USE OF A HIGH-RESOLUTION INFRARED FOURIER SPECTROMETER FOR DETECTION OF ULTRASMALL IMPURITIES IN LIQUIDS AND GASES

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An experimental setup created on the basis of an infrared Fourier spectrometer and intended for an analysis of ultrasmall impurities in liquids and gases is described. Results of experimental studies of the vapor of ultrapure ammonium and nonsymmetric dimethylhydrazine are reported. It is shown that the limiting mole concentration of the detected impurities amounts to about $(3–9)\cdot10^{-4}$% for different types of gases.

Introduction. An experimental specimen of an airborne infrared Fourier spectrometer (IRFS) of high resolution [1, 2] is intended for space monitoring of meteorological characteristics and small gas components in the atmosphere. However, the sphere of application of the device can be extended. It is capable of detecting foreign impurities in different liquids and gases by the absorption or transmission of radiation by these substances within the wavelength range 2–15 μm. The absorption lines for each molecule of a substance are individual, which makes it possible after measurement of the absorption or transmission in them not only to detect the presence or absence of impurities in the tested substance but also to determine the concentrations of these impurities. Unlike the infrared spectrometers of low resolution [3] in which the contour of the absorption band of a liquid substance is investigated, the infrared Fourier spectromerter can distinguish the absorption lines of a gaseous substance that correspond to vibrational-rotational transitions between different energy levels of a molecule.

In the present paper, we discuss the application of an infrared Fourier spectrometer to detection of foreign impurities in the vapor of technical liquids, for instance, of nonsymmetric dimethylhydrazine, and ultrasmall amounts of water admixtures in ammonia of special purity. Such is employed for charging of cooling loops and heat pipes (HPs); therefore, determination of the water contained in ammonia is of particular importance. The presence of water admixtures in ammonia promotes the corrosion of the structural material of heat pipes, while the presence of methane in nonsymmetric dimethylhydrazine can cause the so-called "carbonization" of steel. The only investigation devoted to determination of water in ammonia by the coulometric method seems to be [4]. Here, a study was made only of the samples of liquid ammonia; the minimum determined concentration of water in ammonia amounted to $1.6\cdot10^{-4}$%.

Other nonoptical methods of determination of small water admixtures in liquid ammonia, such as the chromatographic method and titration by the Fischer reagent, are also known. However, all these methods have certain drawbacks; among them, first of all, is the need for an analysis in specially equipped laboratories, elimination of contact of ammonia samples with air, and failure to produce express results. Unlike these methods, the use of the infrared Fourier spectrometer has allowed control and evaluation of the content of

microimpurities in real time; moreover, there are no restrictions on the use of the method only under laboratory conditions.

Calculational Relations. The dependence of the intensity of monochromatic radiation for the wave number ν on the optical thickness τ_ν when natural radiation of a gas can be neglected is described by the equation

$$J_{\text{tr}}(\nu) = J_{\text{inc}}(\nu) \exp(-\tau_\nu) . \tag{1}$$

From the measurement results we construct the dependence of n_ν (a quantity proportional to the logarithm of transmission) on the wavenumber ν:

$$n_\nu = 20 \log \frac{J_{\text{tr}}(\nu)}{J_{\text{inc}}(\nu)} . \tag{2}$$

From expressions (1) and (2) it follows that

$$\tau_\nu = \frac{-n_\nu}{8.686} . \tag{3}$$

On the other hand, the quantity τ_ν can be represented as

$$\tau_\nu = k_\nu l \rho c . \tag{4}$$

Here, the absorption coefficient k_ν for the Lorentz line contour is

$$k_\nu = \frac{S\gamma}{\pi \left[(\nu - \nu_0)^2 + \gamma^2\right]} . \tag{5}$$

The absorption coefficient at the center of the line k_0 is as follows:

$$k_0 = \frac{S}{\pi\gamma} . \tag{6}$$

Substituting (6) into (4), with account for (3) we arrive at the expression for the relative concentration of the tested gas:

$$c = \frac{-n_0 \pi \gamma}{8.686 S l \rho} . \tag{7}$$

Infrared Fourier Spectrometer. The infrared Fourier spectrometer includes an interferometer of the "double pendulum" type and a radiometer having two channels — a shortwave channel (SWC) and a longwave channel (LWC). The optical scheme of the device is shown in Fig. 1.

The radiation investigated passes through inlet window 1 and arrives at light divider 2 with compensator 3, where it is split into two fluxes running to corner reflectors (trihedra) 4. After the secondary passage through the light-dividing unit these fluxes interfere and arrive at dichroic plate 14. The longwave radiation passes through it to objective 5 which focuses the radiation onto detector 6, while the shortwave radiation is reflected from plate 14 and via mirror 15 it arrives at objective 12 and then at detector 13. The objectives 5 and 12 represent high-transmission short-focus lenses. The reference channel of the infrared Fourier spectrometer serves for forming pulses by which interferograms are digitized. It consists of helium-neon laser 7
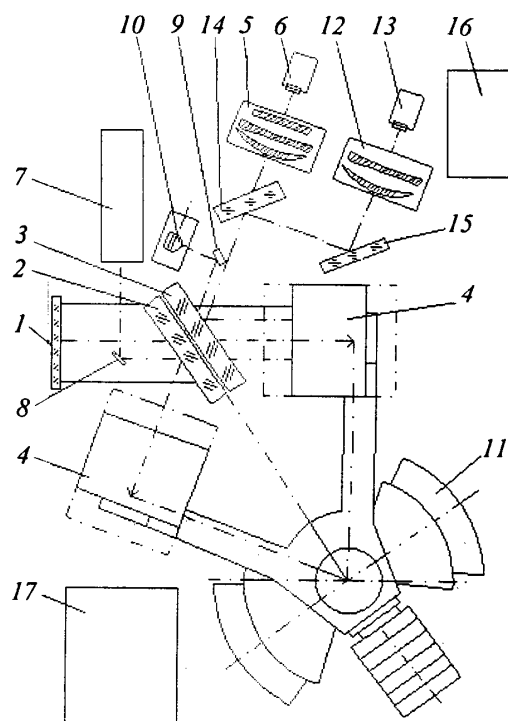
Fig. 1. Optical scheme of the infrared Fourier spectrometer.

as a light source with $\lambda = 0.63$ μm and a beam power of 10 mV, two mirrors 8 and 9, and a receiver of the reference channel 10. The corner reflectors 4 are displaced by linear electromagnetic drive 11 to both sides from the zero optical-path difference. For the infrared Fourier spectrometer operating in a high-resolution mode this displacement is 1.6 cm, and they traverse the entire 3.2-cm path in 4 sec. This is accompanied by recording of an interferogram, which is then used to construct a spectrum on the basis of fast Fourier trans-formation. The nominal frequency of a reference signal recorded by the receiver of the reference channel on displacement of the corner reflectors is 51 kHz. This signal is used in the algorithm of control of the dis-placement of the corner reflectors. The infrared Fourier spectrometer also has preamplifiers of analog signals (interferograms) 16 and analog-to-digital converters 17.

Experimental Setup. A schematic of the experimental setup used for detection of microimpurities is presented in Fig. 2. The radiation from light source LS (a halogen tube with a power of $W = 55$ W) passes through cuvette C filled with the investigated medium and arrives at the infrared Fourier spectrometer. Cu-vette C represents an airtight dismountable stainless-steel cylinder with CaF_2 glasses G1 and G2 installed at the cuvette ends onto ammonia-resistant rubber spacers. Radiation source LS installed in a special casing was connected to the cuvette via diaphragm D. The other end of the cuvette was fastened to the body of the infrared Fourier spectrometer via sylphon bellows.

In determining the microconcentrations of water, it is necessary to weaken as much as possible the influence of the atmospheric moisture on the optical path of the device from light source LS to detector 13 positioned in the body of the infrared Fourier spectrometer. For these purposes, the cuvette was evacuated to a pressure of $P \approx 100$ Pa. The body of the infrared Fourier spectrometer and the casing of LS were not air-tight initially. To remove the atmospheric air in them, the gaseous nitrogen from container Co2 was supplied via reducer R and valve VN4. The nitrogen flow rate was controlled by flow meter FM with a hole area of 0.02 cm^2. The nitrogen flow rate was approximately 1 g/sec. Since the residues of the water vapor were in the cuvette and in the source casing and the detector body, the process of scavenging continued until a con-stant spectrum was obtained. Then the spectrum was recorded and stored as the reference one.
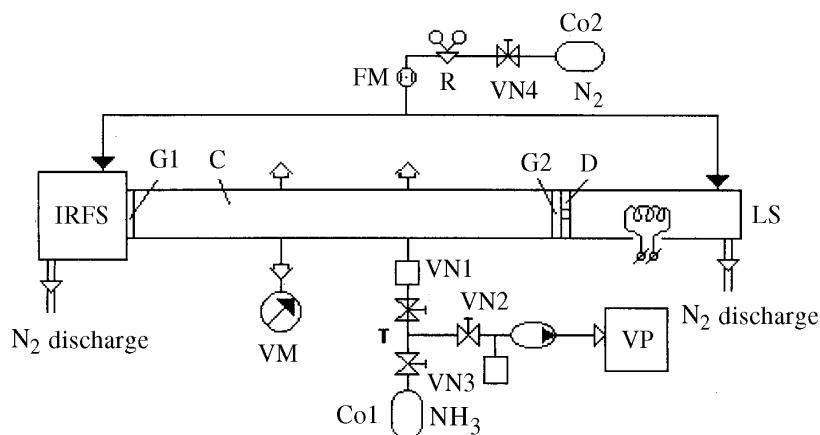
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Fig. 2. Schematic of the experimental setup: IRFS, infrared Fourier spectrometer; C, cuvette; LS, light source; VP, vacuum pump; N_2, nitrogen; NH_3, ammonia; Co1, ammonia container; Co2, nitrogen container; VN1, VN2, VN3, and VN4, valves; G1 and G2, calcium-fluoride glasses; FM, flow meter; VM, vacuum manometer; D, diaphragm; R, reducer; T, tee-joint.

Admission of ammonia was accomplished as follows (see Fig. 2). Ammonia container Co1 was connected via valve VN3 to tee-joint T which, in turn, was connected via valves VN1 and VN2 to the cuvette and vacuum pump VP, respectively. The cuvette and the tee-joint were precleaned in a special way. The cuvette with the tee-joint was evacuated with VN3 shut and with VN1 and VN2 open. The volume of the tee-joint was calculated so that the ammonia filling it was totally evaporated in the cuvette and the cuvette pressure was approximately 100 kPa. The condition of complete evaporation is important for the water contained in ammonia to be able to completely evaporate, too. In this case, the concentration of the water in the ammonia vapor and in the liquid ammonia was the same. Then valves VN1 and VN2 were opened and the tee-joint was filled with the liquid ammonia via valve VN3. After filling the tee-joint and with VN3 and VN2 shut, the liquid ammonia together with impurities evaporated into the cuvette via the opened valve VN1. The pressure in the cuvette was controlled by manometer VM. From the change in the intensity of spectrum lines we can make a judgment about the impurities in ammonia and evaluate them quantitatively.

Measurement Results and Their Analysis. To confirm the correctness of the procedure developed, we measured water impurities on filling the cuvette with nitrogen, methane, and ammonia up to atmospheric pressure. In so doing, we evacuated the cuvette and removed the water impurities following the above procedure. The obtained dependence of n_ν on the wave number ν (transmission spectrum) within the range 1900–6000 cm^{-1} is presented in Fig. 3a. From the plot it is seen that the sensitivity region of a PbSe detector is 2000–5600 cm^{-1}. It should be noted that we failed to eliminate completely the water impurities on the optical path of the device. They are present in the evacuated cuvette, in nitrogen used for scavenging, and in the body of the infrared Fourier spectrometer and the casing of the source. However, this residual amount remains constant during the entire experiment and is assumed to be the reference one. The transmission spectrum also displays the absorption band of a thin oil film formed on the surfaces of optical units in operation of the device.

In determining the concentration of the water in ammonia according to the above procedure, the cuvette was filled with ammonia to a pressure of $P \approx 100$ kPa. The transmission spectrum obtained in this case in the region 1900–6000 cm^{-1} is presented in Fig. 3b. As is seen from the plot, radiation is actively absorbed by ammonia in three regions of the transmission spectrum (3100–3600 cm^{-1}, 4300–4600 cm^{-1}, and 4950–5150 cm^{-1}).
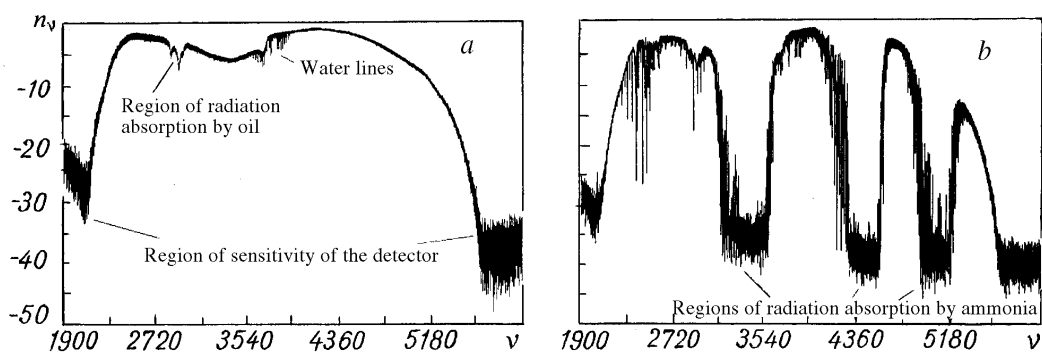
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Fig. 3. Dependence of n_ν on the wavenumber ν: a) for the evacuated cuvette; b) for the cuvette filled with ammonia. n_ν, dB; ν, cm^{-1}.
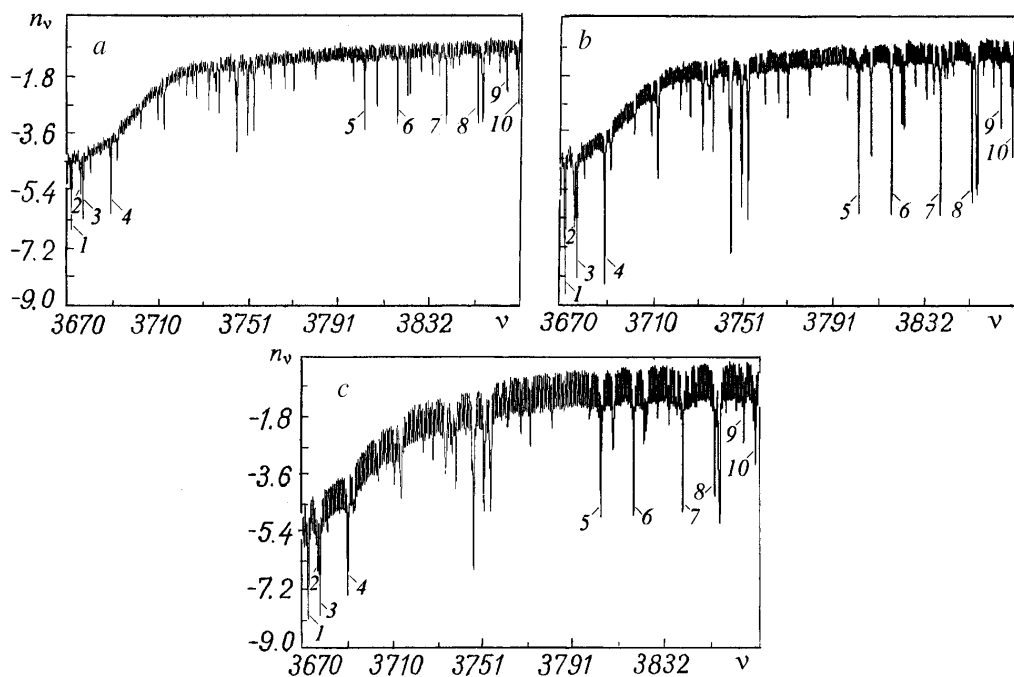

Fig. 4. Dependence of n_ν on the wave number ν in the water-absorption lines within the range 3670–3872 cm^{-1}: a) for the evacuated cuvette; b) for the cuvette filled with nitrogen; c) for the cuvette filled with ammonia.

Consequently, it is necessary to choose such a region of the transmission spectrum where the absorption by ammonia does not occur and the water lines have the highest intensity S. Such conditions are satisfied by the 3670–3872-cm^{-1}-region of the spectrum. In this region, from the plot of the reference transmission spectrum we chose ten individual water lines denoted as 1 through 10 (Fig. 4a). Their main theoretical parameters, such as the intensity S and width $2\gamma_{th}$, are given in Table 1.

The reference quantity n_{ref} and the linewidth $2\gamma_{ref}$ measured from the plot (see Fig. 4a) are presented in Table 1. Figure 4b shows the spectral region investigated on filling the cuvette with nitrogen, while Fig. 4c shows this region on filling the cuvette with ammonia. The occurrence of the sinusoidal component with a period of 0.9 cm^{-1} in the transmission spectrum is explained by the interference on glasses G1 and G2, whose thickness is 0.4 cm. From Fig. 4b and c it is seen that on filling the cuvette with both nitrogen and ammonia, the quantities Δn_{nit} and Δn_{am} as well as $2\gamma_{nit}$ and $2\gamma_{am}$ (see Table 1) undergo changes for each line relative to the reference transmission spectrum (Fig. 4a), which is related to the presence of water in nitrogen and ammonia.

TABLE 1. Parameters of the H_2O Lines in the Spectral Range 3670–3872 cm^{-1}

No. of water line	ν, cm^{-1}	Theoretical parameters [5]		Reference spectrum of the cuvette		Nitrogen cuvette		Ammonia cuvette	
		S, cm^{-1}/(mole·cm^{-2})	$2\gamma_{th}$, cm^{-1}	$-n_{ref}$, dB	$2\gamma_{ref}$, cm^{-1}	$-\Delta n_{nit}$, dB	$2\gamma_{nit}$, cm^{-1}	$-\Delta n_{am}$, dB	$2\gamma_{am}$, cm^{-1}
1	3670.75	$1.79 \cdot 10^{-19}$	0.19	2.32	0.27	1.95	0.34	0.9	0.44
2	3674.959	$8.66 \cdot 10^{-20}$	0.18	1.19	0.27	0.94	0.35	0.5	0.46
3	3676.02	$1.67 \cdot 10^{-19}$	0.2	2.08	0.3	1.71	0.36	1.08	0.42
4	3688.453	$2.12 \cdot 10^{-19}$	0.2	2.39	0.3	2.15	0.35	0.91	0.5
5	3801.42	$2.15 \cdot 10^{-19}$	0.21	2.39	0.3	2.46	0.36	1.4	0.44
6	3816.093	$2.16 \cdot 10^{-19}$	0.2	2.29	0.29	2.67	0.34	1.63	0.42
7	3837.87	$2.29 \cdot 10^{-19}$	0.19	2.32	0.3	2.71	0.35	1.54	0.46
8	3852.058	$1.8 \cdot 10^{-19}$	0.17	2.29	0.28	2.38	0.33	1.1	0.44
9	3865.112	$8.95 \cdot 10^{-20}$	0.18	1.41	0.27	1.08	0.33	0.6	0.39
10	3870.13	$1.32 \cdot 10^{-19}$	0.16	1.79	0.27	1.52	0.32	0.73	0.41

TABLE 2. Mole Concentration of H_2O in Nitrogen and Ammonia

No. of water line	ν, cm^{-1}	Mole concentration of water, %·10^2	
		in nitrogen	in ammonia
1	3670.75	1.663	1.002
2	3674.959	1.705	1.192
3	3676.02	1.655	1.219
4	3688.453	1.593	0.963
5	3801.42	1.849	1.286
6	3816.093	1.886	1.423
7	3837.87	1.859	1.388
8	3852.058	1.958	1.207
9	3865.112	1.787	1.174
10	3870.13	1.654	1.018

The measured linewidth of the water in nitrogen $2\gamma_{nit}$ is 0.32–0.36 cm^{-1}, while the natural Lorentz linewidth of water at atmospheric pressure is approximately 0.2 cm^{-1}. This discrepancy is related to the real spectral resolution of the device ($d\nu \approx 0.15$ cm^{-1}) determined by the maximum optical-path difference, the extension of the light source, and the apodization function (the Blackman–Harris function used in processing the interferograms [6]). On filling the cuvette with ammonia, the linewidth of the water $2\gamma_{am}$ was 0.39–0.5 cm^{-1}, which is related to the elevated (as compared to nitrogen) broadening capability of ammonia.

The concentration of water in the investigated gases is determined by formula (7). For this purpose, use is made of the following parameters from Table 1: line intensity S, quantity Δn, and width 2γ. On their basis one can evaluate the minimum absorption of radiation by water for the present experimental setup. In recording $\Delta n = 0.1$ dB, this quantity is evaluated at $7 \cdot 10^{-4}$% for determination of the mole concentration of the water in nitrogen and at $9 \cdot 10^{-4}$% in ammonia. It is necessary to note that to decrease this quantity, it is necessary to increase the optical path. This can be attained either by increasing the length of cuvette C or by implementing several passes of a light beam in cuvette C by means of the optical system.

The calculated mole concentrations of the water in nitrogen and ammonia for each considered line are presented in Table 2. Here, the arithmetical mean is chosen from the values determined for each line. It amounted to $1.761 \cdot 10^{-2}$% for nitrogen and $1.187 \cdot 10^{-2}$% for ammonia.

TABLE 3. Parameters of the H_2O Calibration Lines

| No. of water line	ν, cm^{-1}	Theoretical parameters [5]		Line parameters in calibration		Mole concentration of water in air, %
		S, cm^{-1}/(mole·cm^{-2})	$2\gamma_{th}$, cm^{-1}	$2\gamma_{cal}$, cm^{-1}	Δn_{cal}, dB	
11	3560.133	$7.72 \cdot 10^{-21}$	0.15	0.3	0.0382	0.999
12	3906.065	$1.59 \cdot 10^{-20}$	0.16	0.32	0.0773	1.047
13	3916.329	$7.89 \cdot 10^{-21}$	0.13	0.32	0.0369	1.008
14	3929.361	$7.59 \cdot 10^{-21}$	0.19	0.35	0.0376	1.167
15	3930.566	$5.42 \cdot 10^{-21}$	0.16	0.29	0.0306	1.102
16	3948.177	$4.75 \cdot 10^{-21}$	0.1	0.26	0.0317	1.168
17	3949.984	$1.12 \cdot 10^{-20}$	0.18	0.34	0.0527	1.077
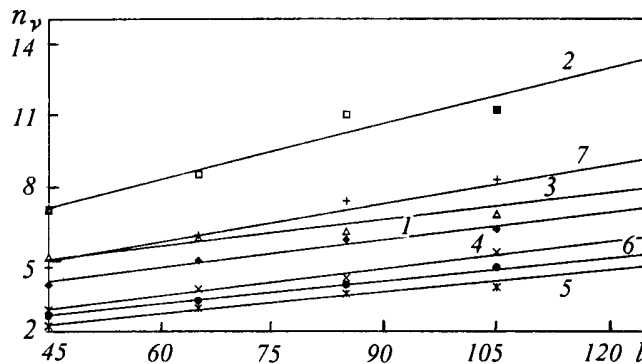
Fig. 5. Calibration dependences for the water lines in air: (1) line 11; (2) 12; (3) 13; (4) 14; (5) 15; (6) 16; (7) 17. l, cm.

Unfortunately, we were unable to measure independently the mole concentration of the water for ammonia and nitrogen by another method. Therefore, to confirm the correctness of the results obtained by the method considered above, we measured the water content in air and compared it to the independent measurement of the moisture content by a "Briz" thermohydrometer. During the experiment, the temperature indoors changed within the limits 20–20.5°, while the relative humidity changed within 48.6–47.6%. Thus, in this case the mole concentration of the water amounted to 1.121–1.127%. In the transmission spectrum, we chose several individual lines of water with an intensity lower than in the lines 1 through 10 considered in Table 1. The theoretical parameters of these lines, i.e., intensity S and width $2\gamma_{th}$, are given in Table 3. Based on such data from Table 3 as the change in n_ν with change in the optical path Δn_{cal} by 1 cm, the linewidth of the water in the air $2\gamma_{cal}$, and the line intensity S, we determined the mole concentration of water indoors by formula (7) (see the last column in Table 3).

Calibration was performed by changing the optical path length l from light source LS to the inlet window of the infrared Fourier spectrometer. The plots of the calibration dependences for lines 11 through 17 (see Table 3) are given in Fig. 5. The average mole concentration of the water determined from these lines amounted to 1.081%.

In performing calibrations on detection of ultrasmall impurities of methane and other gases not constituting the composition of the atmosphere, it is not necessary to scavenge the casing of the light source and the body of the infrared Fourier spectrometer with nitrogen. The samples of methane were injected into the cuvette filled with air to atmospheric pressure. From the experimental results it has been established that the limiting determined mole concentration of methane in air amounts to $3 \cdot 10^{-4}$%. This is explained by the more intense methane lines, as compared to those of water, within the range of wave numbers from 2950 to 3100 cm^{-1}. Similar measurements were carried out for nonsymmetric dimethylhydrazine. The cuvette representing

an airtight steel vessel with a diameter of 8 cm, at the ends of which two 5-cm-diam. quartz glasses were placed at a distance of 1 cm, was filled with liquid nonsymmetric dimethylhydrazine to approximately 1/10 of the volume. The pressure of the nonsymmetric dimethylhydrazine was equal to the saturation pressure. Proceeding from the measurement results, we draw the conclusion that the vapor of nonsymmetric dimethyl-hydrazine contained approximately 7% (by volume) of methane. The developed procedure can also be applied to other liquids and gases.

     Conclusions. As a result of the investigation carried out, we have created an experimental setup on the basis of a Fourier spectrometer. A procedure of detection of microimpurities in the composition of various liquids and gases is developed. It is shown that the minimum detected mole concentration of the water in nitrogen amounts to $7 \cdot 10^{-4}$% and in ammonia it is evaluated at $9 \cdot 10^{-4}$%, while the minimum determined mole concentration of methane in the atmosphere is evaluated at $3 \cdot 10^{-4}$%. This facility makes it possible to obtain in real time results of measuring the concentrations of impurities in various liquids and gases and to track expeditiously the dynamics of change of the impurities.

NOTATION

     $J_{tr}(\nu)$, intensity of the radiation transmitted by the investigated medium; $J_{inc}(\nu)$, intensity of the incident radiation; l, optical path length; ρ, concentration of molecules in unit volume at the given pressure and temperature; S, line intensity; γ, Lorentz line halfwidth; ν_0, wave number at the center of the line; n_0, quantity proportional to τ_ν at the center of the line; λ, wavelength; P, pressure in the cuvette; W, power of the halogen tube; Δn, change in the n_ν value; IR, infrared; H_2O, water; Subscripts: tr, radiation transmitted by the investigated medium; inc, incident radiation; ν, quantity dependent on the wave number; 0, center of the line; th, theoretical parameters of the lines; ref, parameters of the lines in the reference spectrum of transmission; nit, parameters of the lines in the transmission spectrum for the cuvette filled with nitrogen; am, parameters of the transmission lines for the cuvette filled with ammonia; cal, parameters of the water lines in the transmission spectrum in calibration.

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