MEASUREMENTS OF LOW PH₃ CONCENTRATIONS IN GeH₄ WITH THE AID OF A SPECTROMETER EQUIPPED WITH TUNABLE DIODE LASERS

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In order to determine concentrations of impurities such as phosphine (PH₃), arsine (AsH₃), and diborane (B₂H₆) in high-purity gaseous hydrides of germanium (GeH₄) and silicon (SiH₄), gas analyzers with a sensitivity limit of 10⁻⁷ mole % are required [1]. The direct absorption technique used in the infrared part of the spectrum appears promising for such analyses because in this range the impurities listed above have their main absorption bands; the integral intensities $S$ of individual lines reach 1-5 cm⁻²·atm⁻¹. However, since the spectra of the impurities and basic components of the mixtures to be analyzed comprise a large oscillatory-rotatory structure and since the absorption bands overlap, the analyses must be performed at reduced pressure and instruments with a spectral resolution $\leq 10^{-5}$ cm⁻¹ must be employed.

The authors of [2, 3] have shown that when tunable diode lasers on the basis of lead–tin chalcogenides are used as sources of infrared radiation, molecular impurities (SO₂, O₃, NH₃, NO₂, etc.) can be recorded in samples of atmospheric air with a sensitivity of 10⁻⁹ cm⁻¹ with respect to the absorption coefficient; this sensitivity is equivalent to 10⁻⁷-10⁻⁹ mole %. In order to obtain this sensitivity, the authors of [2, 3] have used lasers operated in the CW mode, synchronous signal detection, and multipassage cuvettes with an effective length $L$ of up to 100 m.

It has been shown in [4] that high sensitivity and selectivity can be achieved in pulsed operation of tunable diode lasers. When multipassage cuvettes with $L = 40$ m are employed, the detection limit obtained in [4] was 10⁻⁷ cm⁻¹ on the 3σ level.

We consider in the present work the example of determining the PH₃ concentration in GeH₄ and show that it is possible to record absorption lines with a sensitivity of 10⁻⁷ cm⁻¹ at an optical layer thickness of 1 m. The sensitivity was increased by increasing the emission power of tunable dye lasers, by improving the characteristics of the recording system, and by employing electric filters for suppressing low- and high-frequency signal fluctuations.

Experimental Setup. A tunable PbSnSe diode laser mounted in the cooling junction of a helium cryostat served as the emission source. The laser was pumped with rectangular current pulses. The required range and single-mode generation were established by proper selection of the temperature of the cooling junction and of the parameters of the pumping current [5].

The laser radiation was collimated with a KBr lens to form a parallel beam which was split into two beams with the aid of a light-dividing KBr plate: a main beam (~90% of the intensity) and an auxiliary beam. The main beam was sent through a 100.0 ± 0.2 cm long cuvette filled with the mixture to be analyzed; the beam was recorded with a CdHgTe photodiode. The detector characteristics were as follows: size of the photosensitive area 300 × 300 μm, volt–power sensitivity 500 V/W, and detection limit $D^* = 10^{10}$ W⁻¹·cm⁻¹·Hz¹/₂.

The electric signal obtained from the radiation detector was applied to a low-noise amplifier developed by us ($e_n = 2 \text{nW/Hz}^{1/2}$). The amplifier has adjustable gain and an adjustable transmission band. A 538UNIA integrated circuit was used in the first amplifier stage so that practically the noise limit set by the photodetector was reached ($e_n = 1.5 \text{nW/Hz}^{1/2}$).

Fig. 1. Transmission spectra of PH$_3$ (a) and GeH$_4$ (b, c) in the range 1098.33-1098.63 cm$^{-1}$. The spectra were obtained with a diode laser in pulsed operation. PH$_3$ pressure 0.013 kPa; GeH$_4$ pressure 1.3 kPa; c) spectrum obtained with the gain increased by a factor of 50 and a time constant of 10 usec of the filter of the upper frequencies.

The amplified, filtered signal of the measuring channel was recorded with a digital stroboscopic system on the basis of a V9-5 voltage converter [6] and stored in the memory of an Elektronika DZ-28 microcomputer.

The auxiliary channel of the spectrometer was used for automatically turning the emission frequency of the laser with respect to a reference line [7, 8]. The reproducibility of the frequency was better than 10$^{-4}$ cm$^{-1}$ during the entire time of the measurements.

Selection of the Analysis Conditions. In the range of generation (9-11 μm) of the laser employed, the main absorption bands $\nu_2$ (center of the band at 991 cm$^{-1}$) and $\nu_4$ (1121 cm$^{-1}$) of the PH$_3$ molecule are situated [9]. At T = 300°K, the lines in the range 989-993 cm$^{-1}$ had the highest intensity (≈2 cm$^{-2}$·atm$^{-1}$). But it was not possible to determine the concentration of the PH$_3$ molecules in GeH$_4$ with these lines, because strong absorption by the molecules of the main component takes place in this range. The GeH$_4$ spectrum also comprises two bands $\nu_2$ (930 cm$^{-1}$) and $\nu_4$ (821 cm$^{-1}$) and a large number (up to hundreds per cm$^{-1}$) of frequently overlapping absorption lines of various intensities [10]. It follows from a review of the PH$_3$ and GeH$_4$ spectra that the high-frequency range of 1080-1125 cm$^{-1}$ is to be preferred for analyzing the PH$_3$ concentration in GeH$_4$. Following an experimental study of the PH$_3$ and GeH$_4$ spectra in the range of generation of the laser employed, we selected the PP (2, 2, E) absorption line of the PH$_3$ molecule at the frequency 1098.585 cm$^{-1}$ as the analytic line; the intensity of this line amounted to 3.3·10$^{-4}$ cm$^{-2}$·atm$^{-1}$ [9]. The absorption spectra of the PH$_3$ and GeH$_4$ molecules close to this line were obtained with tunable diode lasers and are shown in Fig. 1. The spectrum represented by Fig. 1c was obtained with a gain which is 50 times greater than that in the case shown in Fig. 1b. Near the analytic line the spectrum of the main component is free of absorption lines and the base line is rather flat.

The optimal pressure p of the mixture was chosen so that the flanks of the GeH$_4$ absorption lines only weakly affected the base line; the corresponding pressure as 1.3 kPa. Owing to collision broadening, the coefficient of absorption was in the maximum smaller than the Doppler broadening by a factor of about 2 so that an improvement by a factor of 5 was obtained in comparison with a pressure of 0.13 kPa.

Method of Measurements and Results. When the tunable diode laser was used in pulsed operation, the emission frequency was tuned during one pulse and the recording of the absorption spectrum was actually reduced to recording the shape of the laser emission pulse which had passed through the cuvette with the substance to be analyzed [5]. It is rather complicated...