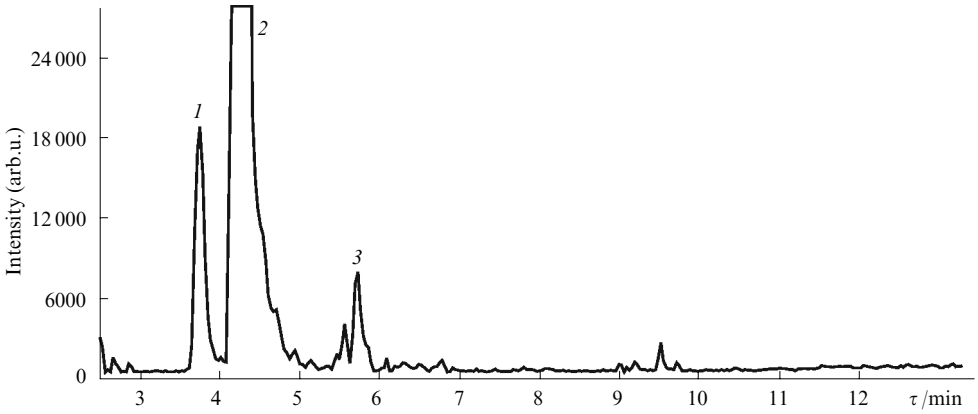


Figure 5. Total ion current chromatogram of a sample of an aqueous solution of UDMH.[31]
(*1*) Acetaldehyde dimethylhydrazone, (*2*) UDMH hydrazone of acetone, (*3*) acetone monomethylhydrazone.

dimethylhydrazone.[31] In this case, for reliable identification, apart from mass spectrometric data, it is necessary to know the order in which these isomeric molecules come out of the chromatographic column (the analyzed isomers are present in comparable amounts) and the fact that the peak of UDMH hydrazone of acetone is located between these two peaks.

The reaction of acetone to prepare hydrazone can also be used to analyze hydrazine. In this case, dihydrazone is formed, its retention time being longer than those of UDMH hydrazone and monomethylhydrazine hydrazone. Mixtures of these compounds can be successfully separated by chromatography and identified by mass spectrometry.

Analysis of the UDMH as the hydrazone was implemented in the 'Procedure for Determination of Impurities in Unsymmetrical Dimethylhydrazine'.[29]

The procedure provides the following:

— measuring of the mass fractions of the most probable (characteristic) impurities (process-related components, transformation products, impurities brought by hydrocarbons);

— detection and identification of any organic impurities and rough estimate of their mass fractions in UDMH samples in the range from 0.005% to 0.5%.

This procedure is not suitable for determining traces of water or mechanical impurities in UDMH. The metrological characteristics of the procedure are summarized in Table 3. A specific feature is the possibility to analyze not only prespecified compounds but also many other compounds that can be identified by CMS. This information is very important for the search of a source of contamination, which can be caused by changes in the production process, for example, switching to a new raw material or failure to observe the rules of fuel transportation, storage or application.

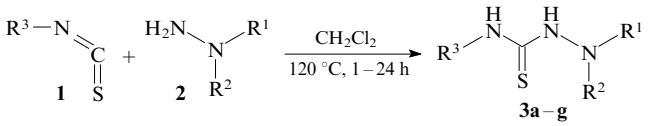
One more way for preparing the UDMH derivative is the reaction with isothiocyanates.[32] The advantage of isothiocyanates as compared with other types of derivatizing reagents (carboxylic acid anhydrides, acyl halides, carbonyl compounds) is the absence of elimination of by-products (hydrogen halides or water) during derivatization, which complicates the analysis. There is no water among the reaction products; therefore, water can be determined according to the proposed version of the procedure, which markedly extends the scope of its application. Since UDMH is highly hygroscopic, the water content in the product must be monitored at any stage of its application.[6, 7, 28]

Table 3. Ranges of measurements (*D*) of the impurities being determined.

Class of impurities	Impurity	*D* (mass %)
Process-related impurities	nitrosodimethylamine	0.010–1.0
	tetramethyltetrazene	0.010–1.0
Transformation products	*N*,*N*-dimethylamino-acetonitrile	0.010–1.0
	N,*N*-dimethylformamide	0.010–1.0
	1-methyl-1,2,4-triazole	0.010–1.0
Hydrocarbon contaminants	toluene	0.005–0.5
	o-xylene	0.005–0.5
	naphthalene	0.0010–0.10
	n-decane	0.005–0.5
	n-dodecane	0.0010–0.10

The reactions of excess isothiocyanate **1** with UDMH and some hydrazines **2** were performed at room temperature in inert solvents to give 1,1-R^1,R^2-4-R^3-thiosemicarbazides **3a**–**g** (Scheme 2).

Scheme 2



$R^1 = R^2 =$ Me: R^3 = Et (**a**), All (**b**), Ph (**c**); R^1 = Me, R^2 = Et: R^3 = All (**d**), Ph (**e**); R^1 = H, R^2 = Me, R^3 = All (**f**), Ph (**g**)

Alkyl isothiocyanates were chosen due to the fact that they contain alkyl substituents and have higher volatility as compared, for example, with aromatic phenyl isothiocyanates.

By surface-assisted laser desorption–ionization mass spectrometry (SALDI-MS), the reaction was found to give no by-products resulting from addition of thiosemicarbazides to the excess of alkyl isothiocyanate. The mass spectra of the UDMH derivatives thus formed exhibit ion peaks at

m/z 148 $[M+H]^+$ of 4-ethyl-1,1-dimethylthiosemicarbazide, m/z 160 $[M+H]^+$ of 4-allyl-1,1-dimethylthiosemicarbazide and m/z 182 $[M+Na]^+$ of 1,1-dimethyl-4-phenylsemicarbazide.

The chromatographic behaviour of the reaction mixture leads to effective separation of thiosemicarbazides and excess of derivatizing reagents, which improves the quantitative determination of UDMH owing to enhanced accuracy of measurement of the peak area for UDMH derivative, which does not overlap with the chromatographic peak of the derivatizing reagent. The GC–MS procedure is applicable to partially resolved and even unresolved chromatographic peaks;[1] however, for reliable quantitative determination of a compound over a broad concentration range, resolution down to the baseline is considered to be optimal.

The mass spectrum of derivative **3a** exhibits an intense molecular ion peak at m/z 147 and two peaks of characteristic ions at m/z 59 and 60, which are presumably caused by elimination of the UDMH ion at m/z 60 and its fragment at m/z 59. It follows from the mass spectrum that the mass to charge ratio and the isotope distribution of the molecular ion resemble those observed in the mass spectra of organosilicon compounds, which are widely used to prepare stationary phases for capillary columns. The presence of equal masses of analyte ions and background peaks of the chromatographic column should be taken into account for analyses in the mass fragmentography mode based on characteristic ions. In this case, the molecular ion together with ions at m/z 59 or 60 should be used for identification of the UDMH derivative in question. The retention time and the shape of chromatographic peaks should serve as additional criteria for identification.

Apart from the molecular ion peak at m/z 159, the mass spectrum of derivative **3b** exhibits two more characteristic ion peaks at m/z 115 and 116, which is very important for increasing the reliability of identification.

The formation of the additional pair of characteristic ion peaks is apparently due to the cyclization of molecular ion of **3b** to give the imidazolidine-2-thione ring followed by elimination of dimethylamino group and formaldehyde methylimine from the molecular ion. The following fragmentation pattern of the molecular ion is assumed (Scheme 3).

The fragment ions are evidently stabilized by either an intramolecular hydrogen bond or tautomer transitions.

The molecular ion peak of **3b** has a relatively low intensity; therefore, when working with minor amounts of this UDMH derivative, the determination sensitivity can be increased by recording mass chromatograms of other characteristic ions — at m/z 59 and/or 60 and 115 and/or 116, which have higher intensity. Corrected retention times or retention indices can serve as additional identification criteria for this procedure.

In the mass chromatograms of compound **3b**, the peak areas (S) of characteristic ions were measured and their ratios recommended for identification of UDMH as isothiocyanate derivatives were determined (Table 4). In all cases, the root-mean-square deviations of the ratio of the characteristic peak areas were $< 15\%$.

Owing to the presence of two pairs of high-intensity characteristic peaks of compound **3b** in the mass spectra, the UDMH derivative can be reliably identified even in the absence of the molecular ion peak and in the presence of

Scheme 3

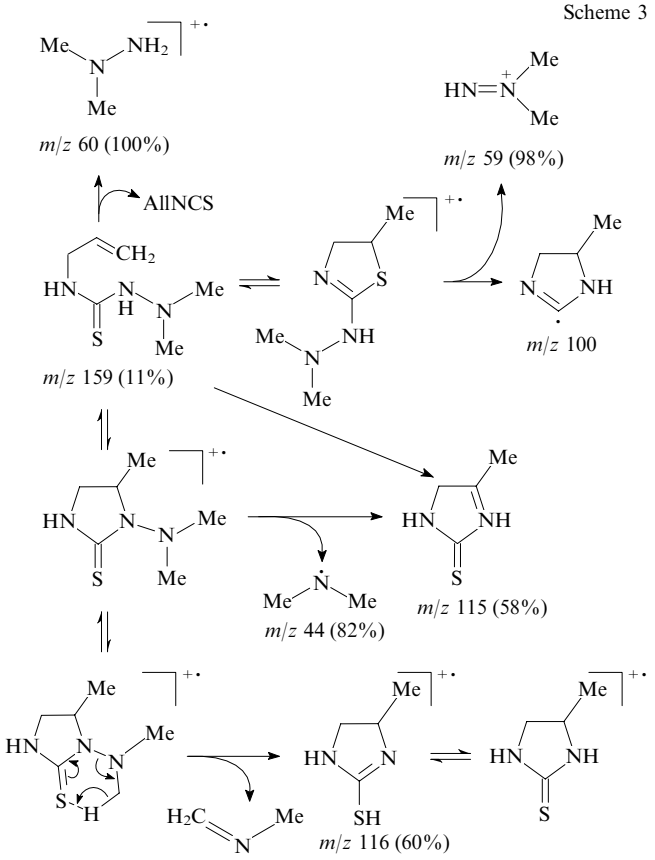


Table 4. Ratio of the peak areas (%) of characteristic ions of compound **3b**.[32]

Run	$\frac{S_{159}}{S_{116}}$	$\frac{S_{159}}{S_{115}}$	$\frac{S_{159}}{S_{60}}$	$\frac{S_{159}}{S_{59}}$	$\frac{S_{116}}{S_{60}}$	$\frac{S_{115}}{S_{59}}$
1	15.2	15.4	10.0	9.7	64.1	62.7
2	19.0	19.2	11.1	11.4	58.2	59.7
3	16.1	15.1	9.1	10.2	56.4	67.6
See [a]	16.8	16.6	10.1	10.4	59.6	63.3
	(11.8)	(13.8)	(10.0)	(8.4)	(6.8)	(6.3)

Note. The subscript at S shows the m/z value of the peak. [a] The average values and root-mean-square deviations (in parentheses) are given.

peaks of the stationary phase. The total ion current chromatogram of derivative **3b** for a small amount of UDMH and, correspondingly, a large amount of the derivatizing reagent, which accounts for intense peaks at $\tau = 10$ min, shows as well the column background, namely, peaks in the ranges $\tau = 12–14$ and 18–19 min. In the mass spectrum of derivative **3b** with low intensity, the molecular ion peak is missing and intense background peaks of organosilicon decomposition products of the stationary liquid phase are present. Meanwhile, even this spectrum is sufficient for reliable identification and determination of UDMH, because identification based on molecular ion can be replaced by identification based on retention times.

The development and application of the isothiocyanate-based procedure of analysis of UDMH demonstrates the potential of GC–MS and reliability of the results of identification.[5, 20] A limitation of the procedure is that

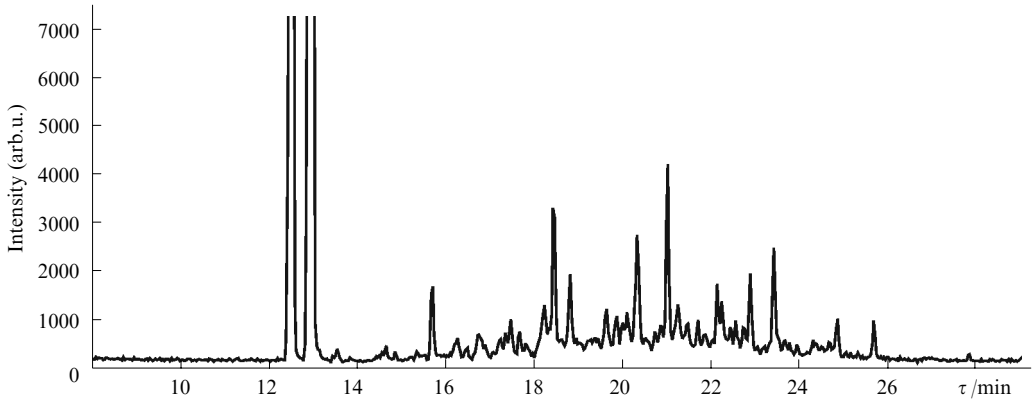


Figure 6. Total ion current chromatogram of the Syntin propellant containing hydrocarbon impurities.[13]

chromatograms contain peaks of the derivatizing reagent. When their retention times coincide with the retention times of unknown UDMH transformation products present in trace amounts, the identification is complicated.

c. Analysis of impurities of a propellant in another propellant

The task of determining the impurities of a propellant in another propellant mainly arises in the use of rocket fuels. Also, these studies may reveal the drawbacks in their storage and transportation processes. This problem is traditionally solved using qualification tests for fuels regulated by GOSTs and/or ASTM standards. However, some of these methods are fairly cumbersome and usually a set of analyses is required to make sure that a fuel is actually contaminated. In order to elucidate the source of contamination, it is often necessary to know the origin and the composition of the contaminating components and, in this case, CMS methods are indispensable.

Gas chromatography–mass spectrometry. The contamination of propellants consisting of several components such as synthetic propellants Syntin and Decilin is determined by CMS. These fuels can be separated from impurities by chromatography or they can be identified by mass spectrometry (if the chromatographic peaks overlap). The mass spectrometric identification is suitable to determine the composition of impurities and, relying on standard samples of fuels, to elucidate the type and the source of contamination.

Figure 6 shows the total ion current chromatogram of Syntin (intense peaks in the range $\tau = 12-14$ min) contaminated by another hydrocarbon fuel (peaks in the range $\tau = 14-26$ min). From the range of retention times, tentative conclusions about the type of contaminating fuels can be inferred. Using the total ion current chromatogram, mass chromatograms of the characteristic ions of Syntin and the detected impurities were measured. The retention times of the target component and the contaminating fuel almost do not overlap, which facilitates identification of the impurities. The group compositions of known hydrocarbon propellants are summarized in Table 5. Considering the data of Table 5 and the data on the boiling range of the fuel, which can also be obtained by CMS, one can draw the conclusion that the contaminant is the fuel T-1PP.

Yet another example is the determination of hydrocarbon impurities that have got into UDMH as a result of violation of rules (*e.g.*, the use of dirty storage tanks, supply pipelines and so on).

Table 5. Contents (%) of groups of compounds in contaminated Syntin propellant and some pure fuels.[13]

Sample	Group of compounds		
	alkanes	cyclanes	aromatic hydrocarbons
Contaminated Syntin [a]	63.8	20.6	14.1
T-1PP	58–63	25–30	8.5–10
Naftil	38–40	60–62	—
T-6	59–61	39–41	—

[a] The content of non-identified compounds is 1.5%.

A total ion current chromatogram of UDMH hydrazone of acetone containing hydrocarbon impurities was obtained. The impurities do not produce a chromatographic pattern with an extensive set of peaks characteristic of hydrocarbon propellants and, hence, the 'fingerprint' identification is impossible. However, mass chromatograms of characteristic ions of UDMH hydrazone of acetone (m/z 100) and detected impurities (m/z 138 and 152), which corresponded to characteristic ions of naphthenes, were measured. Despite the very low intensity of the ion peaks of hydrocarbon impurities, it can be stated with confidence that the contaminant is Naftil.[13]

The results presented above indicate that CMS are quite applicable to the determination of hydrocarbon impurities in UDMH and synthetic hydrocarbon propellants. The identification of the contaminated propellant can be done by both the purely chromatographic 'fingerprint' method, *i.e.*, the identification based on the chromatographic pattern, and the GC–MS version with interpretation of the compositions of all or some contaminating components; this is undoubtedly very important, because contamination sources can be revealed. The use of CMS substantially extended the potential of the 'fingerprint' method because mass chromatograms can be recorded for all groups of homologues and isomers present in the mixture, which increases the number of criteria for further identification.

The opposite task, that is, identification of trace impurities of UDMH in hydrocarbon propellants, can be solved

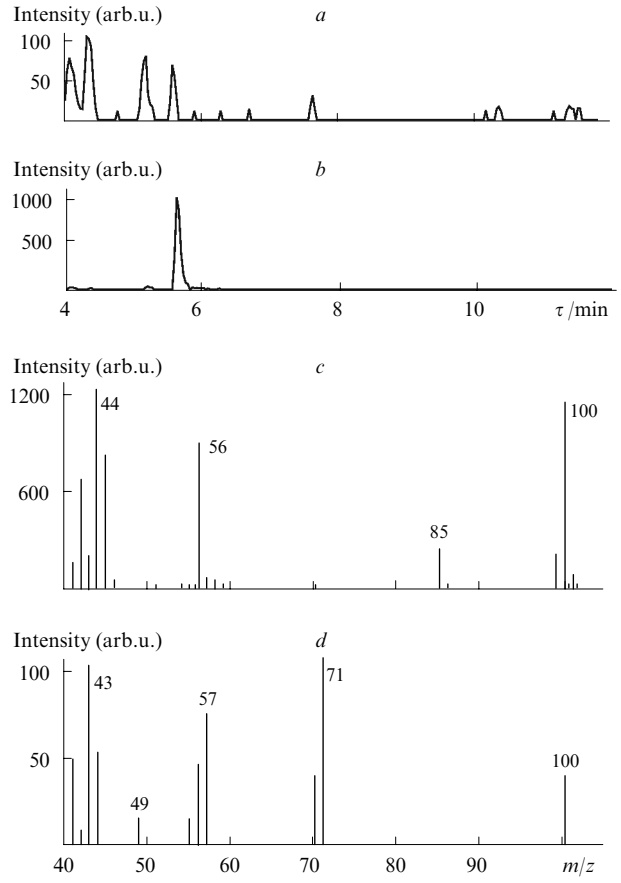


Figure 7. Mass chromatograms of characteristic ions of hydrocarbons and UDMH hydrazone of acetone (*a*, *b*) and mass spectra of co-eluted compounds found in the Naftil propellant sample contaminated by UDMH (*c*, *d*).[13]

by GC–MS, although the retention values of light hydrocarbons may be close to those of UDMH hydrazone and the masses of characteristic ions in the mass spectrum of UDMH hydrazone coincide with the masses of ions formed from hydrocarbon propellants. In this case, the retention time and the mass spectrum should be analyzed to achieve reliable identification.[5, 20] An example of such analysis is illustrated by Fig. 7. Despite almost complete overlap of the chromatographic peaks of UDMH hydrazone of acetone and n-heptane ($\tau \approx 5.6$ min, see Fig. 7 *a*,*b*), the difference between the mass spectra of these compounds (see Fig. 7 *c*,*d*) suffices for their reliable identification. Such detailed information (which is needed, for example, in arbitrage analysis and for industrial process correction) can be retrieved only from CMS data.

For complex mixtures consisting of several fuels, 'more informative' UDMH isothiocyanate derivatives should be used. The physicochemical grounds for determination of UDMH impurity in hydrocarbon propellants with the use of such derivatives were developed. A UDMH impurity in the Syntin and Decilin propellants can be determined by GC–MS using compounds **3a**,**b** even in the presence of the multicomponent Naftil propellant. In GC–MS analysis, the ratios of the peak areas of molecular and characteristic ions can be used for identification purposes apart from the retention time (see Table 4).

Total ion current chromatograms of the UDMH impurity in the form of derivative **3a** in Syntin and Decilin propellants are shown in Fig. 8.[32] The minor component **3a** is hidden by the considerable amount of the Naftil impurity, which hampers identification of **3a** (it is even impossible to isolate the individual chromatographic peak of UDMH derivative).

Nevertheless, the UDMH impurities can be identified based on *m*/*z* 147, 59, and 60 peaks in the mass chromatograms of the molecular and characteristic ions (see above); the error in determination based on the ratio of peak areas of these ions does not exceed 15%.

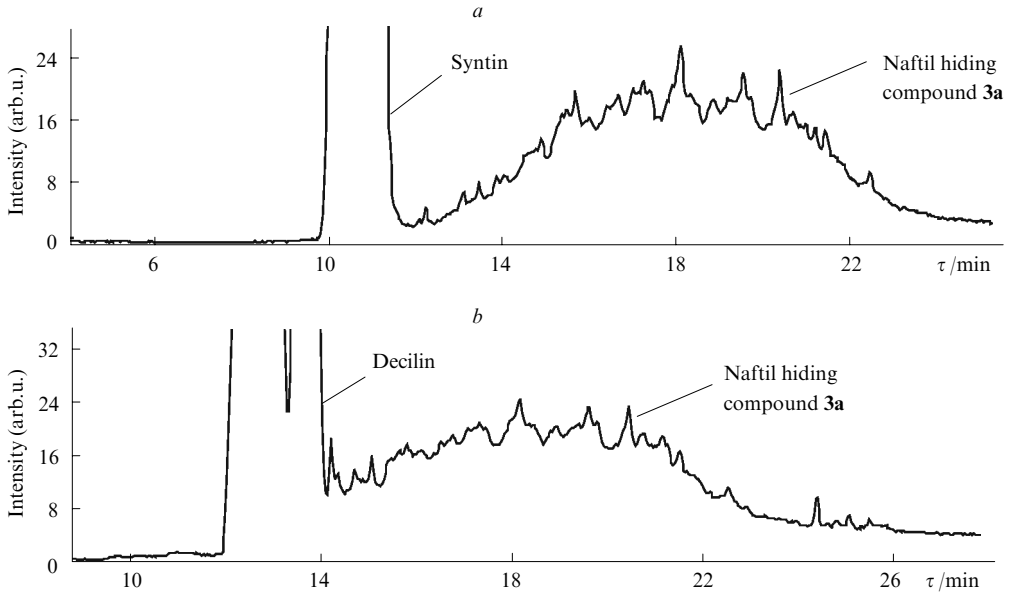


Figure 8. Total ion current chromatograms of compound **3a** and Naftil propellant contaminating Syntin (*a*) and Decilin (*b*) propellants.[32]

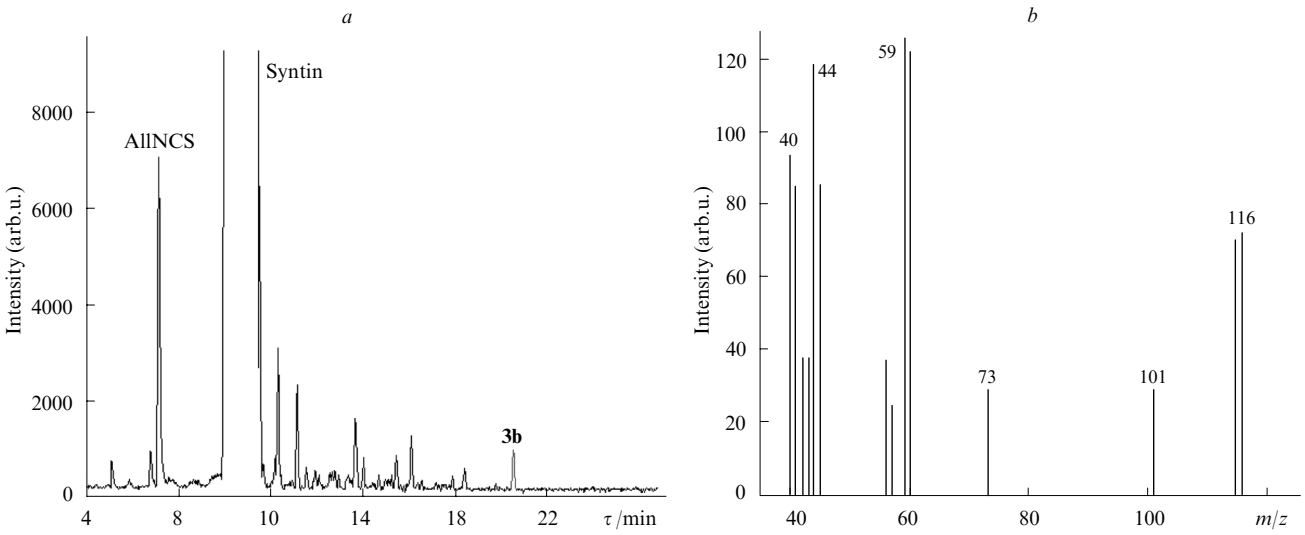


Figure 9. Total ion current chromatogram (*a*) and mass spectrum of UDMH impurity as derivative **3b** (*b*) in Syntin.[32]
$S_{116}:S_{60} = 60\%$, $S_{115}:S_{59} = 59\%$.

In the electron ionization mass spectrum, the molecular ion of compound **3b** has a relatively low intensity. When minor amounts of the compounds are involved, the molecular ion peak may be absent. In this case, analysis can be performed by recording the mass chromatograms of characteristic ions at *m*/*z* 59 and/or 60 and 115 and/or 116 (see above), which are more intense. Using the mass fragmentography mode, the determination sensitivity can be increased ~10–100 fold.[1] The UDMH derivative with allyl isothiocyanate is readily separated from impurities, and both the total ion current and characteristic ion spectra recorded for it are quite informative and applicable for identification (Fig. 9).

The identification of impurities of one hydrocarbon propellant in another is complicated if it is necessary to identify each propellant. In the case of propellants with similar composition, for example, T-1 and T-1PP, the presence of impurities can be confirmed but it is not always possible to identify the contaminating propellant. For such intricate cases, 2D chromatography and mass spectrometric techniques suitable for recording spectra of secondary ions can be used. One more alternative is the search and analysis of the homologue and isomer ratios typical of each propellant and comparative analysis of the test samples and model mixtures of propellants.

Liquid chromatography–mass spectrometry. If UDMH is determined as a trace impurity in the Naftil propellant the components of which are co-eluted with derivatives **3a**,**b**, these compounds are responsible for only a minor fraction of the total ion current and UDMH is difficult to identify. Thus, GC–MS is only partly applicable for such analyses. Therefore, an approach using reverse-phase high-performance liquid chromatography with off-line mass-spectrometric detection was proposed.

A distinctive feature of most popular ionization methods that are used in LC–MS, namely, electrospray ionization and atmospheric pressure chemical ionization, is the reduced fragmentation of the molecular ion as compared with the electron ionization.[2] Moreover, not all classes of organic compounds are readily ionized using these methods. For diode matrix detection of chromatograms, the effect of hydrocarbons is insignificant. Therefore, on-line and off-line CMS methods for the detection of UDMH impurities in complex hydrocarbon propellants can be developed. A proposed procedure [33] includes extraction of UDMH derivatives **3a–c** from the Naftil propellant in the Diapak cartridges for solid-state extraction and reverse-phase HPLC on the Hypercarb sorbent of the extracted compound. The chromatograms obtained during the determination of UDMH impurity as some derivatives in Naftil are shown in Fig. 10. By varying the derivatizing reagent, it is possible to change the chromatographic retention values of the derivatives and thus to level the possible influence of the impurities of unknown origin. The recovery of UDMH increased 98% and the degree of preconcentration was 1.

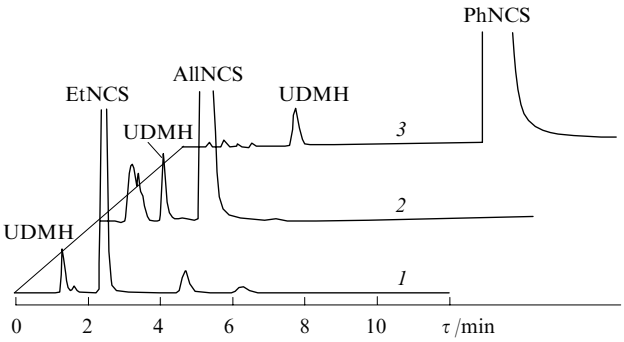


Figure 10. Chromatograms of UDMH impurities as derivatives **3a–c** in Naftil.[133]
Hypercarb sorbent, mobile phase flow rate 0.5 ml min^{-1}, elution with MeOH–H_2O, UV detection at 240 nm, UDMH concentration 1 mg $litre^{-1}$.

The analytical characteristics of the procedure for determination of UDMH impurities are summarized in Table 6. The detection limits are determined by the concentration of UDMH released from the fuel to the gas phase, mainly in

Table 6. Analytical characteristics of reverse-phase HPLC using Hypercarb sorbent (sample volume 20 μl).[33]

Compound	Detection limit /μg litre^{-1}	A /μg litre^{-1} (see [a])	Calibration equation	R^2 (see [b])
3a	5	25–500	$y = 0.1216x + 0.013$	0.9997
3b	5	25–500	$y = 0.15x + 0.0714$	0.9998
3c	7	25–250	$y = 0.0863x + 0.5403$	0.9994

[a] The range of linear dependence of the concentration on the intensity and detector signal. [b] Correlation coefficient.

Table 7. Detection limits of UDMH as derivatives **3a**–**c** by MALDI-MS with various matrices (signal/noise ratio ~10).[33]

Derivative	Detection limit (mg litre^{-1}) with the matrix		
	CHCA [a]	DHBA [b]	dithranol
3a	–	0.1	10
3b	1	1	10
3c	1	0.01	1

[a] Cyano-4-hydroxycinnamic acid. [b] 2,5-Dihydroxybenzoic acid.

the work area, and are limited by the maximum allowable concentration (MAC).

For increasing the reliability of qualitative determination of UDMH, it was proposed to use, apart from the retention times, the MALDI–MS technique providing information about the analyte molecular mass and structure. The sequence of the key stages of the analysis is presented below:

— fractions corresponding to the chromatographic peaks of the analytes are isolated;

— aliquots (1 μl) of the obtained fractions are applied onto the MALDI–MS target;

— the mass spectra containing peaks for protonated molecular ions of UDMH derivatives **3a**–**c** are recorded (Fig. 11).

The informational content and the intensity of the recorded mass spectra can be increased by doping the samples with alkali metal ions (usually sodium or potassium) or their mixtures. Although the detection limits of UDMH proved to be poorer for MALDI–MS detection than for reverse-phase HPLC (which is caused by the smaller amounts of the injected sample and lower sensitivity of MALDI–MS relative to derivatives **3a**,**b**, see Table 7), these results were adequate to the solution of this task. It was shown [33] that phenyl isothiocyanate has to be used as the derivatizing reagent and 2,5-dihydroxybenzoic acid should serve as the matrix, and samples of larger volume should be injected into the mass spectrometer. The advantage of this approach is in the possibility of fast analysis of large numbers of samples of propellants contaminated by UDMH.

The application of LC–MS to fuel analysis is now limited to only several examples, but in the future, this method can be expected to find more extensive use. Some LC–MS procedures for analysis of the environmental consequences of the aerospace activities are given below (see Section III).

Evidently, in the upcoming years, liquid rocket propellants will also be widely used and the operations related to their handling will become more automated.[34] An important trend is development of cryogenic and low-temperature gelled propellants, monofuels and propellants based on ionic liquids,[35] including combined ones with non-toxic

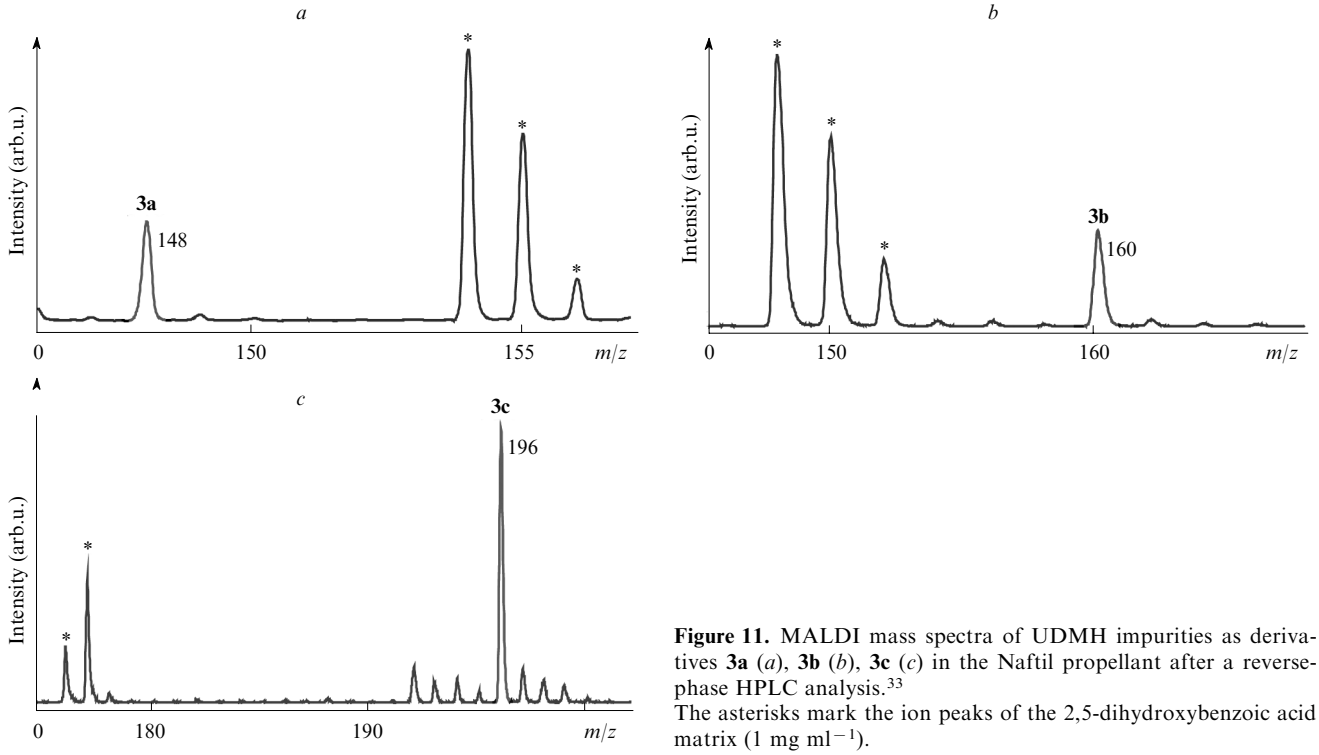


Figure 11. MALDI mass spectra of UDMH impurities as derivatives **3a** (*a*), **3b** (*b*), **3c** (*c*) in the Naftil propellant after a reverse-phase HPLC analysis.[33]
The asterisks mark the ion peaks of the 2,5-dihydroxybenzoic acid matrix (1 mg ml^{-1}).

oxidants.[36] However, some new propellants based on ionic liquids still include conventional components, in particular, UDMH.[37] Analysis of such propellants may require various CMS techniques including already developed ones.

2. Oxidants

Chromatography – mass spectrometry is not used to determine hydrogen peroxide,[38] although it can be used as an alternative to chromatography to monitor the production process. Dinitrogen tetroxide, nitric acid and oxygen are determined by traditional methods;[6,7] however, CMS can also be used to quantify these compounds (especially when they are used in microengines where the effect of minor impurities is enhanced). An important role can be played by LC – direct electron ionization MS[39] and plasma ionization mass spectrometry.[40]

3. Solid fuels

Currently, CMS is not widely used to study solid fuels, although size exclusion chromatography – mass spectrometry is applicable for analysis of the molecular-mass distribution of a polymer binder, while IC – ICP-MS can be used to analyze trace impurities in inorganic materials (for example, in ammonium perchlorate) that affect their decomposition.[41]

A broad range of organic compounds, first of all, nitrogen compounds,[42] are used to improve the composition of solid fuels in order to develop environmentally safe materials free from chlorine.[43] However, the application of such fuels is subject to strict control of evolution of toxic products, in particular hydrocyanic acid and its derivatives.[44] The most reliable quantitative monitoring of the gas phase composition and identification of unknown compounds can be performed by CMS.

A promising trend is the development of solid fuels based on hydrides.[45] The properties of such products, in particular, aluminium hydride,[46] are studied by time-of-flight mass spectrometry. It is evident that for more intricate compositions, CMS will also be demanded.

One more important trend is the creation of hybrid propellants,[47] which usually consist of a solid propellant and a liquid oxidant, most often, oxygen, hydrogen peroxide[48] or nitric acid,[49] although ammonium perchlorate is also used. In the future, it would be possible to use CMS for the control of production and application of these propellants. For example, GC – MS was used to study pyrolysis of polyacrylamide, which serves as a combustion booster for aluminium – water fuel.[50] Twenty four products of pyrolysis were identified two of which were previously unknown. Presumably, the combustion processes can be intensified by using optimal amounts of polyacrylamide.

III. The use of gas and liquid chromatography with mass spectrometric detection for analysis of environmental media

The environmental impact of aerospace activities is diversified and the consequences are not always immediately revealed.[51] The most obvious effect comes from the production and use of rocket fuels and also from contingency events. Solid rocket fuel is believed to be less harmful to the environment than liquid fuel. The major combustion products are highly dispersed metal oxides and nitrogen and sulfur oxides,[52] which can be determined merely by sensors; in the case of the possible formation of, for example, hydrocyanic acid and its derivatives, CMS is required.

Perchlorate-containing solid fuel compositions are most hazardous for the environment. The hazard arises from both perchlorates themselves and their combustion products, in particular, polychlorinated dioxins, which are most toxic among the industry-generated environmental pollutants.[53] For reliable determination of these compounds, high performance gas chromatography and high-resolution mass spectrometry are required. The top instrument-making companies manufacture high-resolution GC – MS instruments, specially adjusted for analysis of polychlorinated dioxins. Noteworthy is the problem of environmental pollution by proper perchlorates upon explosive disposal of rocket equipment: large-scale air, water and soil pollution occurs at the disposal sites, resulting in the subsequent accumulation of pollutants in food products and, hence, in animal and human bodies. Perchlorates are determined by HPLC; in the case of intricate matrices, it is expedient to use a mass spectrometer as the detector.

Research into the impact of liquid rocket fuel components on the environment has become a political issue both in Russia and abroad due to the lack of information about aerospace activities and, in particular, about the effect of particular components, first of all, hydrazine and its derivatives, on the human health in the affected areas. In recent years, numerous publications appeared concerning the environmental changes in the areas strongly affected by the consequences of aerospace activities (see, for example, Refs 54 – 63).

Analysis of the pollution of environmental media is one of the fields where CMS have considerable advantages over other methods. First of all, this is the possibility of determination of several target compounds in one analysis. For example, using LC – MS or GC – MS, it is possible to determine simultaneously unsymmetrical dimethylhydrazine and the products of its transformations — dimethylamine, nitrosodimethylamine and tetramethyltetrazene (*i.e.*, compounds with known MAC).

Hydrocarbon propellants, which are widely used in the aerospace industry, do not basically differ from the propellants used in other branches but can contain highly toxic components. Analysis of the environmental pollution by hydrocarbon propellants by means of CMS has been reported in detail in some reviews and monographs;[64 – 66] therefore, it is nor considered in detail here. Naturally, the whole inventory of CMS techniques and all possible detection options are used for such analyses.[67,68] This can be exemplified by the study[69] in which GC – MS was invoked to develop a procedure for the analysis of jet propellant used for military purposes by NATO countries. The procedure is suitable for analyzing vapours and aerosols of this propellant, for determining its overall content and for quantification of particular components. The procedure has been validated and is used in toxicological studies. Note that the simultaneous determination of the overall content and the contents of particular components is possible only by using methods based on chromatographic separation; this accounts for the use of CMS. Particular attention should be paid to analysis of polyaromatic hydrocarbons — highly hazardous compounds with proven carcinogenic properties.[70] These compounds are traditionally quantified by liquid chromatography with a UV detector

but the analysis of complex samples taken from various types of soils may require LC–MS.

The unsymmetrical dimethylhydrazine is used not only in the aerospace industry but also in pharmacology for the synthesis of drugs and in chemical industry for the production of pesticides. The production and application of this compound is associated with high environmental risks.[71–73] Its use in any areas of human activity is associated with possible pollution of the environment. This pollution comes from fuel combustion;[74] fuelling of launch vehicles and railway tanks used for transportantion; falling of the detachable parts of launch vehicles; disposal of industrial effluents formed upon washing of storage and fuelling facilities; emergency spills cannot be ruled out either.[75] In all of these cases, atmospheric air is polluted. Due to high reactivity and water solubility of UDMH, aqueous solutions are formed containing transformation products which contaminate soils and for which MAC values have been established only recently.[73] Some transformation products are more toxic than parent UDMH,[72] and for some of the compounds there are still no sanitary and hygienic standards. Some of the transformation products of UDMH have not yet been identified.[13, 31]

Unfortunately, in most cases, the impact is estimated using mainly information about the concentrations of UDMH but the data about the transformation products are scarcely involved. This is one of the reasons why the environmental consequences of the impact of liquid rocket fuel components are so difficult to predict. The effect of the transformation products that have been reliably determined by CMS was taken into account in the prediction of the environmental situation in the areas where detachable sections of the launch vehicles fall on the Earth on the Baikonur launching site.[61–63]

In view of the foregoing, it can be seen that the problem of analysis of UDMH and the products formed upon its transformations in the environmental media is challenging and requires the whole range of CMS techniques for solution.

In the atmospheric air[76] and in the industrial work area,[77] UDMH can be determined directly after preconcentration on the sorbents. Determination of UDMH in air is done after it has been converted to a derivative, in particular, with acetone,[78] and hence it can be detected when mixed with hydrazine derivatives. By using more sensitive detectors, first of all, mass spectrometers, it is possible to decrease substantially (by 1–2 orders of magnitude) the limits of detection. Low limits of detection of UDMH (down to half of the MAC for the air of populated areas) are necessary because pollution of, in particular, inner compartments of a International Space Station (ISS) by this compound and the products of its transformations may come from the outer surface of the station.

During extravehicular activity, astronauts contact with the outer surface of the station, their space suits can be contaminated by UDMH and products of its decomposition. In the case of emergency and contingency situations, astronauts might get into the engine operation area. Inside the station, the space suit and gloves become the source of air pollution, and the level of such pollution may exceed the maximum allowable concentration of UDMH; therefore, the level of air pollution in the air lock and crew compartments of the station are subject to sanitary and chemical surveillance. It is assumed that UDMH and nitrogen-containing products of its incomplete combustion are chemisorbed on the station surface due to hydrogen bonding and due to the formation of salts with nitric and nitrous acids, which arise upon destruction of the oxidant.

In water, soils and food products, UDMH is quantified by gas chromatography after converting it to derivatives with various compounds (most often, with aldehydes). Mass spectrometer is the most frequently used detector for these analyses.[79–82] Liquid chromatography is also used with success to determine UDMH and its derivatives, the analysis being often preceded by sorption preconcentration.[83, 84] When a mass spectrometer is used as the detector, the reliability and the information content of the analysis increase. Ion and ion pair chromatography are promising methods for quantification of hydrazine, monomethylhy-

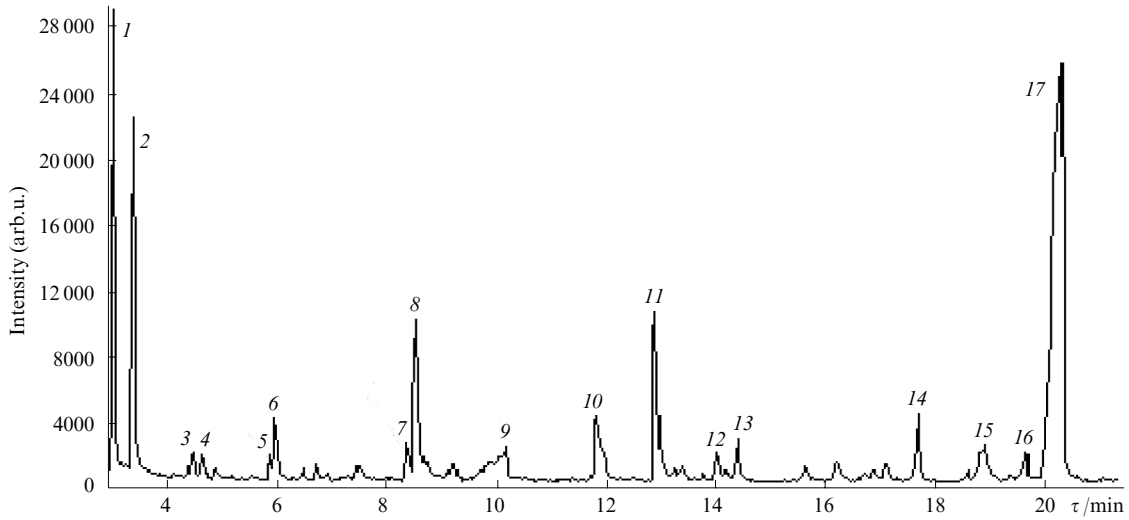


Figure 12. Total ion current chromatogram of the extract of a model aqueous solution of UDMH.[31]
For (*1–17*), see Table 8

drazine and UDMH, because this analysis can be carried out without sample preparation and derivatization.[85–88] In this case, by using a mass-spectrometric detector, the detection selectivity can be increased and the transformation products can be determined.

An example of total ion current chromatogram, which displays the presence of UDMH transformation products formed in the model aqueous solution after storage for a year, is presented in Fig. 12. The UDMH transformation products are characterized in Table 8.

Table 8. Compounds and their concentrations in the mixture of UDMH transformation products after long-term storage.[31]

Run	Time /min	Compound	*c* /mg litre^{-1}
1	3.07	acetaldehyde dimethylhydrazone	27.20
2	3.4	acetone dimethylhydrazone	30.40
3	4.47	nitrosodimethylamine	3.00
4	4.66	dimethylaminoacetonitrile	2.26
5	4.91	1-methyl-1*H*-pyrazole	1.41
6	5.93	*N*,*N*-dimethylformamide	0.36
7	8.41	acetone azine	3.93
8	8.57	1-methyl-1*H*-1,2,4-triazole	16.90
9	10.19	guanidine	10.80
10	11.83	dimethyltriazole	11.90
11	12.92	non-identified	19.41
12	14.04	the same	2.83
13	14.41	"	4.48
14	17.71	"	7.73
15	18.91	"	8.86
16	19.66	"	3.14
17	20.29	glyoxal bis(dimethylhydrazone)	107.00

The compounds were qualitatively identified using library search programmes and by analyzing the regularities of UDMH reactions, the properties and reactivities of the intermediates and final products. The quantitative analysis was based on the assumption that the ionization cross-section of the standard coincides with the ionization cross-sections of the analytes. Naturally, this is a rough approximation; reference standard samples are to be used for quantitative analyses; however, for comparative assay of a series of like samples, this approach is quite justified. For non-identified compounds, this semiquantitative analysis is almost the only way to evaluate the contamination rate.

Apart from the unreacted UDMH, the mixture contains transformation products including non-identified ones (see Fig. 12 and Table 8). The latter are mainly nitrogen-containing compounds of various classes. These data confirm once again the need for CMS methods because information about the detected products (even non-identified ones) is very important for investigation of the transformation mechanisms of hydrazine propellants in the environment and for selecting the treatment procedures.

On relatively short-term storage (up to one month), nitrosodimethylamine and formaldehyde dimethylhydrazone are the first to be formed.[89] At high UDMH concentration, tetramethyltetrazene is formed, probably, according to the reaction (1):

$$Me_2N-NH_2 + Me_2N-NO \xrightarrow{[O]} Me_2N-N{=}N-NMe_2 \qquad (1)$$

As the storage time and UDMH concentration increase, heavier products are accumulated such as glyoxal bis(dimethylhydrazone), which is formed by the reaction

$$Me_2N-NH_2 + \begin{matrix} O & O \\ \| & \| \\ H & H \end{matrix} \longrightarrow \qquad (2)$$

$$\longrightarrow Me_2N-N{=}CH-CH{=}N-NMe_2 + 2\,H_2O$$

A quantitative comparison of the results obtained for different initial concentrations of UDMH showed that at high UDMH concentrations, more stable products are accumulated in solution and remain unchanged for long periods, while at low concentrations, UDMH decomposes to give mainly volatile products (nitrogen, formaldehyde, methane and methyl- and dimethylamines), which is correlated with published data.[89, 90]

Chromatograms obtained for samples of industrial effluents (No. 1, No. 5) formed upon washing of equipment and lines at a storage facility are shown in Fig. 13. The effluents were stored in steel tanks under atmospheric air. The identified products and their amounts are presented in Table 9. It can be seen that the mixture contains considerable amounts of UDMH transformation products; for some compounds the maximum allowable concentrations are exceeded by orders of magnitude. For comparison, values for the samples taken from the other steel tank (sample No 2) and two concrete tanks (samples No 3 and No 4) are also presented. For one of the samples, there are also data obtained after storage for 175 days at room temperature with addition of a catalyst accelerating the destruction of UDMH and the products of its transformation. The concentration difference may be caused by different amounts of UDMH in the samples, while different qualitative compositions are due to different sample prehistory. The major compounds are acetaldehyde dimethylhydrazone, hydrazine (as acetone azine), tetramethylurea and glyoxal bis(dimethylhydrazone). Hydrazine may be formed upon destruction of dimethylhydrazine and may also be present as an additive in the initial fuel. These fuel mixtures, for example Aerozine, are known and consist of equal amounts of hydrazine and dimethylhydrazine.[6, 7, 27, 28] The presence of monomethylhydrazine will obviously attest to destruction processes, because monomethylhydrazine-based fuels, although known, are barely used in Russia.

Acetaldehyde dimethylhydrazone is formed in both model and real samples. The closest homologue is formaldehyde dimethylhydrazone formed upon the reaction of formaldehyde with the initial dimethylhydrazine

$$CH_2O + Me_2N-NH_2 \longrightarrow Me_2N-N{=}CH_2 + H_2O \qquad (3)$$

The appearance of formaldehyde is usually attributed to the formation and decomposition of hydroperoxides.[89] Alternatively it could form upon the direct reaction of methyl radicals with oxygen. Relying on these mechanisms, it can be assumed that acetaldehyde dimethylhydrazone arises according to a similar reaction, which, however, involves acetaldehyde (formed from formaldehyde and a methyl radical) instead of formaldehyde. Acetaldehyde dimethylhydrazone is an isomer of acetone methylhydrazone, which appears when the sample preparation procedure involves acetone. It is important to separate and

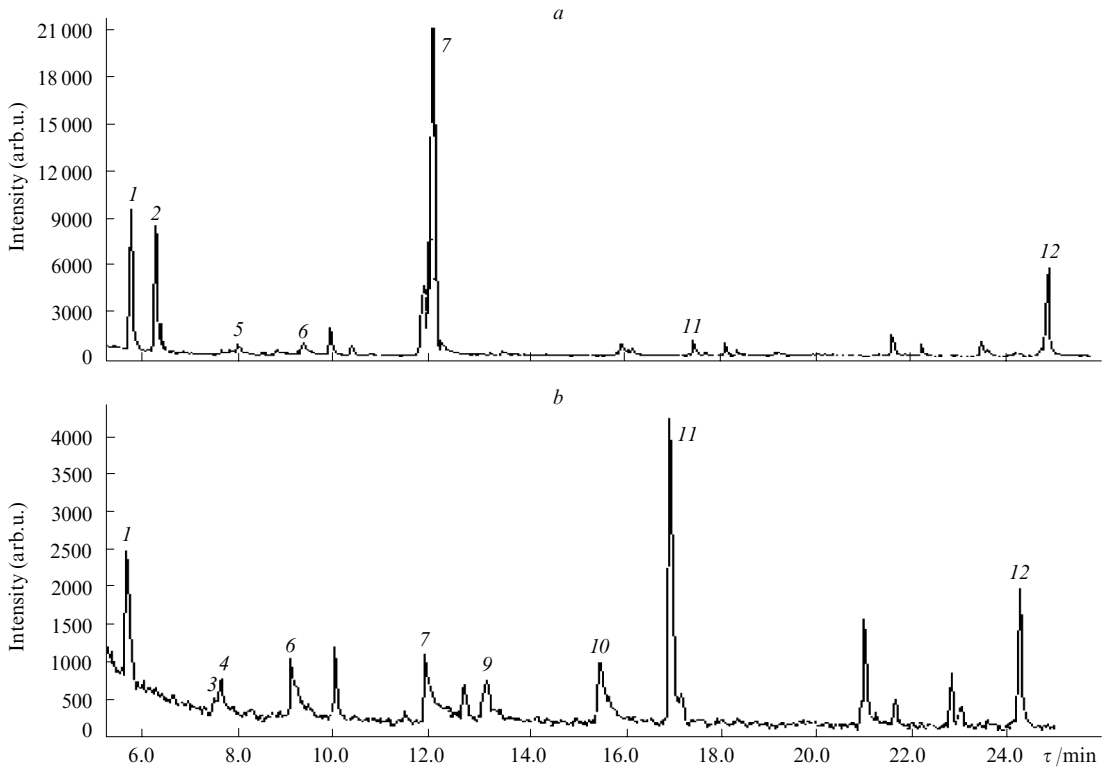


Figure 13. Total ion current chromatogram of extracts of industrial effluents.[31]
(*a*) Sample No. 1, (*b*) sample No. 5; For (*1–12*), see Table 9

identify these products by CMS for evaluation of the mechanisms of destruction processes in UDMH solutions.

The problem of pollution by the fuel of launch areas and areas where the detachable parts of launch vehicles fall on the Earth is mainly specific to Russia because the US and European detachable parts of launch vehicles containing fuel tanks and motor units with the remainder of toxic propellants and the oxidant usually fall into the ocean.

Buryak *et al.*[91] carried out a GC–MS study of the transformations of UDMH on the sorbents that simulated real soils. Using this informative method, the key products of UDMH transformation on various model sorbents were identified. For clay samples, kinetic curves for UDMH decomposition and product accumulation were plotted.

The GC–MS method was also utilized[92–95] to study the products of transformation of UDMH in model systems and real soils. The authors were able to confirm the complex multistage mechanism of transformation of UDMH in soils and to identify numerous transformation products.

GC–MS analysis of soils is compatible with any sample preparation procedure: analysis of the equilibrium vapour phase above the soil, vapour preconcentration on various

Table 9. Products of transformation of UDMH and their concentrations in industrial effluents of various types.[31]

Run	Compound	Concentration (mg litre^{-1}) in the sample					
		No. 1	No. 2	No. 3	No. 4	No. 4[a]	No. 5
1	acetaldehyde dimethylhydrazone	0.43	–	920	890	–	6.26
2	acetone dimethylhydrazone	0.29	0.2	1000	900	0.853	0.32
3	nitrosodimethylamine	0.05	0.03	0.16	0.15	0.359	1.24
4	dimethylaminoacetonitrile	0.03	–	33	31	0.447	1.95
5	acetone methylhydrazone	0.05	0.04	–	–	–	–
6	*N*,*N*-dimethylformamide	0.13	0.08	11	10	1.22	3.27
7	acetone azine	2.57	2.73	330	280	13.3	5.82
8	1-methyl-1*H*-1,2,4-triazole	0.29	0.21	12	11	0.05	–
9	guanidine	0.04	–	32	32	–	3.06
10	dimethyltriazole	0.15	0.17	21	20	–	4.52
11	tetramethylurea	0.15	0.05	110	100	0.524	12.70
12	glyoxal bis(dimethylhydrazone)	0.47	–	0.07	0.42	7.87	5.98

[a] After 175 days of storage with the addition of a catalyst accelerating the destruction of UDMH.

types of sorbents and analysis of aqueous or organic extracts.

A group of researchers [92–95] optimized the stages of vapour extraction: they studied the effect of temperature and incubation time† for various types of samples (sand, clay, clayish soil) and a model sorbent (crushed glass). The optimal conditions of sample injection, chromatographic separation and detection for the total ion current and separate ion modes were selected. The rapidity of GC–MS analysis allowed the researchers to study a multitude of samples from the falling area of the Baikonur launching site contaminated by UDMH and the products of its transformation. This integrated approach increased the reliability and information content of the analysis by extending the range of transformation products being determined.

The use of LC–MS for analysis of the environmental pollution is still held up by high cost of instrumentation and, hence, quantifications; therefore, these studies are few.

The HPLC–MS method has been successfully used [96] to quantify the products of oxidative transformation of UDMH in soils. A new product was identified — formic acid dimethylhydrazide, which can be hydrolyzed to give free UDMH. The detection of this product may account for the abnormal increase in the amount of free UDMH in soil after it has regularly decreased. Procedures for quantification of this product in soil extracts based on ion chromatography coupled with detection by chemical ionization mass spectrometry under atmospheric pressure were developed.[97]

By means of HPLC–MS, it is possible to solve topical problems of analysis of the products formed in reactions of UDMH with biopolymers — polysaccharides, proteins, DNA and RNA.[98] However, these problems are too sophisticated and are rarely tackled by biologists and ecologists. For example, it was shown [99] that exposure of bee moth larvae to UDMH gives rise to peptides modified by methyl groups at the glutamic and aspartic acid residues and at C-terminal amino acids in the larvae body. In addition, the amount of low-molecular-mass (1–3 kDa) peptides increases. The authors suggested that by studying the contents of such products, it is possible to predict the long-term effects of application of rocket fuels (see also other publications [51, 54–56, 71, 72]).

Note that the LC–MS method covers a large range of substances as regards both the molecular mass and the presence of reactive functional groups and that options for coupling of a chromatograph and a mass spectrometer are being developed and the equipment becomes less expensive. Therefore, considering the prospects of using CMS to determine hydrazine, methylhydrazine, UDMH and the products of its transformation suggests that, as for other types of specimens,[100] the ratio of GC–MS and LC–MS methods being used (first of all, for newly developed procedures) would shift toward a higher share of the latter.

IV. Chromatography – mass-spectrometry for analysis of the surface of structural materials

Studies of contaminated surfaces by means of traditional CMS analysis [1, 66] usually require preliminary sample preparation and washing from the surface or taking samples for pyrolysis when the pyrolytic procedure is used.[64] In the case of ion chromatography coupled with ICP-MS, elemental analysis of the surface is possible with determination of elements in various oxidation states.[101] It is possible to carry out thin layer displacement chromatography followed by matrix/surface-assisted laser desorption–ionization (MALDI/SALDI) analysis or fast atom bombardment, which allows preconcentration and analysis of trace impurities on the surface. The MALDI/SALDI techniques can also be used to construct the distribution diagrams of pollutants on the surfaces of structural materials.[102]

Most popular is GC–MS, which is used to monitor the state of the surface of the International Space Station (ISS) and surface contamination by fuel and transformation products. This is an important practical problem that needs to be solved for maintenance of the station, crew safety and reliability of functioning of optical devices. Special experiments were carried out for determining the qualitative and quantitative compositions of pollutants; for this purpose, plate containers with various materials were mounted at the station.[103]

Similar experiments were carried out at the Mir station (Kromka experiments).[104, 105] The photo images of the plates from the containers (Fig. 14) show areas contaminated by the products of fuel transformations. The total ion current chromatogram of the acetone washing from the strip used to fasten the plate container at the Mir station is shown in Fig. 15. It can be seen that a very complex mixture was analyzed, and not in all cases, complete chromatographic separation was attained. The presence of micro and macro components in the mixture also supports the choice of CMS for this analysis. Meanwhile, complete chromatographic separation and reliable identification may require two-dimensional processes (GC/GC–MS/MS). Quite a few nitrogen compounds were found among the contaminants (Table 10). Presumably, the reactions giving these products involve nitrogen monoxide and dioxide, UDMH and products of its incomplete combustion. After these compounds

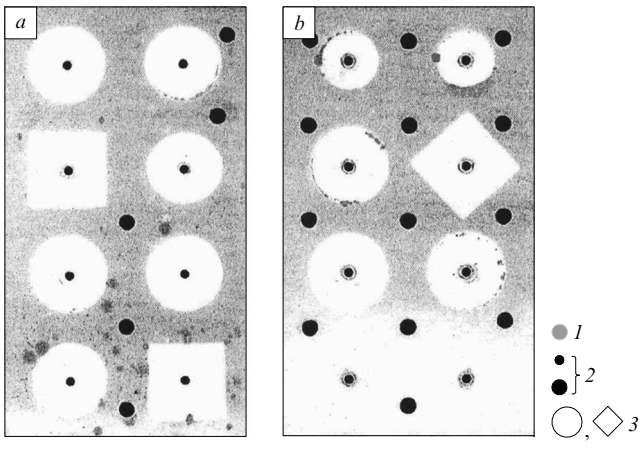


Figure 14. Photo images of the control plates from the containers used in the experiments 'Kromka 1-0' (*a*) and 'Kromka 1-1' (*b*).[104] (*1*) Traces of drop contamination by rocket fuel components on the surface, (*2*) working holes, (*3*) traces of the structural materials exposed on the container.

† The time of maintenance at a definite temperature in a closed vial for vapour-phase analysis.

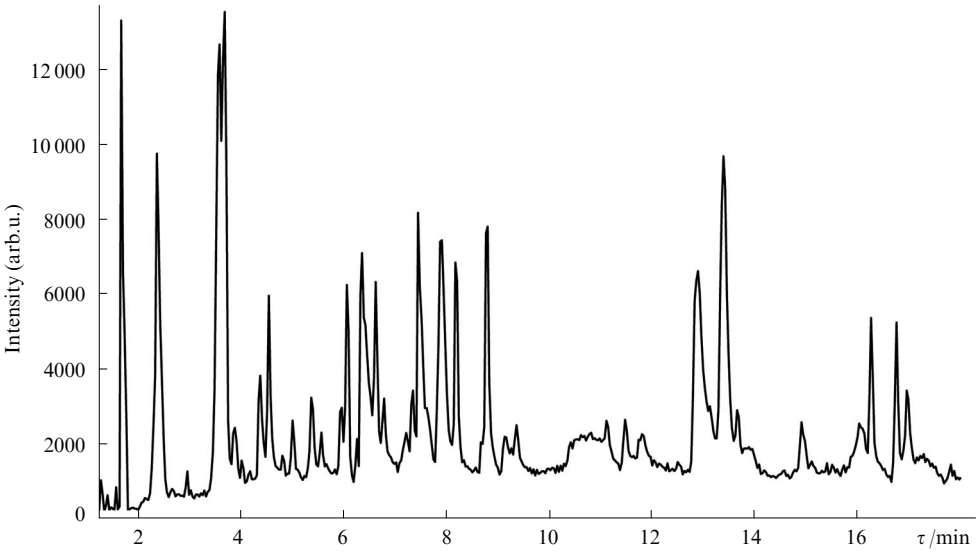


Figure 15. Total ion current chromatogram of acetone washing from the strip used to fasten the case with the material contaminated by products of incomplete combustion of the fuel.[13]

Table 10. The principal composition of the washing from the strip contaminated by the propellant and products of its transformation.[13]

τ /min	Compound	*m*/*z*	*c* /μg g^{-1}
1.8	cyanate 1	56	5.43
2.4	1,3,5-triazine	81	5.80
2.9	acetone dimethylhydrazone [a]	100	0.63
3.6	nitrosodimethylamine	74	4.23
3.7	dimethylaminoacetonitrile	83	25.02
4.4	*N*-methylformamide	59	2.06
4.6	*N*,*N*-dimethylformamide	73	2.23
5.0	dimethyl-1*H*-4,5-dihydropyrazole	83	4.52
5.3	cyanate 2	56	7.06
5.4	amino-4-methyl-1*H*-1,2,4-triazole	97	0.99
6.0	4-methylpyrimidine	94	1.01
6.1	1,5-dimethyl-1*H*-4,5-dihydropyrazole	98	1.53
6.4	1-methyl-1*H*-1,2,4-triazole	83	31.45
6.6	3,5,5-trimethyl-1*H*-4,5-dihydropyrazole	97	6.92
6.8	2,5-dimethylpyrrole	94	0.58
7.2	guanidine	59	6.83
7.4	non-identified	107	0.29
7.5	*N*,*N*-dimethyl-*N*′-dimethylamino-formamide	115	24.33
7.7	*N*,*N*-diethylacetamide	58	6.98
7.9	hydroxymethyltriazole	42	24.03
8.2	3,5-diamino-1*H*-1,2,4-triazole	99	3.22
8.8	non-identified	107	1.30
9.1	methylimidazole	82	0.73
9.4	dimethyl-1*H*-1,2,4-triazole	97	7.73
12.9	*N*,*N*-dimethylurea	44	4.86
13.3	aminotriazole	127	0.76
13.4	non-identified	102	3.34
14.9	4-nitro-1*H*-pyrazole	113	0.71
16.3	non-identified	120	0.83

[a] The amount of UDMH is indicated.

have been sorbed on the strip, they are further oxidized to give more intricate products.

Washings from various sites of the ISS surface and exposed samples were investigated by GC. Compounds were identified by mass spectrometry. Nitrogen-containing compounds formed from UDMH were detected.[103–106] The data averaged over trhe exposure time are presented in Table 11. The content of the transformation products varies over a broad range, which is caused by the relative positions of sampling points, and the qualitative composition resembles the composition of the transformation products formed under earth conditions.[31,95]

Table 11. Compounds detected on the surface of the International Space Station and their relative contents for different samples.[13]

Run	Compound	*m*/*z*	*c* (%)
1	nitrosodimethylamine	74	0–1.5
2	dimethylaminoacetonitrile	83	20.3–24.9
3	*N*,*N*-dimethylformamide	73	23.1–25.6
4	1-methyl-1*H*-1,2,4-triazole	83	17.6–19.6
5	dimethyl-1*H*-1,2,4-triazole	97	16.2–16.9
6	guanidine	71	17.4–17.9

Important results were obtained in the studies of contamination of various areas of the solar batteries of the Mir station.[106] Their surface was found to bear products of transformation of rocket fuel components.

Based on the above results, it can be considered proven that fuel gets on the station surface and that substantial amounts of UDMH transformation products, including highly toxic ones, are formed. The most reliable and informative method for such investigations is GC–MS.

When CMS is used, the reliability of the results is beyond doubt but when interpreting the results, it should be borne in mind that reactions of the fuel and fuel transformation products with various surfaces afford secondary

products the composition of which depends on the reaction conditions and the surface properties. Surprising is the presence of fuel transformation products on the station surface under high vacuum of space and the fact that these products are retained for long periods of time, although their boiling points are relatively low (in the range of 50–200 °C). One of the causes is high sorption activity of the transformation products consisting mainly of nitrogen-containing compounds having acidic or basic properties and forming adducts with one another, which can be preserved on the surface for long periods; another cause is the formation of salts of nitric and nitrous acids (resulting from conversion of the oxidant) with amines (resulting from conversion of the propellant). Detailed investigation of these salts and adducts for predicting their stability on the surface requires various CMS procedures. To choose the procedures for removal of these deposits and reduce the deposition rate, CMS determination of the heats of adsorption of the transformation products on the surfaces of materials used for the manufacture of outer coatings of ISS may be useful.

The GC–MS technique was used [107] to study the surface and bulk properties of the textiles meant for protection from UDMH contamination. The key products of transformation of UDMH on the surfaces of various types of textile were identified and their amounts were determined. Hydrazine, methylhydrazine, nitrosodimethylamine, tetramethyltetrazene and some other compounds were shown to be formed as major products. The textiles differed in the catalytic activity towards UDMH decomposition and sorption capacity with respect to UDMH (that remained unchanged). The obtained results indicate that the protective properties of textiles such as FTsM and TD-3 brands are caused by physicochemical processes that take place on their surface — physical adsorption in the two-component sorbent system and chemical reactions between the chemical sorbent (copper ferrocyanide) and UDMH. The obtained results formed the basis for development of chemical protective clothing for UDMH-handling personnel.[108, 109]

Gulidov *et al.*[110] carried out investigations, in particular, by GC–MS, of the influence of the chemical properties of the surface on the service life of the fuel tanks of ocean-spanning ballistic missiles. No UDMH transformation products were found on the outer surface of fuel tanks, which attests to corrosion resistance of the tank material. Trace amounts of process-related contaminants representing components of lubricants and cutting fluids were detected. Analysis of the obtained data and the results of other methods provide important information for the development of methods for their conservation and extending the service life of the articles.[111]

Organic impurities were studied by GC–MS in the cooling system of the rocket engine RD170 (see Ref. 112). Mainly hydrocarbons were identified and their amounts were determined. On the basis of the results obtained by gas chromatography and microprobe analysis with electron microscopy, conclusions were drawn on minimum amounts of deposits on the surface of the fire wall and, hence, on proper operation of the engine.

By solid-state NMR and GC–MS studies, the relationships were found between the formation of aromatic compounds and accumulation of deposits during thermal decomposition of jet fuels of various types.[113] The transformations of mono- and bicyclic hydrocarbons into aromatic compounds and accumulation of polyaromatic compounds were established. HPLC analysis confirmed the formation of polyaromatic compounds; however, only those compounds for which standard samples were available were identified. Evidently, HPLC–MS is needed for detailed identification of all components of the mixture and for validation of the scheme of deposition.

The thermal decomposition of rocket and jet fuels was studied by means of gas chromatography and mass spectrometry: changes in the fuel composition after heating under pressure in contact with structural materials were elucidated. [114–116] The experiments simulated the behaviour of the fuel when used to cool the combustion chamber, *i.e.*, outside the jacket. The GC–MS technique was used for comparative analysis of the initial samples and the samples subjected to short-term heating under pressure. It was found that with temperature rise, the amount of light hydrocarbons considerably increases, the total amount of alkanes decreases, whereas the amounts of mono- and bicyclic alkanes, alkylbenzenes, indans, tetralins and naphthalene derivatives increase.

The integrated information about the fuel composition after heating and the chemical composition of the wall deposits can be used to predict the quantity called 'cooling capacity' of the fuel, and, finally, the engine service life.

V. The use of chromatography–mass-spectrometry for evaluating the efficiency of removal of fuel components at different facilities

This Section deals with the CMS studies involved in the development of procedures for the mitigation of environmental consequences of aerospace activities and monitoring of detoxification of rocket propellant components during their production and application at different facilities. Using CMS, it is possible to rapidly evaluate the degree of detoxification, accumulation of the transformation products and the consumption of the reagents used. The application of CMS is especially efficient in the development and comparison of various industrial processes and evaluation of new processes. The efficiency is due first of all to the high information content of CMS.[1–5]

The GC–MS method was used to evaluate the gas-phase process of UDMH decomposition induced by electric discharge. The transformation products formed under different conditions were identified and the process being developed was concluded to be advantageous.[117] Using GC–MS, the formation of cyanogen and accumulation of nitrosodimethylamine following an increase in the time of electric discharge treatment in an air – helium mixture was established. This result makes it possible to define more precisely the scope of applicability of the process being developed and to plan measures for improvement of the technique.

The operation efficiency of a bioreactor for degrading the industrial wastes obtained after absorption of methylhydrazine and hydrazine from the gas phase with citric acid [118] was monitored by a set of analytical methods including GC–MS. The most important finding, *i.e.*, the absence of transformation products of methylhydrazine, attests to effective operation of the bioreactor.

The results of evaluation of the process of treatment of UDMH in water with potassium permanganate [119] are presented in Fig. 16. The total ion current chromatogram

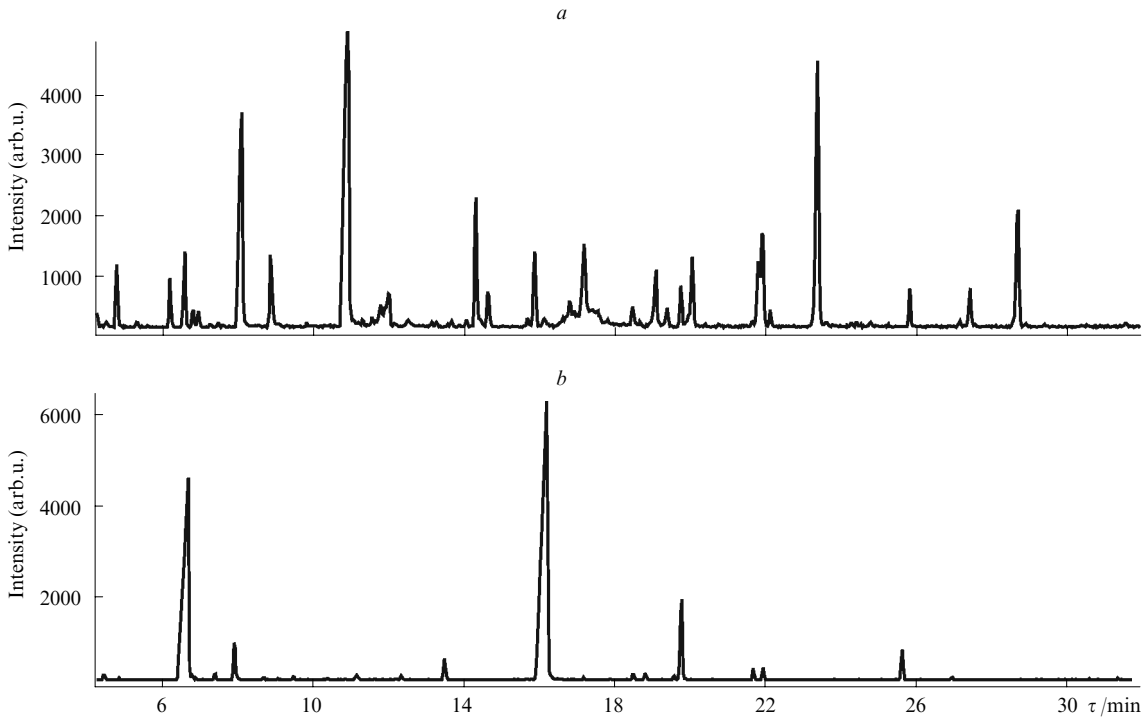


Figure 16. Total ion current chromatograms of an aqueous solution of UDMH at different stages of potassium permanganate decontamination.[120]
(*a*) intermediate stage of decontamination; the most intense peaks were not identified and disappeared upon further oxidation; (*b*) after decontamination; the peak at $\tau = 6.3$ corresponds to nitrosodimethylamine; the peak at $\tau = 16.2$ was not identified.

(see Fig. 16 *a*) shows the presence of UDMH transformation products formed in the intermediate stage of treatment: the mixture contains 13 compounds three of which have not been identified. During treatment, some UDMH transformation products disappear but some other are accumulated (see Fig. 16 *b*). Among the latter, nitrosodimethylamine was detected and an unknown compound, which is of special hazard because it lacks even a theoretical value of MAC. It is clear that this treatment process is inapplicable and should be modified. It was planned to increase the process efficiency by combining potassium permanganate with hydrogen peroxide but in this case, too, the formation of toxic transformation products could not be avoided.[120]

The GC–MS method was used to evaluate another process for the removal of UDMH, which is based on ozonolysis.[121] It was found that during treatment, no significant accumulation of toxic transformation products takes place, and after completion of the process, the concentrations of all compounds present in the initial mixture reduced to a safe level. This process was recommended for practical use.

The development of treatment processes is faced by additional complications if the solutions to be treated contain not only UDMH and products of its transformations but also washing reagents. Usually, 0.5%–5% solutions of washing reagents are used.[122, 123] The presence of such considerable amounts of reagents may have adverse effect on the results of detoxification. Analysis of the total ion current chromatograms of extracts from the solutions after ozone-based treatment that contain a washing reagent and a salt of *m*-nitrobenzoic acid (MNBA), demonstrated that ozonolysis decreases the concentrations of the washing reagent and UDMH transformation products. The results of determination of the concentrations of contaminants in the treated solution are summarized in Table 12. The calculations showed that the contents of all compounds present in the solution after treatment do not exceed the maximum allowable levels for domestic water supply.

Table 12. Concentrations of contaminants in a 0.5% solution of MNBA contaminated by UDMH (the initial concentration of UDMH was 500 mg litre^{-1}) 3 and 10 h after the beginning of ozonolysis.[123]

τ /min	Compound	Content /mg litre	
		after 3 h	after 10 h
3.4	nitromethane	0.008	–
9.9	nitrosodimethylamine	1.7	0.0045
28.8	dinitrobenzene	0.51	0.2
29.1	MNBA methyl ester	0.062	0.0006
32.0	MNBA	3.6	0.004
32.1	2,4,6-trinitrobenzoic acid	0.005	0.008

Catalyzed oxidation with air oxygen [124, 125] and hydrogen peroxide [126, 127] under various conditions was monitored by chromatography and by GC–MS where trace impurities were analyzed and the oxidation products were identified. These detailed analyses are important because optimal processes for detoxification of solutions containing UDMH and the products of its transformation have not been developed as yet.[128]

Soil is one of the most stubborn media for the control of UDMH spills. At different depths of penetration into the soil, the UDMH transformation processes have different mechanisms. In deep layers in the absence of air, UDMH is conserved. In addition, various mineral components of soils have different catalytic effects. Therefore, the composition of UDMH transformation products is different for different types of soil. Several processes for soil decontamination from UDMH have been developed;[128–131] however, none of them provides a satisfactory solution to this problem. Golub *et al.*[132, 133] proposed and practically tested a process for the control of UDMH spills by means of a material manufactured based on a natural sorbent called shungite. CMS has been used in all stages of the work: for identification of micro and macro components, for analysis of model solutions and real samples and for comparison of various types of shungite materials. The natural shungite material shows catalytic activity in decomposition of UDMH but decomposition is slow. More pronounced catalytic and sorption properties are achieved by modification of shungite.

Golub *et al.*[132, 133] studied washings from model soil samples and shungite-bearing model soil samples that were treated with aqueous solutions of UDMH with different concentrations (10% – 90%) and then (after 24 h) washed with acetone. The studies were carried out in the temperature range from −15 to 20 °C. It all cases, the contaminant concentrations were reduced. This was attributed to sorption and subsequent decomposition of UDMH and its transformation products on the sorbent surface.

From the temperature dependence of the UDMH concentration in the washings from soil surface, it follows that the concentration of UDMH on the surface decreases as the temperature increases. The content of UDMH in shungite-bearing soils is much lower. The use of shungite rock provides a considerable (5 – 10-fold) decrease in the contaminant concentration as soon as after 24 h. No products of transformation of UDMH were detected in washings from shungite-containing samples at levels exceeding 0.001 mg g^{-1}, whereas model samples accumulated compounds that are usually formed upon UDMH decomposition in soils, including highly toxic nitrosodimethylamine and tetramethyltetrazene.

The mass chromatograms of molecular ions of acetone dimethylhydrazone (m/z 100) and benzene as the standard (m/z 78) for washings from a shungite rock sample are presented in Fig. 17 *a*,*b*. Since acetone was used as the solvent, UDMH was determined as the acetone hydrazone. Apart from UDMH, the chromatogram was found to show sulfur-containing impurities (Fig. 17 *c* – *e*). According to GC – MS identification, these were dimethyl disulfide and dimethyl trisulfide. These compounds may be of human or natural origin. Most likely, they are formed upon UDMH destruction on the surface of shungite grains. The oxidative destruction of UDMH is known to give free radicals. Presumably, methyl radicals can react with sulfur, which is present in the shungite rock to give methyl derivatives.

It is necessary to take into account the formation of volatile sulfur compounds, because their presence complicates the sensor analysis of the environmental situation in the region of emergency spills. In addition, the offensive odour of dimethyl polysulfides complicates the work. The most toxic of the detected compounds, dimethyl disulfide, has a MAC of 0.04 mg $litre^{-1}$ in water and 0.7 mg m^{-3} in air (upon short-term exposure, this is comparable with the MAC of UDMH, which is 0.2 mg $litre^{-1}$ in water and 0.1 mg m^{-3} in work area air).[72]

These results formed the basis for development of a process[134] for effective and environmentally safe removal of UDMH spills. The reliability of this process is based on the CMS monitoring of the quality of solutions used for treatment and degree of conversion.

In some cases, on the basis of analytical CMS data alone, it is possible to predict the efficiency of a process

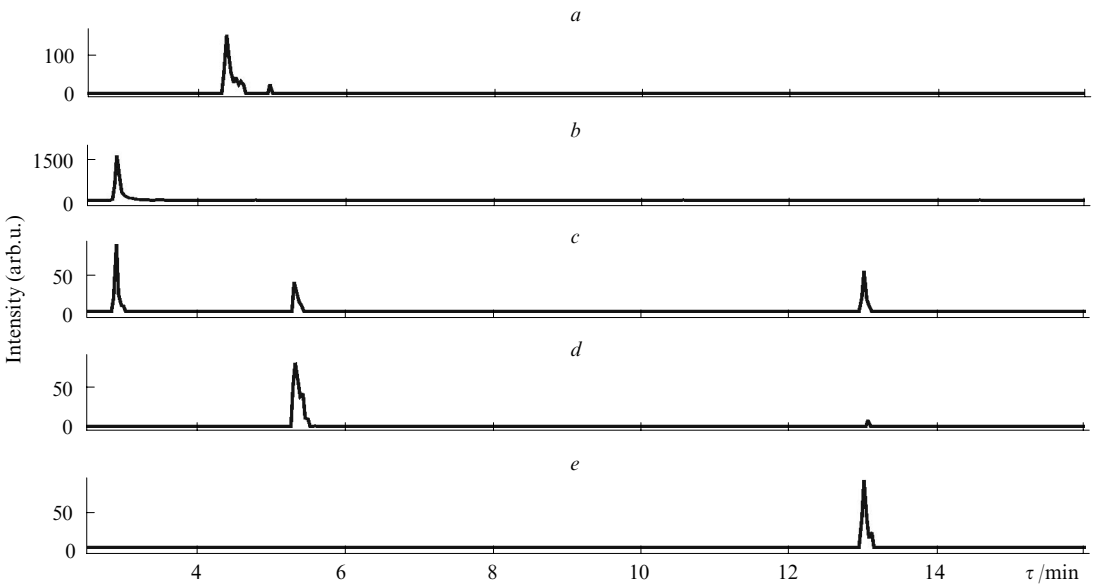


Figure 17. Mass chromatograms of characteristic ions of acetone dimethylhydrazone (*a*), benzene (*b*), dimethyl disulfide (*c*, *d*) and dimethyl trisulfide (*c*, *e*).[133]
m/z 100 (*a*), 78 (*b*), 94 (*c*), 79 (*d*), 126 (*e*).

planned to be developed and to evaluate the practicability of this process. In particular, the problem of control of hydrocarbon propellant spills can be successfully solved using GC – MS procedure for determination of JP-8 propellant components in soils.[135] The authors demonstrated by experiments with a real propellant and a standard hydrocarbon mixture that the major components of the propellant cannot be detected in soils as soon as after 15 days. Thus, the procedure for predicting the concentrations of the major propellant components in soil depending on time, the type of soil and environmental conditions may serve as the basis of a detoxification process for soils contaminated with the propellant of this type.

VI. Conclusion

The considered examples and the cited literature do not cover, naturally, all possible aerospace applications of CMS; it should be noted that in the future, CMS will be used for a major part of fuel analyses. An important CMS application that has been barely considered in the review should be conduction of arbitrage analyses in order to evaluate the analyses performed by other methods according to GOSTs.

The environmental consequences of the aerospace activity would be evaluated to a large extent by using gas and liquid chromatography with mass-spectrometric detection. Extensive use of LC – MS may be expected in the analysis of biological specimens.

One more trend that is still to gain popularity is the CMS analysis of the surface chemistry of structural materials. Within this trend, of particular value would be liquid and ion chromatography coupled with various mass-spectrometric detectors for determination of organic and inorganic components that are deposited on the surface of structural materials and are present in fuels, lubricants and starting fluids.

The speed, reliability and efficiency of the processes being developed would largely depend on the degree to which CMS techniques are employed. In the future, they might be used in all types of processes.

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