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DETERMINATION OF THE STRUCTURE OF IMPURITIES IN TRYETHYLENE GLYCOL BY NMR AND HPLC-MS/MS OF HIGH RESOLUTION

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The process of natural gas drying leads to accumulation of unstudied organic impurities in the used absorbent solutions. These impurities reduce the drying capacity of triethylene glycol. In order to increase the effectiveness of installations for drying natural gas it is necessary to purify triethylene glycol from the accumulated impurities. The absence of information on the structure and properties of these impurities considerably complicates the purification of the absorbent solutions. In this study the structures of impurities accumulated in triethylene glycol were determined by NMR and high resolution mass-spectrometry coupled with chromatography (HPLC-MS/MS). The obtained results will enable to improve the existing methods for the purification of the working solutions of the absorbent.

Keywords: *high performance liquid chromatography, high resolution mass spectrometry, nuclear magnetic resonance, triethylene glycol.*

Introduction

In the course of absorptive drying of natural gas, various impurities are accumulated in glycol absorbents. These impurities include highly volatile and slow-evaporating organic compounds, inorganic substances, reagents used at previous steps of raw materials processing etc. [1–3]. It was established in studies carried out before that absorbent samples providing and not providing the required degree of raw materials drying statistically authentically differ from each other in the content of some organic compounds [4, 5]. It is assumed that these compounds impede the process of moisture absorption by triethylene glycol. In order to test this assumption it is necessary to establish the structure of the found impurities.

In this work we carried out comparative analysis of absorbent samples taken in various periods of operation of an installation for natural gas drying in Yamburg gas field. We obtained high-resolution NMR and HPLC-MS/MS spectra of compounds accumulated in working solutions of the absorbent. On the basis of the

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obtained results we determined the structures of components affecting the absorbing capacity of ethylene glycol.

Experimental

The analysis of samples by high-resolution HPLC-MS/MS was carried out with the use of a Dionex Ultimate 3000 liquid chromatograph combined with a Q-Exactive hybrid high-resolution mass spectrometer of firm (Thermo Scientific, USA). NMR studies were carried out with the use of an Avance III HD a spectrometer (Bruker, USA).

Besides, the following equipment and reagents were used: a NANOPure installation for obtaining deionized water (Thermo Scientific, USA); a Concentrator Plus vacuum concentrator (Eppendorf); a Hypersil Gold aQ analytical column 100 mm long, with an internal diameter of 2.1 mm, sorbent particles diameter of 1.9 μm (Thermo Scientific, USA); Discovery DSC-18 cartridges for solid-phase extraction with C18 bonded phase and sorbent capacity of 500 mg (Supelco, USA); acetonitrile for gradient HPLC (Merck, Germany); 98% formic acid (Panreac, Spain); dimethyl sulfoxide-d_6 containing 99.9% of deuterium (Cambridge Isotope Laboratories, USA).

In order to carry out the study we selected two regenerated samples of the absorbent from the block for fire regeneration of an installation for natural gas drying of JSC Yamburggazdobycha at the moments of conformity and non-conformity of the dew-point temperature (DPT) of dried raw materials to the standard requirements for moisture content[1].

Analysis of triethylene glycol samples by HPLC-MS/MS

Preparation of the absorbent samples for HPLC-MS/MS analysis was carried out according to [4].

The conditions of the chromatographic analysis and mass-spectral detection are presented in Table 1.

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[1] Industrial Standard OST 51.40-93. Flammable natural gases delivered and transported through cross-country gas pipe-lines. Technic specifications.

Table 1. HPLC-MS/MS analysis conditions

Chromatographic separation parameters			
Elution mode: gradient	Time	Content of mobile phase A, % (0.1% solution of formic acid in water)	Content of mobile phase B, % (0.1% solution of formic acid in acetonitrile)
	0.00	100	0
	1.00	100	0
	10.00	5	95
	13.00	5	95
	13.01	100	0
Mobile phase flow rate	0.35 ml/min		
Analysis duration	17 min		
Sample volume	1 μl		
Mass-spectral detection parameters			
Ionization method	Electrostatic spraying		
Detection mode	Recording of positively/negatively charged ions		
Mode of parent ions recording	By total ion current within the range 100–900 Da		
	Resolution 70000		
Mode of daughter ions recording	By total ion current within the range 50–900 Da		
	Resolution 17000		
	Range of fragmentation energies of the collision cell 15–70 eV		

No pronounced peaks of compounds were found in absorbent samples when using the mode of negatively charged ions recording. However, an essential increase of the background by total ion current was noted in the range of retention times 1–5 min (Figure 1) in a sample taken from the installation at an insufficient extent of raw materials drying.

This result can be explained by a higher content of organic impurities in the second sample. They have carboxyl groups –COOH in the structure. Such compounds are weakly retained in a reverse-phase chromatography column and form, as a rule, negatively charged ions upon ionization in the mass spectrometer source [6–9].

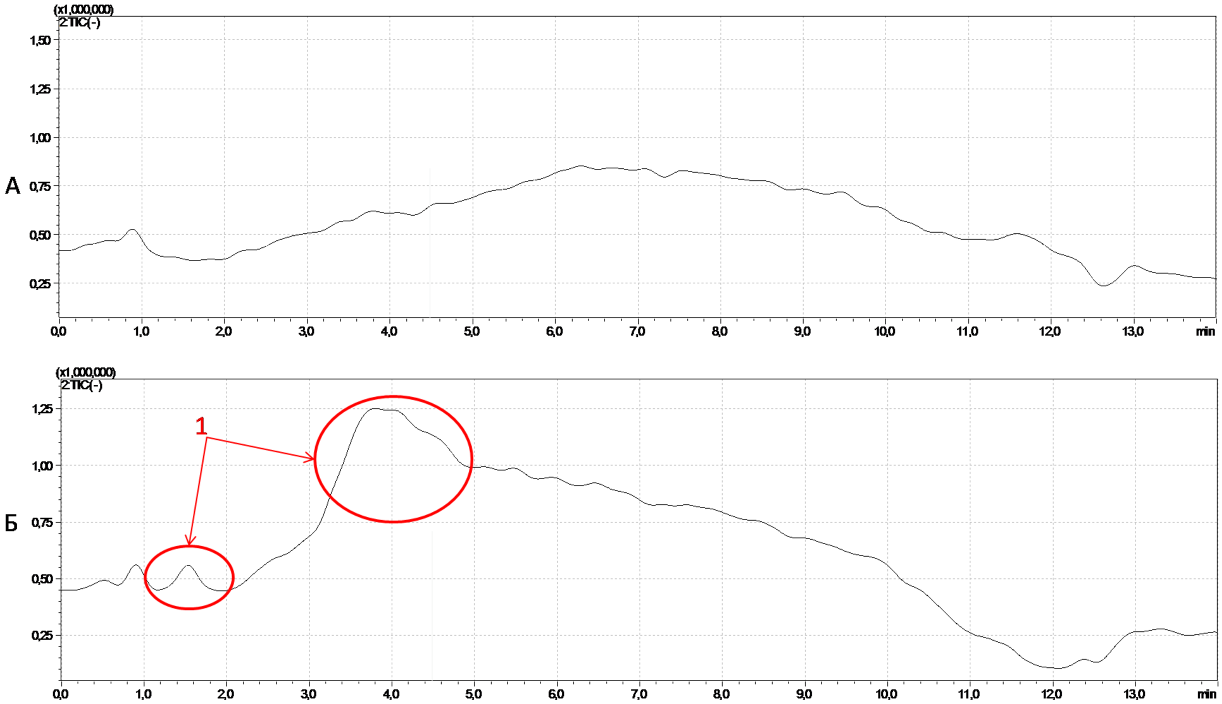

Figure 1. Chromatograms of analyzed absorbent samples by total ionic current
upon recording negatively charged ions:
A – triethylene glycol sample taken from the installation
at a sufficient extent of raw materials drying;
B – triethylene glycol sample taken from the installation at an insufficient extent
of raw materials drying (1 – areas higher background in sample B).
[А means A; Б means B]

When recording positively charged ions in the absorbent samples, intensive peaks of two types of compounds were found:

Group 1 – compounds that are present in each of the samples;

Group 2 – compounds contained only in the second sample taken from the installation at an insufficient extent of raw materials drying.

Figure 2 presents a chromatogram of the analyzed absorbent samples upon recording positively charged ions.

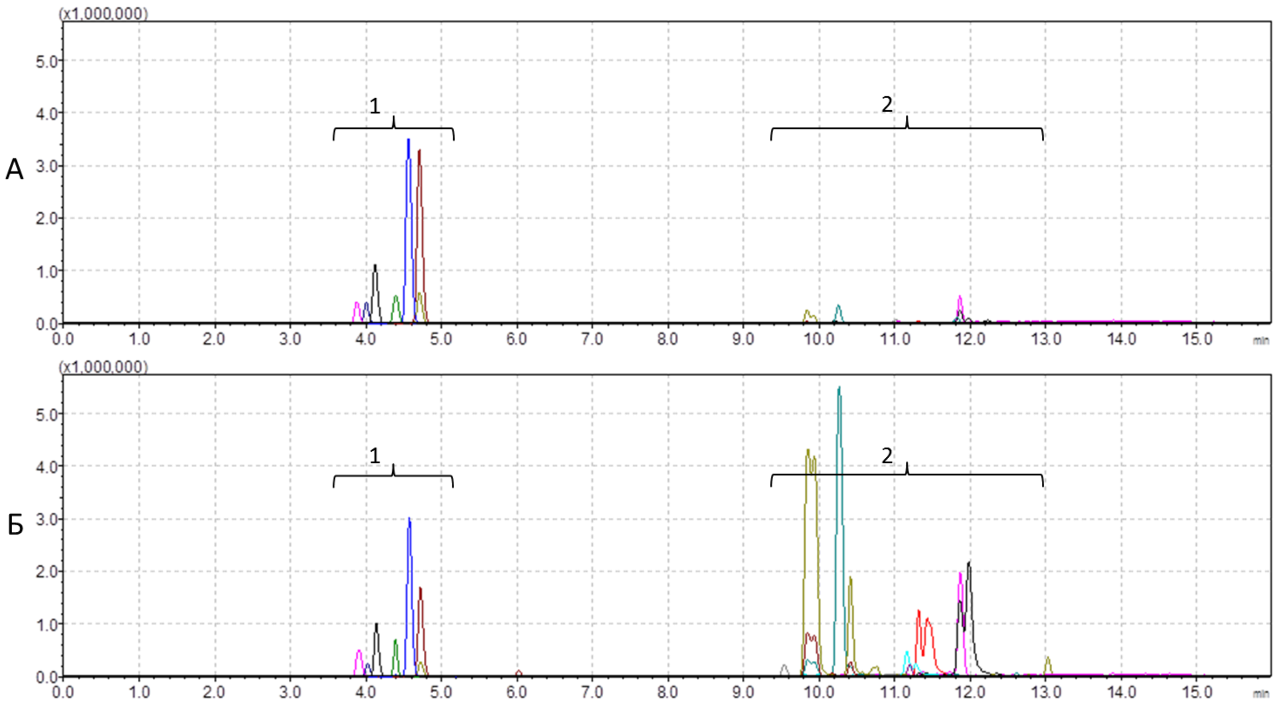

Figure 2. Chromatogram of analyzed absorbent samples by isolated ions upon recording positively charged ions:
A – triethylene glycol sample taken from the installation at a sufficient extent of raw materials drying;
B – triethylene glycol sample taken from the installation at an insufficient extent of raw materials drying (1 – group of compounds that are present in each of the samples;
2 – group of compounds that are present only in sample B).
[А means A; Б means B]

It can be seen from Figure 2 that the samples of the second group differ considerably in the content of compounds. As noted in [4, 5], these compounds presumably affect both the physico-chemical properties of ethylene glycol and its absorbing capacity.

Using the exact masses of positively charged ions of the first and second group compounds their gross formulas were calculated. On the basis of the calculated gross formulas it was found that the following elements are a part of the impurities: C, H, O, N.

In order to study further the properties of the compounds we analyzed the daughter spectra of the parent ions obtained at various fragmentation energies in the collision cell.

Figure 3 presents typical second order mass spectra of some compounds from the first group obtained upon fragmentation in the collision cell at energy 20 eV.

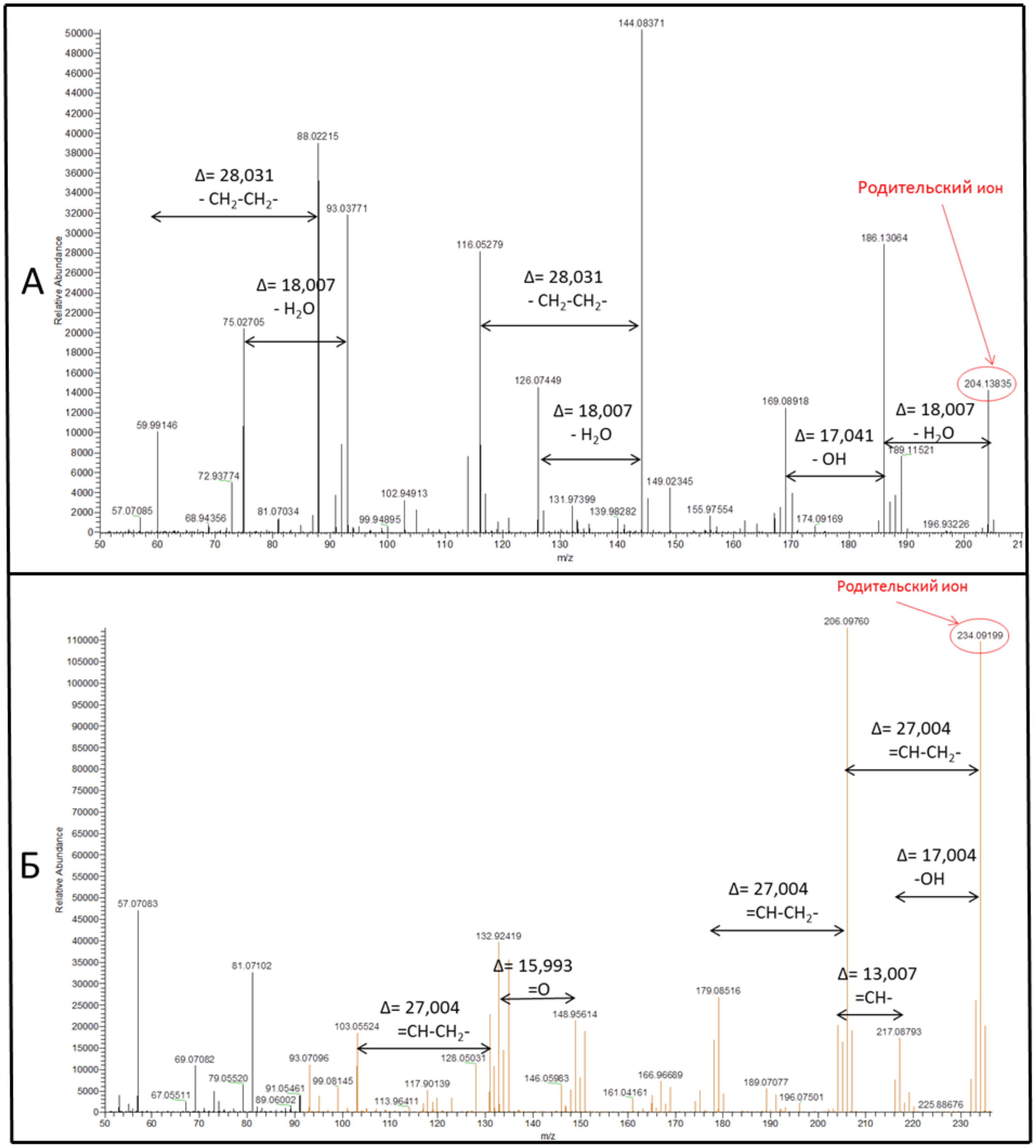

Figure 3. Characteristic daughter mass spectra of compounds of the first group at fragmentation energy 20 eV:
A – second order mass spectrum of a compound from the first group with *m/z* =204.1383 Da;
B – second order mass spectrum of a compound from the first group with *m/z*=234.0919 Da.
[A means A; Б means B; Родительский ион means Parent ion]

It can be seen from Figure 3 that when fragmentation of compounds of the first group occurs at collision cell energy 20 eV, the second order mass spectra contain residues of parent ions, as well as a number of fragments with differences corresponding to elimination of functional groups –OH, $=CH–CH_2–$, –C≡C– etc. This indicates the aliphatic nature of the compounds with non-uniform distribution of electron densities. Such fragmentation of parental ions is typical of aliphatic compounds containing various functional groups and multiple bonds [6–9].

Figure 4 presents typical second order mass spectra of some compounds of the second group obtained upon fragmentation in the collision cell with energy 55 eV.

It can be seen from Figure 4 that when fragmentation of compounds of the second group occurs at collision cell energy 55 eV, no parent ions remain in the second order mass spectra. Instead, a number of fragments differing from each other by a $–CH_2–$ functional group are found, which is typical of the fragmentation of unsaturated cyclic compounds [6–9]. Because *m/z* of the parent ions is in the range 350–400 Da, it is possible to say that each of the compounds consists of several alicyclic rings bonded with each other.

It should be noted that the structures of compounds of the second type should include such functional groups as –OH and $–NH_2$. These functional groups are easily protonated forming positively charged ions in a mass spectrometer source [6–9]. Without these groups it would be impossible to record the spectra of polycyclic compounds upon ionization by means of ionic spraying.

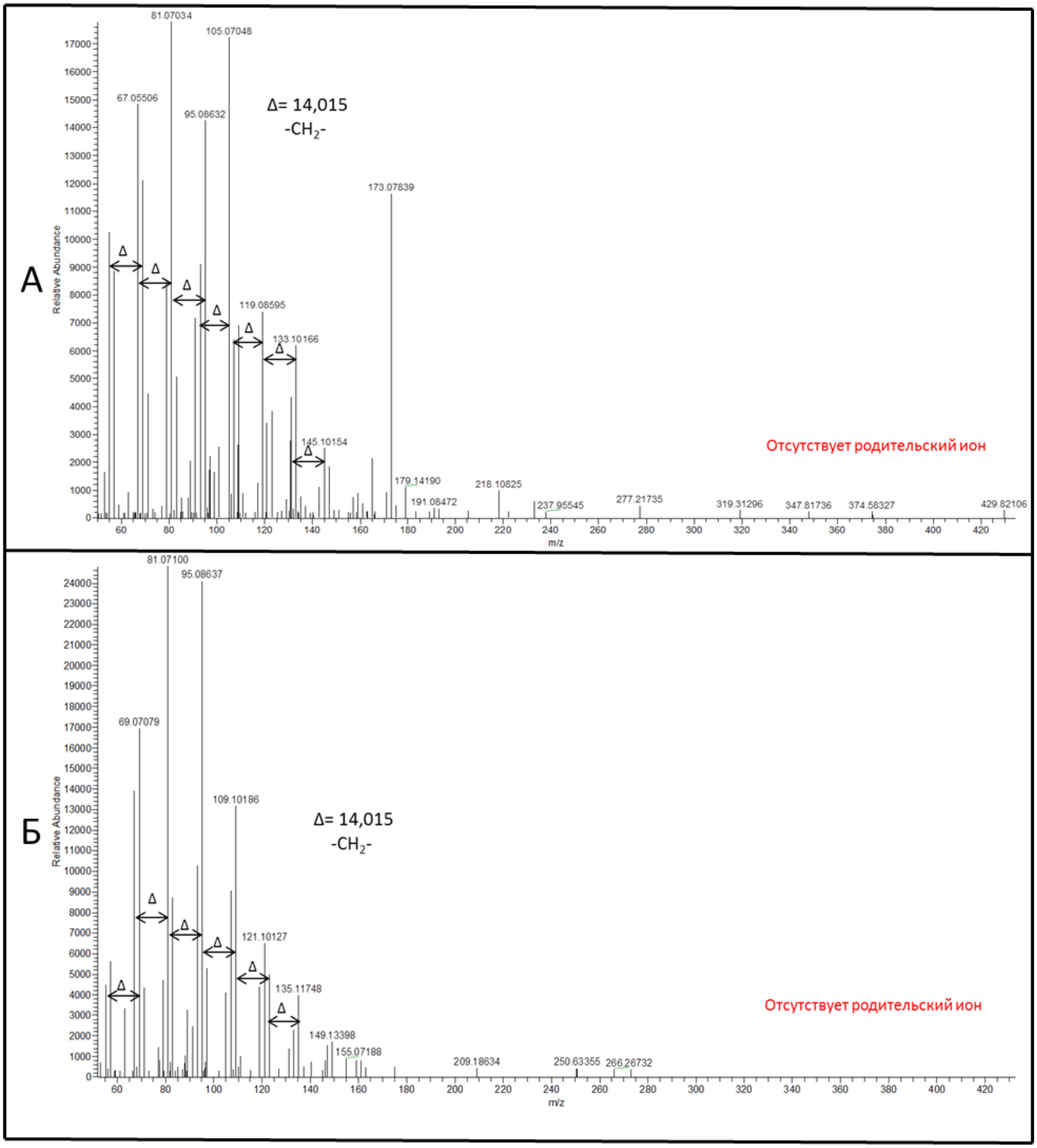

Figure 4. Characteristic daughter mass spectra of compounds of the second group at fragmentation energy 55 eV:
A – second order mass spectrum of a compound of the second group with *m/z*=427.2466 Da;
B – second order mass spectrum of a compound of the second group with *m/z*=435.3561 Da.
[А means A; Б means B; Отсутствует родительский ион means No parent ion]

Generalized analytical characteristics of compounds of the first and second groups obtained by HPLC-MS/MS are presented in Table 2.

Table 2. Analytical characteristics of compounds of the first and second groups

Characteristics	First group compounds	Second group compounds
Retention times	2–5 min	9–14 min
m/z of parent ions	150–350 Da	350–500 Da
Elements included in the structure of the compounds	C, H, O, N	C, H, O, N
Energy of collision cell, at which fragmentation of parent ions occurs	20 eV	Above 50 eV
Fragmentation character	Fragmentation is partial, parent ions are found in the spectra of daughter ions	Fragmentation is complete, no parent ions are found in the spectra of daughter ions
Fragments found in the spectra of daughter ions	Obtained by elimination of various functional groups: –OH, OH, =CH–CH_2–, C≡C– etc.	Obtained only by elimination of –CH_2– fragments

Thus, on the basis of the results obtained by HPLC-MS/MS it is possible to say that the absorbent sample taken from the installation for natural gas drying at the at the moment of non-conformity of the DPT of dried raw material to the standard requirements[1] contains polycyclic unsaturated compounds with functional groups –OH and –NH_2 in the structure.

Analysis of TEG samples by NMR

To confirm the results obtained by HPLC-MS/MS we recorded ^{1}H NMR spectra of compounds contained in the absorbent samples. For this purpose the found impurities were concentrated by means of solid-phase extraction and purified from triethylene glycol as follows. A cartridge was sequentially treated with 1 ml of dichloromethane and 1 ml of deionized water. Then 3 ml of a TEG sample was added, and the sorbent was washed with 3 ml of deionized water. The target fraction of the impurities was extracted with 2 ml of dichloromethane, and the extracts were collected in 2.5 ml vials. The collected aliquot was evaporated to dryness in a vacuum evaporator at 60 °C and 2000 rpm. The concentrated sample was dissolved in 0.6 ml of DMSO-d_6.

Conditions for carrying out ^{1}N NMR are presented in Table 3.

Table 3. Conditions for recording NMR spectra

Parameter	Value
Sample temperature	298 K
Scanning frequency	600 MHz
Signal accumulation time	5 min

Figure 5 presents ^{1}H NMR spectra of the analyzed samples of the absorbent.

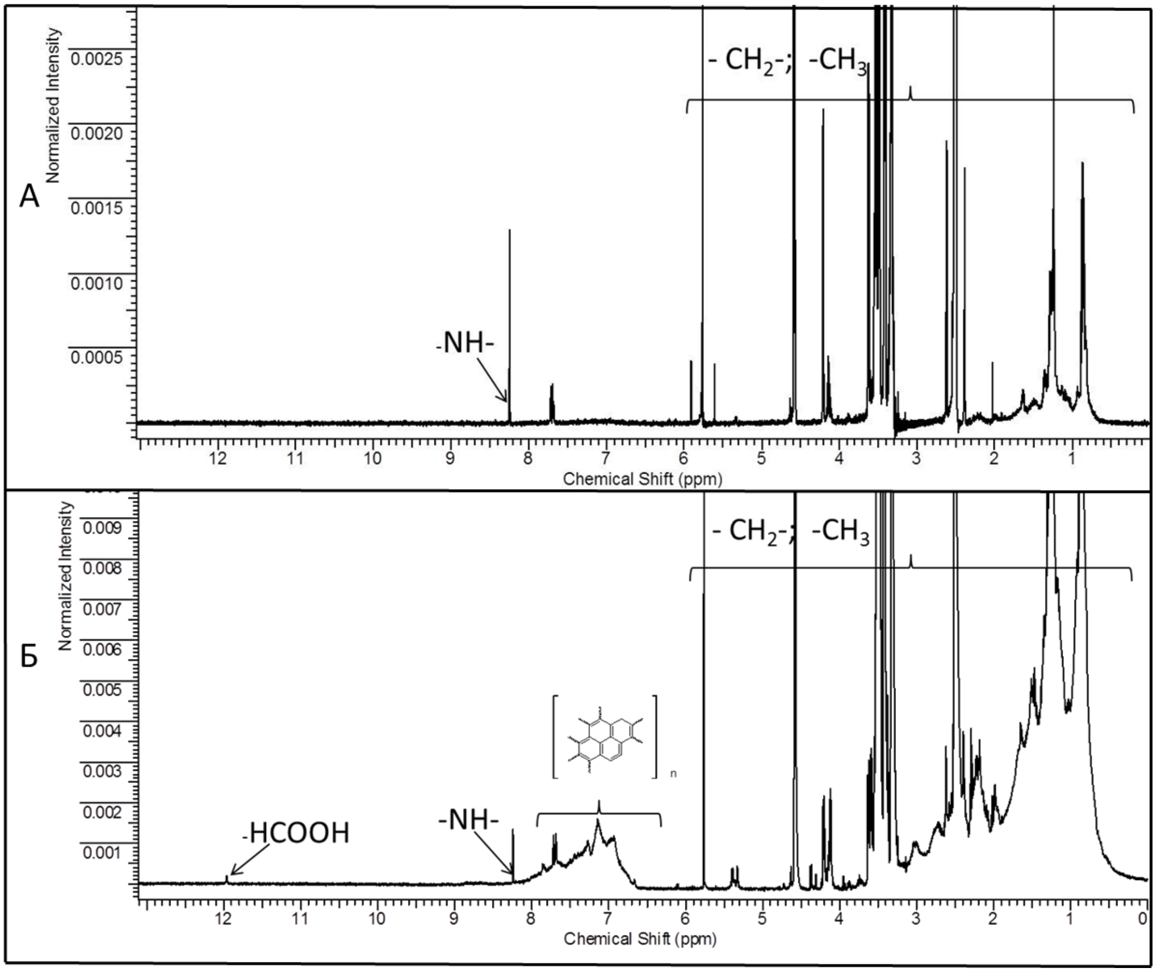

Figure 5. ^{1}H NMR spectra of impurities accumulated in working solutions of the absorbent:
A – triethylene glycol sample taken from the installation at a sufficient extent of the gas drying;
B – triethylene glycol sample taken from the installation at an insufficient extent of the gas drying.
[A means A; Б means B]

The broadened signals in the NMR spectra indicate a wide variety of compounds of similar structure, as well as the fact that dynamic processes between them may occur.

Conclusions

In this study samples of working solutions of absorbents providing and not providing the required degree of natural gas drying were obtained by high resolution HPLC-MS/MS and NMR. When processing the results, it was established that:

1) Each of the samples contains a comparable amount of aliphatic impurities having functional groups –OH, =CH–CH_2–, –C≡C– etc. in the structure.
2) The absorbent sample taken from the gas drying installation at an insufficient degree of raw materials drying contains, in addition to aliphatic compounds, a large amount of polycyclic unsaturated impurities having hydroxyl and amino groups in the structure, as well as trace amounts of organic compounds having carboxyl groups –COOH.

Because the results of two used methods are in agreement, it is safe to say that among impurities having negative impact on the absorbing capacity of triethylene glycol are, mainly, polycyclic unsaturated compounds containing hydroxyl and amino groups in the structure.

This conclusion is in agreement with the previous studies [10–12], which confirms the adequacy of the obtained results and indicates the expediency of using the described approach for monitoring the loss of triethylene glycol quality in installations for natural gas drying during production.

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