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CLEANING OF SATURATED ABSORBENTS USED IN NATURAL GAS CLEANING BY THREE-STAGE FILTRATION METHOD AND ANALYSIS OF THEIR PROPERTIES

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Abstract: The article presents the results of research on the purification of aqueous solutions of used-saturated ethanolamines from toxic compounds by a three-stage filtration method. In the study, the purification process of ethanolamines by three-stage filtration (sand, charcoal - bentonite and anionite (Tulsion (USA) A-23 and AV-17-8 of the Russian Federation strong base gel type anionites)) was studied, it was found to be the most effective method, and their properties were analyzed done.

Keywords: ethanolamine, natural gas, H_2S, SO_2, mercaptans, absorbent, monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA), resinous substances, anions, quartz sand, activated carbon, mechanical compounds, heat resistant salts.

Introduction. The annual volume of extraction of natural gas and its purification from various toxic compounds in Uzbekistan reached 60 billion m3. Natural gases of this volume contain 80-90% of sulfur compounds (H_2S, mercaptans (R-SH), COS, CS_2), and when using gases as raw materials in industry and sending

them to the public economy as commodity gas, it is necessary to purify them from such toxic compounds.

In the gas processing plants of our republic (Muborak GRF, Shortanneftgaz JSC, Shortan GCC JSC) the absorption method is widely used to purify natural gas from H2S, CO2, COS, CS2 and other sulfur compounds. Due to the presence of low-sulfur gases in Shortanneftgaz JSC, the adsorption method is also used in this enterprise. But in our republic, the most effective method of cleaning natural gases from toxic compounds is the absorption method, which uses 25-30% aqueous solutions of ethanolamines (monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA)) as an absorbent [1].

Today, 30% aqueous solution of MDEA is used in the gas purification process of Shortan GCC JSC, DEA and Mubarak GRF LLC. During the purification of natural gas from toxic compounds in these solutions, the absorption process takes place at high pressure and the desorption process takes place in these solutions at high temperature, and as a result of this process continuing continuously, it was observed that the absorption solution became saturated and became useless during the gas purification process. It was determined from the analysis that the temperature and pressure continuously change during the absorption gas cleaning process, the formation of various compounds (oxygen, metal oxides and hydroxides) in the solution causes the destruction and polymerization of ethanolamines, and the accumulation of resinous substances in the solution. In addition to resinous substances, the absorbent solution contains nitrogen, sulfur compounds, formic acid, glycolates, acetates, bisin, oxalate, nitrate, sulfate, chloride salts, iron sulfide from hard rocks, iron oxide and hydroxides, and other impurities.

Analyzing the samples of ethanolamine working solutions used in the absorption process and the main parameters of the technological mode, the ways of destabilizing the working mode of absorption devices in the purification of natural gas from H_2S, SO_2, COS, CS_2 and other harmful compounds, the reasons for the foaming of the ethanolamine solution under the influence of chemical compounds and its exit from the system were determined. in order to prevent or reduce them in the future, ways of improving the technological process of absorption-desorption purification of natural gas were chosen.

Based on the results of the conducted studies, it was determined that the most effective method of cleaning the used ethanolamines from harmful compounds is the combined method based on the ionization method.

Table 1 shows the composition analysis of the DEA solution used in the gas purification process of Shortan GCC JSC, MDEA used in "Mubarak GRF " LLC and MEAs used in Navoiyazot JSC.

Table 1. Composition of saturated solutions of MEA, DEA and MDEA used in gas purification.

T.r.	Composition of ethanolamine solutions	The amount of substances in the analyzed samples			
		Sample 1		Sample 2	
		DEA	MDEA	DEA	MDEA
1	Concentration of formic acid, g/l	0, 2 4	0, 27	0,32	0,34
2	SO_2, concentration g/l	11 , 16	11,24	19.65	19,72
3	Mass fraction of bound ethanolamine in the solution, %	3.44	3.23	6.26	5.86
4	Concentration of resinous substances, g/l	2,075	2,18	2,050	2.062
5	of SO_4^{2-} in solutions share , %	0.19	0,20	0.30	0.32
6	In solutions Mass fraction of Cl^-, %	0.028	0.032	0.032	0.0 36
7	The density of the solution, g/cm ^{3}	1,017	1,018	1,028	1.0 32
8	Hydrogen index, rN	10,25	10,4	10.00	10.03
9	NO_3 in solutions, mg/l	57	59	252	256
10	The total concentration of sulfur in the solution, mg /l	677.4	6 61 , 7	703.94	704,04
11	Mass fraction of MEA , MDEA and DEA in solutions, %	26.56	26, 77	23.74	24,14
12	Mass fraction of mechanical impurities in the solution, %	0.134	0.137	0,142	0,143

Based on the results of the conducted research, we decided to use the combined method, which is carried out in successive filtration processes, for the purification of ethanolamine solutions from harmful additives. For this, first of all, GOST 20301-74; GOST 20255.1-89; According to GOST 20255.2-89, gel-type anionites of strong base A-23 of Tulsion (USA) and AV-17-8 of the Russian Federation were prepared [2,3].

AG-3 type activated carbon is thoroughly washed with highly demineralized water and cleaned of mechanical impurities and other substances. River sand, AG-3 activated carbon and bentonite were washed, chemically and thermally treated and prepared.

It is required to clean the used-saturated ethanolamine solution from mechanical impurities, TBT, salts, DDM and other organic compounds. For this purpose, first of all, quartz river sand with a particle size of 0.34-1.0 mm prepared in advance is passed through 100 cm^3 of river sand at a temperature of 65-75^o C and a speed of 1.5-2.1 l/h.

After the first-stage filtering process, the composition of the ethanolamine solution, the amount of harmful compounds SO_2 and Cl^- almost did not change, the total concentration of tarry substances was DEA 1.83 g/l and MDEA 1.97 g/l, the mass fraction of mechanical impurities was DEA 0.007% and MDEA was found to be reduced to 0.005% (Table 2, stage I).

In the second stage of filtration, activated carbon of AG-3 type, washed with demineralized water, separated from the precipitated cloudy part by filtration, purified from the amorphous part, various mechanical impurities and washed and treated with 0.1 normal hydrochloric acid solution, Navbahor bentonite was used.

Table 2. The composition of the ethanolamine solution purified by the three-stage filtration method.

T.r	Composition of ethanolamine solutions	Initial sample composition		**Stage I** filtration with quartz river sand 1.5-2.1 l/h		**Stage II** AG-3 filtration with activated carbon and bentonite 1.5-2.1 l/h		**Stage III** A-23 (AV 17-8) filtration with ionites 1.5-2.1 l/h	
		DEA	MDEA	DEA	MDEA	DEA	MDEA	DEA	MDEA
1	Concentration of formic acid, g/l	0, 32	0, 34	0, 32	0, 34	0.04	0.05	0.032	0.041
2	SO_2 concentration g/l	19.65	19, 72	19.65	19, 72	5.08	6 , 17	4.97	5,86
3	Total mass fraction of nitrogen in solutions, %	2.79	2, 81	2.79	2, 81	2.44	2.52	2.44	2.52
4	Mass fraction of bound ethanolamine in the solution , %	6.26	5.86	5.89	5.63	1.05	1.06	0.7	0.6
5	Concentration of resinous substances, g/l	2,050	2.0 62	1.83	1.91	0, 28	0.26	0, 25	0.26
6	Mass fraction of SO_4^{2-} in solutions, %	0.30	0.3 2	0, 30	0.32	0, 28	0.29	0.008	0.008
7	In solutions Mass fraction of Cl^-,%	0.032	0.036	0.032	0.036	0.0 30	0.034	0.0 03	0.002
8	The density of the solution , g / cm ^{3}	1,028	1.032	1,013	1,014	1,013	1,014	1,013	1,014
9	Hydrogen ion activity indicator, rN	10.00	10.03	10.00	10.0 3	10, 3 5	10.03	10.95	10.03
10	NO_3^- in solutions, mg/l	252	256	233	214	224	201	25	21
11	The total concentration of sulfur in the solution , mg / l	703.94	704,04	689.41	691,39	19	21	8	8
12	Mass fraction of MEA , MDEA and DEA in solutions , %	23.74	24, 14	23.74	24,14	23.01	24,04	23,01	24,04
13	Mass fraction of mechanical compounds in the solution, %	0.142	0.143	0.007	0.005	0.006	0.005	0.006	0.005

The second filtration process was treated with ethanolamine solution filtered through a sand filter and purified. At the same time, the ethanolamine solution passed through the sand filter at a speed of 1.5-2.1 l/h at a temperature of 60-70 °C passes through the second-stage coal and bentonite layer and is cleaned of tarry substances, organic compounds and destruction products.

100 cm^3 of adsorbents prepared by pre-washing and thermal treatment were taken and placed in separate flasks. Saturated absorbent solution is successively passed through a layer of adsorbent filters at a rate of 1.5-2.1 l/h and is cleaned of harmful compounds (Table 2, stage II).

100cm^3 of adsorbents prepared by pre-washing and thermal treatment were taken and placed in separate flasks. Saturated absorbent solution is passed successively through a layer of adsorbent filters at a speed of 1.5-2.1 l/h and is cleaned of harmful compounds. In the first stage of the absorbent solution filtration process, the purified ethanolamine solution passes through a sand filter at a temperature of 65-75 ^oC, in the second stage through AG-3 activated carbon and bentonite at a temperature of 60-70 ^oC, 1.5-2.1 l/h at a temperature of 45-50 ^oC at speed A-23 (AV-17-8) is purified from TBT and other salts by passing through anionite (Table 2, stage III). After each filtering process, the purity level of the solution is checked (chromato-mass spectroscopy and elemental analysis) and analyzed [4,5].

When analyzing the initial component of the 30% solution of MDEA and DEA taken for the sample, the concentration of formic acid in the absorbent solution was from 0.24 g/l to 0.34 g/l, and the amount of SO_2 was from 11.18 g/l to 19.65 g /l, the total concentration of tarry substances is from 2.05 g/l to 2.45 g/l, the mass fraction of SO_4^{2-} in solutions is from 0.13% to 0.30%, the mass fraction of Cl^- is from 0.014% to 0.032 %, the concentration of NO_3^- was from 244 g/l to 252 g/l, the total sulfur concentration was from 615.93 mg/l to 703 mg/l.

To clean the obtained samples in a three-stage combined cycle, the anionic was washed and treated with a 5% sodium hydroxide solution, its sorption power was restored, washed with water, and the used ethanolamine solution was used for cleaning. The activated carbon is thoroughly cleaned, soaked in demineralized boiled water for 2 hours, processed, and transferred to the filtration process.

Purification of absorbent solutions in the combined ion exchange method, the solution was purified in the laboratory device in the following order (Fig. 1).

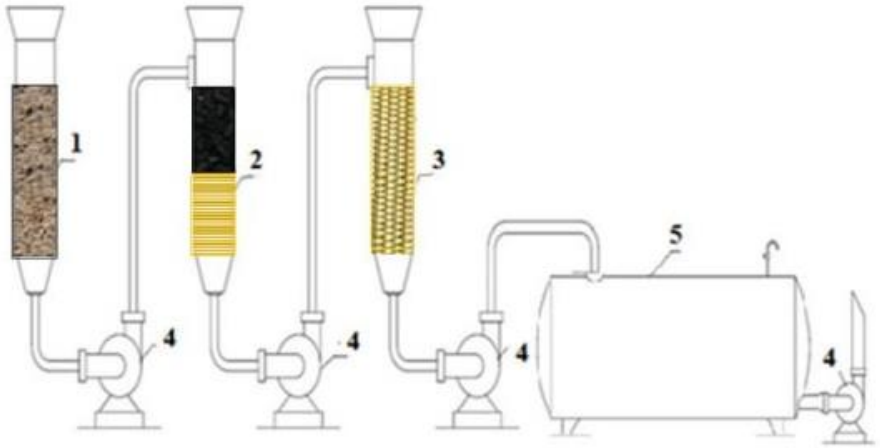

Figure 1. Purification of the used DEA solution by filtration.
1- Sand filter, 2- Activated carbon and bentonite filter of AG-3 type, 3- A-23 or AV-17-8 anionite filter, 4- pumps, 5- tank for storing purified technical DEA solution.

In the first filtration, pre-processed and prepared quartz with a particle size of 0.34-1.0 mm is passed through 100 cm^3 of river sand at a temperature of 65-75 ^oC and a speed of 1.5-2.1 l/h and cleaned with river sand. Then mechanical impurities in the ethanolamine solution decreased to 0.007% in DEA and 0.005% in MDEA. The amount of harmful compounds in the ethanolamine solution, the amount of SO_2, Cl^- and SO_4^{2-} almost did not change, the total concentration of resinous substances in the DEA content was 1.83 g/l and in the MDEA content up to 1.91 g/l, the concentration of NO_3^- in the DEA content was 233 mg/l and MDEA content up to 214 mg/l, total sulfur concentration was found to be partially reduced to 689.41 mg/l in DEA content and 691.39 mg/l in MDEA content. Purification of mechanical impurities in solution up to 59-63% was achieved.

In column 1, the absorbent solution purified from mechanical impurities was passed through column (2) where activated carbon of type AG-3 and Navbahor bentonite, separated from each other by filter paper, were placed in a previously prepared diethanolamine solution to remove tarry substances and organic compounds in the solution.

In the second stage of filtration, AG-3 type activated carbon and specially treated Navbahor bentonite were used. The ethanolamine solution was passed through a 100 cm^3 layer of coal and bentonite at a temperature of 60-70 ^oC at a rate of 1.5-2.1 l/h. During such filtration, it was found that formic acid, bound ethanolamine compounds, tarry compounds, sulfur compounds and other organic compounds were absorbed and were present in the solution.

If the carbon layer placed in the column (2) cleans the solution from organic compounds, heavy oxygen substances such as bitcins, bound ethanolamine compounds and tarry substances, the bentonite layer in the filter will partially absorb the salts along with the tarry substances contained in the solution. From the results of the analysis, we saw that when the DEA working solution was filtered in bentonite, bentonite absorbed well the polarized molecules contained in the absorbent working solution. This means that the cleaning of TBT dissolved in the solution using a bentonite layer is more effective than other methods [6,7].

A sample of technical DEA solution purified with a 30% solution of used-saturated DEA was analyzed by chromatography-mass spectroscopy.

The results of the chromatography-mass spectroscopic analysis in Figure 2 show that in the saturated absorbent solution, the products of thermal destruction of amines, organic compounds, TBT, inorganic salts and other amines polymerized by temperature and pressure are more than the norm. This indicates deterioration of the physico-chemical and working properties of the absorbent solution.

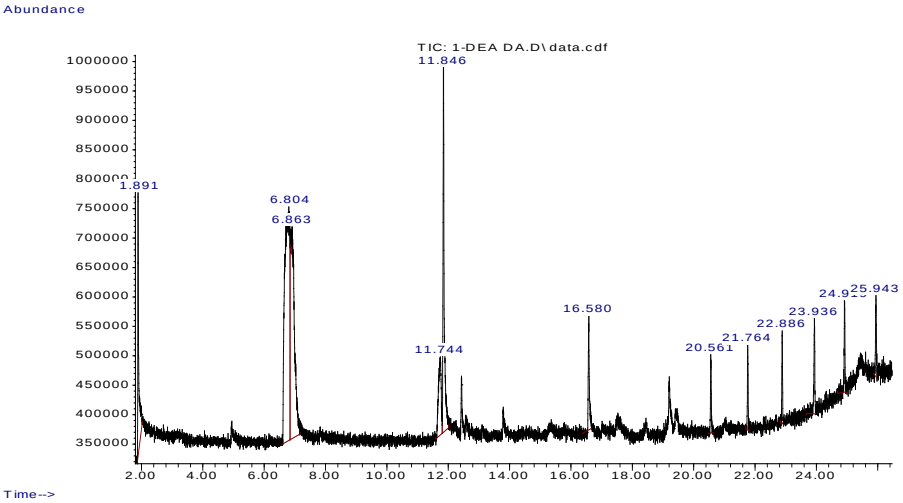

Figure 2. Spent-Saturated DEA Solution Chromatomass Spectroscopy Analysis.

After the three-step purification process, the second sample obtained from technical DEA was also analyzed by chromatography-mass spectroscopy.

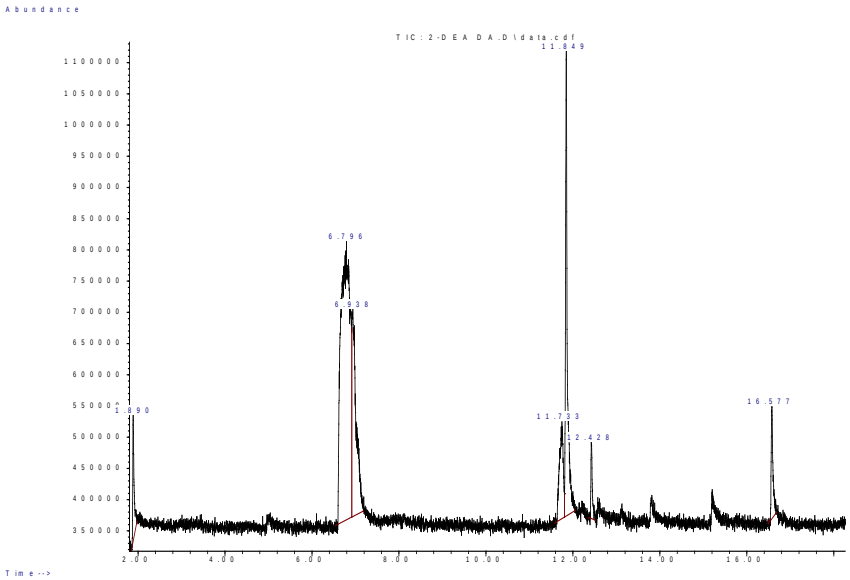

Figure 3. Chromatomass-spectroscopy analysis of working DEA solution purified by combined method.

The pure DEA obtained for the sample, used in the gas purification process and purified by the combined method was investigated by infrared (IR) and Raman-spectroscopy, and gas chromatographic methods[8].

It is known that the IR-spectroscopy method can provide complete information about functional groups in organic compounds. The IR analysis method was carried out on a Fure-IR-spectrometer device.

Theoretically, nonlinear compounds have 3N–6 vibrations, and most of these vibrations are observed by IR spectroscopy, and some by Raman spectroscopy. Therefore, the study of the studied compounds using IR and Raman spectroscopy methods gives a

positive result. In IR-spectroscopy methods, functional groups with a bond dipole moment different from zero give intense absorption, while in Raman spectroscopy, on the contrary, functional groups with a bond dipole moment close to zero give intense absorption. Raman spectra of the DEA sample were analyzed on the Renishaw InViaRaman spectrometer (laser wavelength 785 nm) at the Institute of Ion-Plasma and Laser Technologies of the Academy of Sciences of the Republic of Uzbekistan, and IR on the Carry-IQ-Fure spectrometer of the same institute.

For DEA, there are (3·21-6) 50 vibrations, most of which are observed in the IR spectrum. However, since the molecule is symmetrical (the presence of similar groups), the vibrations corresponding to the groups of substances in the studied solution give absorption peaks at one frequency. Symmetric valence vibrations of the methylene group in the molecule of the substance combine with peaks caused by asymmetric vibrations.

Comparing the IR spectrum (Figures 5, 7, 8) and the Raman spectrum of ethanolamines used in the purification of natural gas with pure DEA solution revealed the following (Figures 4, 6, 9): the main absorption lines of DEA in the Raman spectrum are 2950, We see that 2878, 2799, 1457, 1296, 1129, 1045, 943, 872, 752, 532, 468 and 343 cm $^{-1}$ are observed in the fields (Fig. 4).

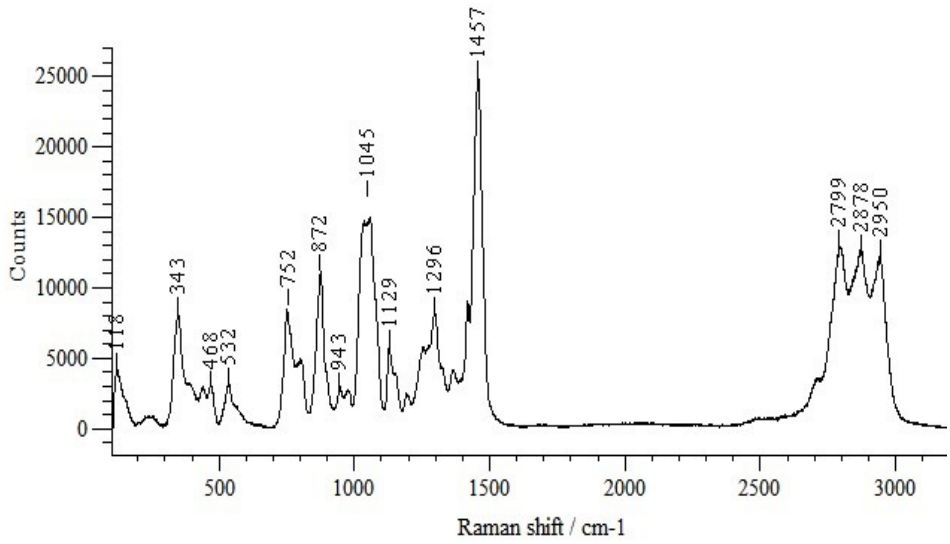

Figure 4. Pure DEA ramen spectrum.

DEA in the IR– spectrum main peaks of methylene groups valent and strain ts ion vibrations and OH, C –N and C –O vibrations, as a result, surface came are peaks. For example, high frequency intense peak in the field (3359 cm $^{-1)}$ OH of groups valent vibrations as a result surface came C –O and C –N absorption lines suitable 1034 and 1201 cm $^{-1,}$ respectively in the field it was determined to occur (figure 5).

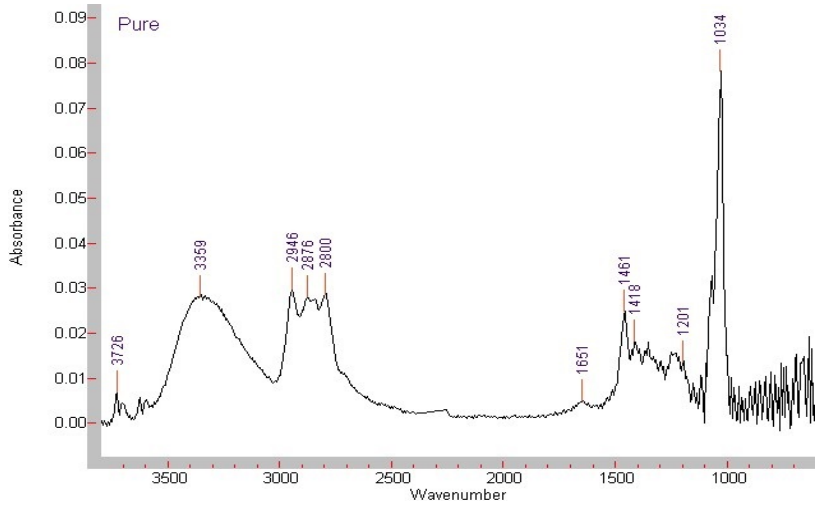

Figure 5. IR spectrum of pure DEA.

DEA is structural part quantitative in the analysis less presence of DEA in quantity shown. It is known that two DEA 's in a comfortable environment influence as a result, piper dine is formed will be

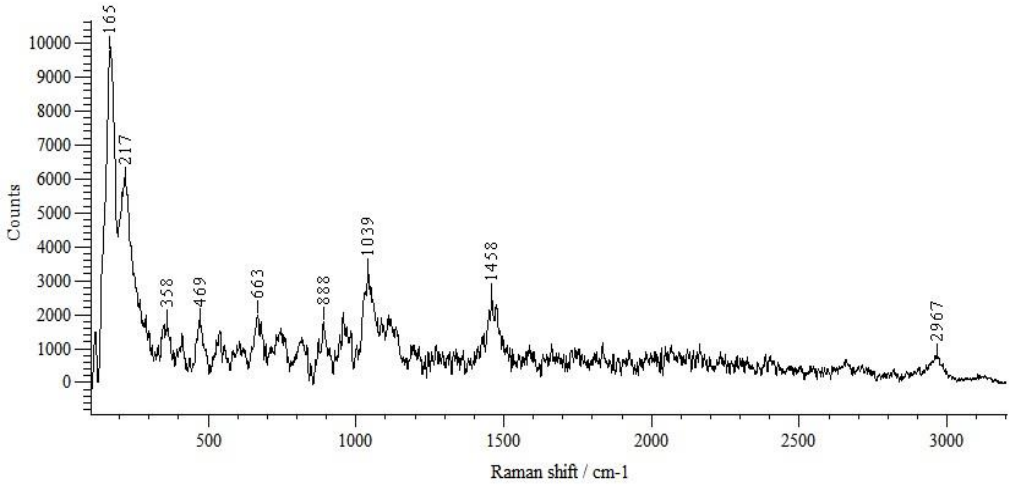

Figure 6. Unrefined DEA raman spectrum.

Not cleared of the DEA raman in the spectrum signal-to-noise ratio many high signals at 2967, 1458, and 1039 cm $^{-1}$ relative intensity clean to the sample relatively difference to do was determined. That is, not cleaned a peak at 1039 cm $^{-1}$ remained in the sample for two relatively intensive (Fig. 6).

Same as well as in the IR spectrum both ON and S–O groups vibrations as a result surface came lines intensity clean and not cleaned in samples from each other difference to do was determined (Figure 7).

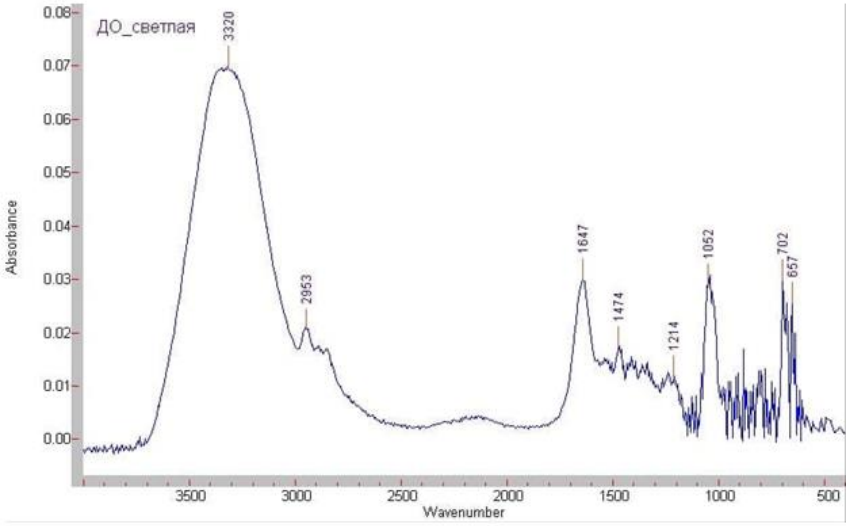

Figure 7. Not cleared DEA IR spectrum.

Also, when we compared the IR spectra of DEA that was not used for the sample, used in the gas purification process, and purified by the ionization method, it was seen that the intensity of ON, S–O absorption lines in the purified DEA spectrum coincided with the intensities of the same groups of lines in the clean sample (Fig. 8).

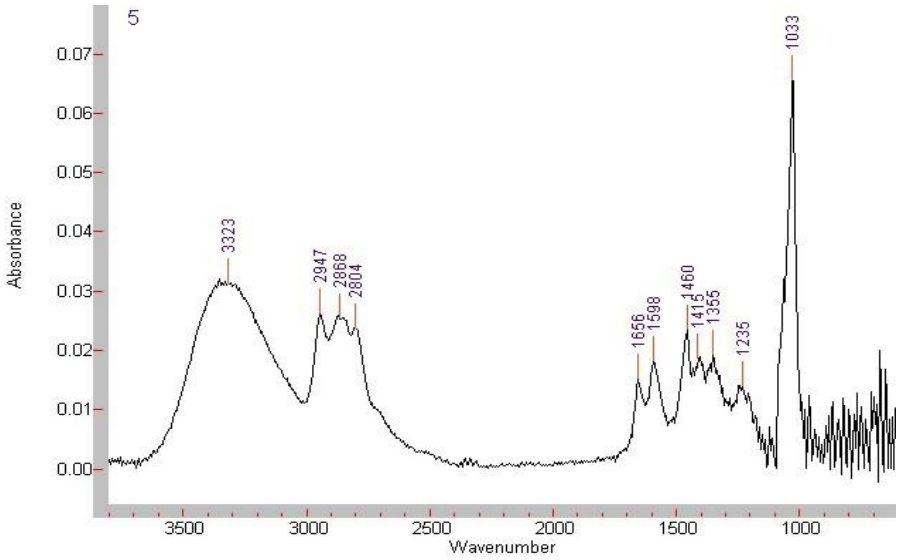

Figure 8. IR– spectrum of purified technical DEA sample.

Clean from the sample different, cleaned sample in the IR– spectrum addition lines (1656, 1598 cm $^{-1)}$ lines existence was determined.

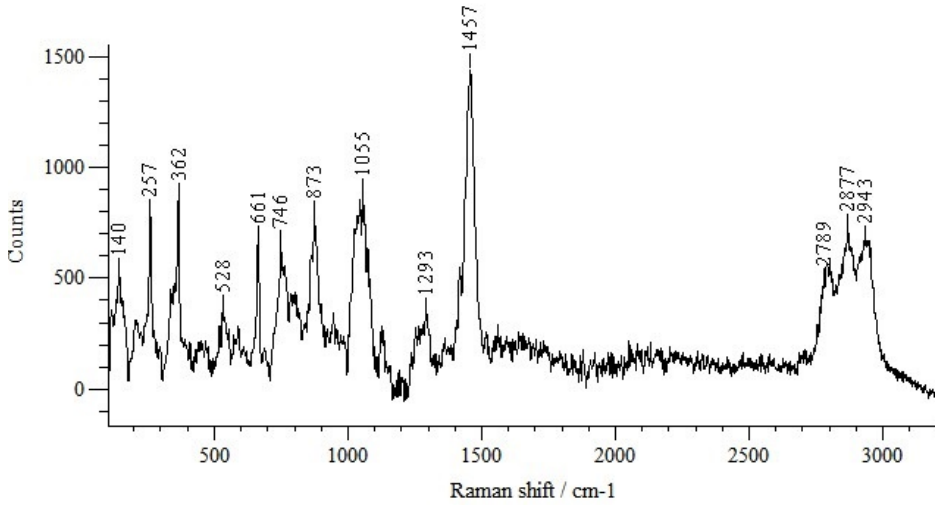

Figure 9. T previous technical DEA raman spectrum.

When we compared the Raman spectra of DEA obtained for three different samples, virgin DEA, used in the gas purification process, and DEA purified by vacuum extraction method, we saw that there are significant changes in the spectrum of purified DEA (Fig. 9). As a result of purification, the differences in the relative intensities of the peaks in the untreated sample and the observation of one peak in the region of 2800-3000 cm^{-1} disappeared[9].

Thus, it was found that the most effective method of cleaning the saturated ethanolamine solution from toxic compounds and using them again in the gas purification process is the three-stage filtration method. The used ethanolamine solution was passed through sand, bentonite, activated carbon, and anionite filters to clean it. The temperature and environment suitable for each filtration process were studied and analyzed, and the optimal conditions were selected. Using this method, 60-70% of the saturated ethanolamine solution was purified, technical ethanolamine was obtained, and it was possible to reuse natural gas for purification of toxic compounds.

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