

The content of acidic components in the technical gas and their impact on the environment

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Abstract. The analysis of the current trend of gas processing enterprises related to chemical industries is carried out in this article. The impact of technical gases emitted by oil and gas industry enterprises on the environment and population has been studied in detail. The content of hydrogen sulfide (H₂S), carbon disulfide (CS₂) and carbonyl sulfide (COS) components in technical gases has been analyzed. Studies have been carried out in order to determine the amount of hydrogen sulfide, carbon disulfide and carbonyl sulfide components in Gazli-TG gas sample (technical gas) from the Gazli gas processing plant, Ustyurt-TG gas sample (technical gas) from the Ustyurt gas chemical complex, Muborak-TG gas sample (technical gas) from Mubarek gas processing plant and Shurtan-TG (technical gas) from Shurtan gas-chemical complex LLC. It has been established that the content of acidic components in the sample of the Ustyurt-TG technical gas is greater than in the samples of the technical gas of other industrial enterprises.

1 Introduction

It is known that the technical gases released in all production enterprises belonging to the chemical industries in Uzbekistan have a negative impact on the environment. In order to determine the priorities of state policy in the field of environmental protection, prevent the violations of laws in the field of nature protection, introduce the effective mechanisms for their detection and prevention, strengthening the personal responsibility of state bodies, heads of economic entities and citizens for the sanitary and ecological condition of the republic settlements, as well as to ensure the achievement of national goals and objectives in the field of sustainable development in the period until 2030, the concept of environmental protection of the Republic of Uzbekistan until 2030 has been approved by the Decree of the President of the Republic of Uzbekistan No. PD-5863 dated October 30, 2019 [1].

At present, the available gas reserves of the Gazli region are 182 billion cubic meters. During 2017-2020, 8 new gas condensate deposits were opened as a result of geological exploration in this area (Tomaris, Southern Kulbeshkak, Andakli, Shorqum, Shortak, Eastern Khatar, Ortakum, Southern Oqqum). In 2020, natural gas production is expected to be 33.6 billion cubic meters, gas condensate 1 million 415 thousand tons, oil 204 thousand tons. For

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this, 121 new wells were drilled and put into operation, 600 wells were fully and modernly repaired, and 42 technological facilities were built. As it is known, JSC “Uzbekneftgaz” works on increasing the indicators of hydrocarbon production in the next year. In 2023, the volume of natural gas production is expected to be 33.9 billion cubic meters [2].

The trial process of production at the Ustyurt gas-chemical complex was started in 2015. In 2015, more than 54.9 thousand tons of liquefied hydrocarbon gas and more than 34 thousand tons of gas condensate were produced. More than 1.8 billion cubic meters of ethane and gas were supplied to the main gas pipelines, and more than 87.5 thousand megawatts of electricity were delivered to the energy system of the JSC “Uzbekenergo”. At the moment, the pyrolysis distillate is sent to the Bukhara oil refinery for the preparation of gasoline. Polyethylene and polypropylene are exported to a number of foreign countries. In 2016, more than 186,000 tons of polyethylene and polypropylene worth about 150 million dollars were shipped to Central and Eastern Asia, the CIS and European countries. According to data, the volume of polyethylene production increased 4.1 times in 2020 [3].

On August 28, 2020, at the Mubarak gas processing plant, the 4th branch of the Installation of propane-butane mixture extraction (IPBME), which allows the production of 38.400 tons of liquefied gas per year, was put into operation. Based on the words of Alisher Sultanov, the Minister of Energy of republic: “Today, we are commissioning a new facility, the construction of which began 3 years ago and has been continued rapidly despite the difficulties caused by the pandemic. Therefore, today's event is not only the opening of a new enterprise, but also an example of overcoming various obstacles on the way to achieving the set goal”. Moreover, “the launch of new industrial facilities in the oil and gas sector means new technologies aimed not only at high efficiency, but at the same time at energy saving and minimal impact on the environment”. The commissioning of the 4th branch of IPBME will help to increase the production of compressed natural gas at the Mubarak gas processing plant. These opportunities serve to satisfy the growing demand for this product by industrial enterprises and residential and communal enterprises of our republic. The new propane-butane mixture production facility will allow processing of 3 billion cubic meters of gas and more than 38.000 tons of liquefied gas per year. About 70 employees will be employed as a result of its launch. In addition, it can be said that the project on the construction of a new Installation of propane-butane mixture extraction at Mubarak gas processing plant was implemented in accordance with the decisions of the President of the Republic of Uzbekistan No. PD-2745 dated January 26, 2017 and No. 3874 dated July 19, 2018. The value is 58.25 million. financing of this projector equal to USD is carried out from the own funds of “Uzbekneftgaz” JSC, and payback period is 6 years (2021-2026) [4].

Among the enterprises in the JSC “Uzbekneftgaz” system, the Mubarak gas processing plant has a high rate of emissions into the atmosphere, and in order to eliminate this problem, it is planned to build a sulfur production unit to compensate for the out-of-service capacity at the plant.

“Shortan gas chemical complex” LLC, which is one of the largest production enterprises in Uzbekistan, also has a very negative impact on atmospheric pollution (Table 1).

Table 1. Composition of waste gases emitted into the atmosphere by "Shortan Gas-Chemical Complex" LLC in 1 year.

No.	The name of waste gases	Amount, ton per year
1	The amount of waste gases released in 1 year	2561.425
2	Nitrogen (IV) oxide (NO ₂)	448.229
3	Nitrogen (II) oxide (NO)	742.814
4	Carbon (IV) oxide (CO ₂)	1016.569
5	Hydrocarbons (CnHm)	73.870
6	Sulfur (IV) oxide (SO ₂)	2.930
7	Methane (CH ₄)	6.858

8	Soot	42.596
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The methods of cleaning, processing, recuperation and neutralization of waste gases are different, and they mainly depend on the type of acidicce emitting gases, its chemical composition, amount, concentration, temperature and similar parameters [5].

2 Research method

In order to determine the amount of hydrogen sulfide (H_2S), carbon disulfide (CS_2) and carbonyl sulfide (COS) components in technological gases, the chromatographic method has been used [6, 7].

The chromatographic method of gas analysis is based on the physical separation of mixed components on a sorbent. Due to different absorptivity, the movement speed of the gas mixture components in the carrier gas flow through the immobile sorbent bed is not the same. The greater the absorption capacity of a substance, the slower it moves through the chromatographic column and, therefore, the longer its retention time.

Under conditions of constant separation, the retention time is constant for each component. The carrier gas sequentially removes the individual components of the mixture from the column in a certain order. In the analysis of technical gases of carbon disulfide production, first, hydrogen sulfide and carbonyl sulfide are removed from the chromatographic column, and after a long time, carbon disulfide is also removed.

The device shown in Figure 1 has been assembled for analysis. Its basis is a chromatographic column 7, 1.5 m long, consisting of two sections of 0.75 m each, made of glass tubes with a diameter of 4.5 mm. The column filler is made of diatomite brick with a grain size of 0.5-1.0 mm, washed from dust and burned at 300 °C for 3 hours.

50 g of diatomaceous sand is poured into a Wurtz flask and filled with a solution containing 15 g of petroleum jelly in 50 ml of chloroform. The contents of the flask are stirred, after which the chloroform is distilled off on a water bath, and the charge is dried to constant weight at 110°C.

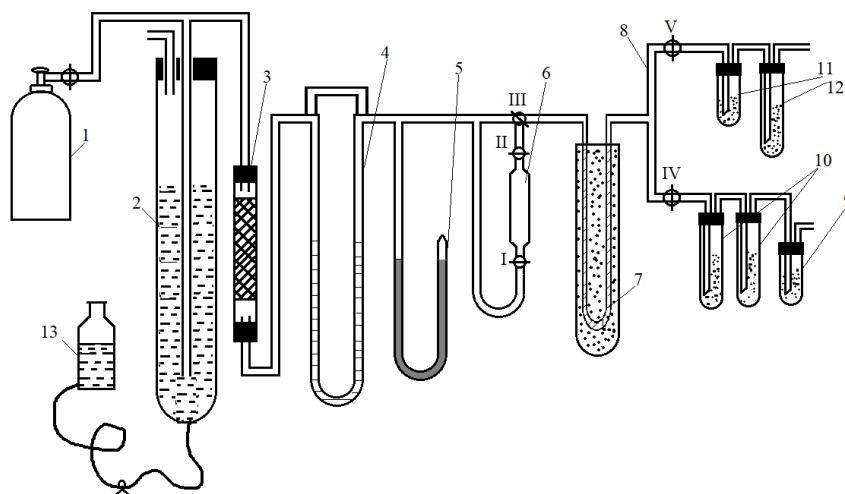


Fig. 1. Experimental device for chromatographic determination of hydrogen sulfide (H_2S), carbon disulfide (CS_2) and carbonyl sulfide (COS) components. 1- cylinder filled with nitrogen; 2- manostat; 3- drying column; 4- rheometer; 5- manometric tube; 6- a pipette with a gas sample; 7- chromatographic column; 8- bidirectional pipe; 9, 10- absorbers for hydrogen sulfide and carbonyl sulfide; 11, 12- absorbers for carbon disulfide; 13- distribution tank; I, II, III, IV, V- taps.

The flow of nitrogen from the cylinder is adjusted at a rate of 60 ml/min using a rheometer so that nitrogen bypasses gas pipette 6 by opening valves III and IV in the tube. After that, valves I and II are opened and the gas sample is sent to the chromatographic column with the three-way valve III. First, gas absorbers are directed through 10 (25% NaOH solution) and 9 (10% alcoholic solution of KOH), and after 6 minutes a stream of absorbers 11, 12 (alcohol alkali) is passed through the second network and is passed through them for 24 minutes. Then, according to the iodometric method described above, the composition of absorber 10 is analyzed for hydrogen sulfide, and the composition of absorbers 9 and 11 is analyzed for carbonyl sulfide and carbon disulfide, respectively. Other methods of chromatographic determination of sulfur-containing gases are also described in the literature [8, 9].

The amount of hydrogen sulfide x (vol.%) is calculated according to the following formula:

$$x = \frac{(25-a)(273+t) 760 \cdot 22414 \cdot 100}{2 \cdot 10000 \cdot 273 \cdot P \cdot V} = 312 \cdot \frac{(25-a)(273+t)}{PV} \quad (1)$$

The total amount of carbon disulfide and carbonyl sulfide (vol.%) is calculated according to the following formula:

$$y = \frac{b(273+t) 760 \cdot 22414 \cdot 2.5 \cdot 100}{10000 \cdot 273 \cdot P \cdot V} = 1550 \cdot \frac{b(273+t)}{PV} \quad (2)$$

where a is 0.1 n. $\text{Na}_2\text{S}_2\text{O}_3$ solution used for titration of excess iodine, ml; b is amount for titration of 0.1 n. iodine solution, ml; t is temperature during sampling, °C; P is atmospheric pressure, mm Hg.; V is the volume of the gas pipette, ml.

3 Research results and their discussion

Separate determination of carbon disulfide and carbonyl sulfide can be done by combining volumetric analysis with gravimetry. However, this method is more complicated and takes longer and does not always give reliable results.

Simple and accurate quantitative determination of hydrogen sulfide, carbon sulfide, and carbonyl sulfide in technical gases can be performed using a simplified chromatographic method developed by Belyaeva and Levit.

1) The amount of hydrogen sulfide in the TG gas sample (vol.%) is calculated as follows:

$$x_{(\text{H}_2\text{S})} = \frac{(25-a)(273+t) 760 \cdot 22414 \cdot 100}{2 \cdot 10000 \cdot 273 \cdot P \cdot V} = 312 \cdot \frac{(25-a)(273+t)}{PV} = 312 \cdot \frac{(25-3)(273+35)}{375.031 \cdot 1000} = 5.64\%;$$

The total amount of carbon disulfide and carbonyl sulfide in TG gas sample (vol.%):

$$y_{(\text{CS}_2+\text{COS})} = \frac{b(273+t) 760 \cdot 22414 \cdot 2.5 \cdot 100}{10000 \cdot 273 \cdot P \cdot V} = 1550 \cdot \frac{b(273+t)}{PV} = 1550 \cdot \frac{3(273+35)}{375.031 \cdot 1000} = 3.82\%;$$

2) The amount of hydrogen sulfide in Ustyurt-TG gas sample (vol.%) is calculated as follows:

$$x_{(\text{H}_2\text{S})} = \frac{(25-a)(273+t) 760 \cdot 22414 \cdot 100}{2 \cdot 10000 \cdot 273 \cdot P \cdot V} = 312 \cdot \frac{(25-a)(273+t)}{PV} = 312 \cdot \frac{(25-2)(273+40)}{375.031 \cdot 1000} = 5.99\%;$$

The total amount of carbon disulfide and carbonyl sulfide in the Ustyurt-TG gas sample (vol.%):

$$y_{(\text{CS}_2+\text{COS})} = \frac{b(273+t) 760 \cdot 22414 \cdot 2.5 \cdot 100}{10000 \cdot 273 \cdot P \cdot V} = 1550 \cdot \frac{b(273+t)}{PV} = 1550 \cdot \frac{5(273+40)}{375.031 \cdot 1000} = 6.47\%;$$

3) The amount of hydrogen sulfide in the Mubarak-TG gas sample (vol.%) is calculated as follows:

$$x_{(\text{H}_2\text{S})} = \frac{(25-a)(273+t) 760 \cdot 22414 \cdot 100}{2 \cdot 10000 \cdot 273 \cdot P \cdot V} = 312 \cdot \frac{(25-a)(273+t)}{PV} = 312 \cdot \frac{(25-4)(273+35)}{375.031 \cdot 1000} = 5.38\%;$$

The total amount of carbon disulfide and carbonyl sulfide in the Mubarak-TG gas sample (vol.%):

$$y_{(\text{CS}_2+\text{COS})} = \frac{b(273+t) 760 \cdot 22414 \cdot 2.5 \cdot 100}{10000 \cdot 273 \cdot P \cdot V} = 1550 \cdot \frac{b(273+t)}{PV} = 1550 \cdot \frac{4(273+30)}{375.031 \cdot 1000} = 5.01\%;$$

4) The amount of hydrogen sulfide in the Shortan-TG gas sample (vol.%) is calculated as follows:

$$x_{(H_2S)} = \frac{(25-a)(273+t) \cdot 760 \cdot 22414 \cdot 100}{2 \cdot 10000 \cdot 273 \cdot P \cdot V} = 312 \cdot \frac{(25-a)(273+t)}{PV} = 312 \cdot \frac{(25-5)(273+35)}{375.031 \cdot 1000} = 5.12\%;$$

The total amount of carbon disulfide and carbonyl sulfide in the Shortan-TG gas sample (vol.%):

$$y_{(CS_2+COS)} = \frac{b(273+t) \cdot 760 \cdot 22414 \cdot 2.5 \cdot 100}{10000 \cdot 273 \cdot P \cdot V} = 1550 \cdot \frac{b(273+t)}{PV} = 1550 \cdot \frac{3(273+35)}{375.031 \cdot 1000} = 3.82\%;$$

The total amount of hydrogen sulfide, carbon sulfide, and carbonyl sulfide in the technical gas, determined as a result of the calculations, is shown in Table 2.

Table 2. Content of acidic components in the technical gas.

Name of the sample	Amount of acidic components, %	
	H ₂ S	Total amount of CS ₂ and COS
Gazli-TG	5.64	3.82
Ustyurt-TG	5.99	6.47
Muborak-TG	5.38	5.01
Shortan-TG	5.12	3.82

It is shown in Table 2 that the amount of hydrogen sulfide in the Gazli-TG gas sample is 5.64 vol.% and the total amount of carbon disulfide and carbonyl sulfide is 3.82 vol.%, the amount of hydrogen sulfide in the Ustyurt-TG gas sample is 5.99 vol.% and the total amount of carbon disulfide and carbonyl sulfide is 6.47 vol.%, the amount of hydrogen sulfide in the Mubarak-TG gas sample is 5.38 vol.%, and the total amount of carbon disulfide and carbonyl sulfide is 5.01 vol.%, the amount of hydrogen sulfide in the Shortan-TG gas sample is 5.12 vol.% and the total amount of carbon disulfide and carbonyl sulfide is 3.82 vol.%.

Using the experimental device shown in Figure 1, research on the amount of hydrogen sulfide, carbon disulfide and carbonyl sulfide components in four different technological gas samples, i.e. Gazli-TG gas sample obtained from the Gasli gas processing plant, Ustyurt-TG gas sample obtained from the Ustyurt gas-chemical complex, Muborak-TG gas obtained from the Mubarak gas processing plant Shortan-TG gas samples obtained from “Shortan gas-chemical complex” LLC was carried out. Each gas sample was run for 36 hours in the experimental device. In fact, simple and accurate quantitative determination of hydrogen sulfide, carbon sulfide, and carbonyl sulfide in technical gases was carried out using a simplified chromatographic method developed by Belyayev and Levit, and the experimental results were included in Table 3.

Table 3. Content of acidic components in technical gas.

Name of the sample	Amount of acidic components, %		
	H ₂ S	CS ₂	COS
Gazli-TG	5.64	2.63	1.19
Ustyurt-TG	5.99	3.95	2.52
Muborak-TG	5.38	2.94	2.07
Shortan-TG	5.12	2.13	1.69

Table 3 shows that the amount of hydrogen sulfide in the Gazli-TG gas sample is 5.64 vol.% and the total amount of carbon disulfide and carbonyl sulfide is 3.82 vol.%, of which: 2.63% carbon disulfide and 1.19% carbonyl sulfide; the amount of hydrogen sulfide in the Ustyurt-TG gas sample is 5.99 vol.%, and the total amount of carbon disulfide and carbonyl sulfide is 6.47 vol.%, of which: 3.95% is carbon disulfide and 2.52% is carbonyl sulfide; the amount of hydrogen sulfide in the Mubarak-TG gas sample is 5.38 vol.%, and the total amount of carbon disulfide and carbonyl sulfide is 5.01 vol.%, of which: 2.94% is carbon disulfide and 2.07% is carbonyl sulfide; the amount of hydrogen sulfide in the Shortan-TG gas sample is 5.12 vol.%, and the total amount of carbon disulfide and carbonyl sulfide is 3.82 vol.%, of which: 2.13% is carbon disulfide and 1.69% is carbonyl sulfide; all the results were determined in the experimental device using chromatographic method [10].

4 Conclusions

When analyzing the amount of hydrogen sulfide (H_2S), carbon disulfide (CS_2) and carbonyl sulfide (COS) components in technical gas samples, i.e., Gazli-TG obtained from the gas processing plant, Ustyurt-TG obtained from the Ustyurt gas-chemical complex, Mubarak-TG obtained from the Mubarak gas processing plant, Shortan-TG obtained from the “Shortan gas-chemical complex” LLC, we can come to the following conclusion. Each sample was taken from a volume of 1000 ml and was held under a pressure of 0.5 MPa and a temperature in the range of 30-40 °C. Based on the indicators presented in Table 1, it was found that the content of acidic components in the Ustyurt-TG technical gas sample is more than the technical gas samples obtained from other industrial enterprises. Simple and accurate determination of hydrogen sulfide, carbon sulfide, and carbonyl sulfide in technical gases was carried out using a simplified chromatographic method developed by Belyaeva and Levit, and producing various products from acidic components in the future is advisable and promising.

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