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AN ANALYSIS OF THE CHEMICAL COMPOSITION OF THE ATMOSPHERE OF VENUS ON AN AMS OF THE VENERA-12 USING A GAS CHROMATOGRAPH

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AN ANALYSIS OF THE CHEMICAL COMPOSITION OF THE ATMOSPHERE OF VENUS ON AN AMS [Avtomaticheskaya mezhplanetnaya stantsiya Robot space station] OF THE VENERA-12 USING A GAS CHROMATOGRAPH

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When studying planets of the Earth group, the study of /1*
the chemical composition of the atmosphere is of particular interest inasmuch as the data on the composition of the atmosphere makes it possible, to a significant degree, to judge the evolution of the planet.

For solving this problem, Sigma gas chromatographs were installed on the SA [Silovoy agregat, power unit] AMS of the Venera-11, 12. The distinguishing feature of the Sigma chromatograph is the use of a high sensitivity ionization detector in it based on the use of the Pennig effect in rare gases (Rotin, 1974). Selection of the detector, to a considerable degree, was determined by the general structure and meteorologic characteristics of the chromatograph.

A block diagram of the Sigma chromatograph is presented in Figure 1.

An analysis of the gas sample and the calibration mixture was carried out on three sequentially located columns and detectors. The first column, 2 m long, is filled with a modification polysorb designed for separating sulfur compounds H_2S, COS, SO_2 and moisture in carbon dioxide. Separation of low-boiling gases--helium, hydrogen, argon with oxygen, nitrogen, krypton, methane and carbon monoxide--

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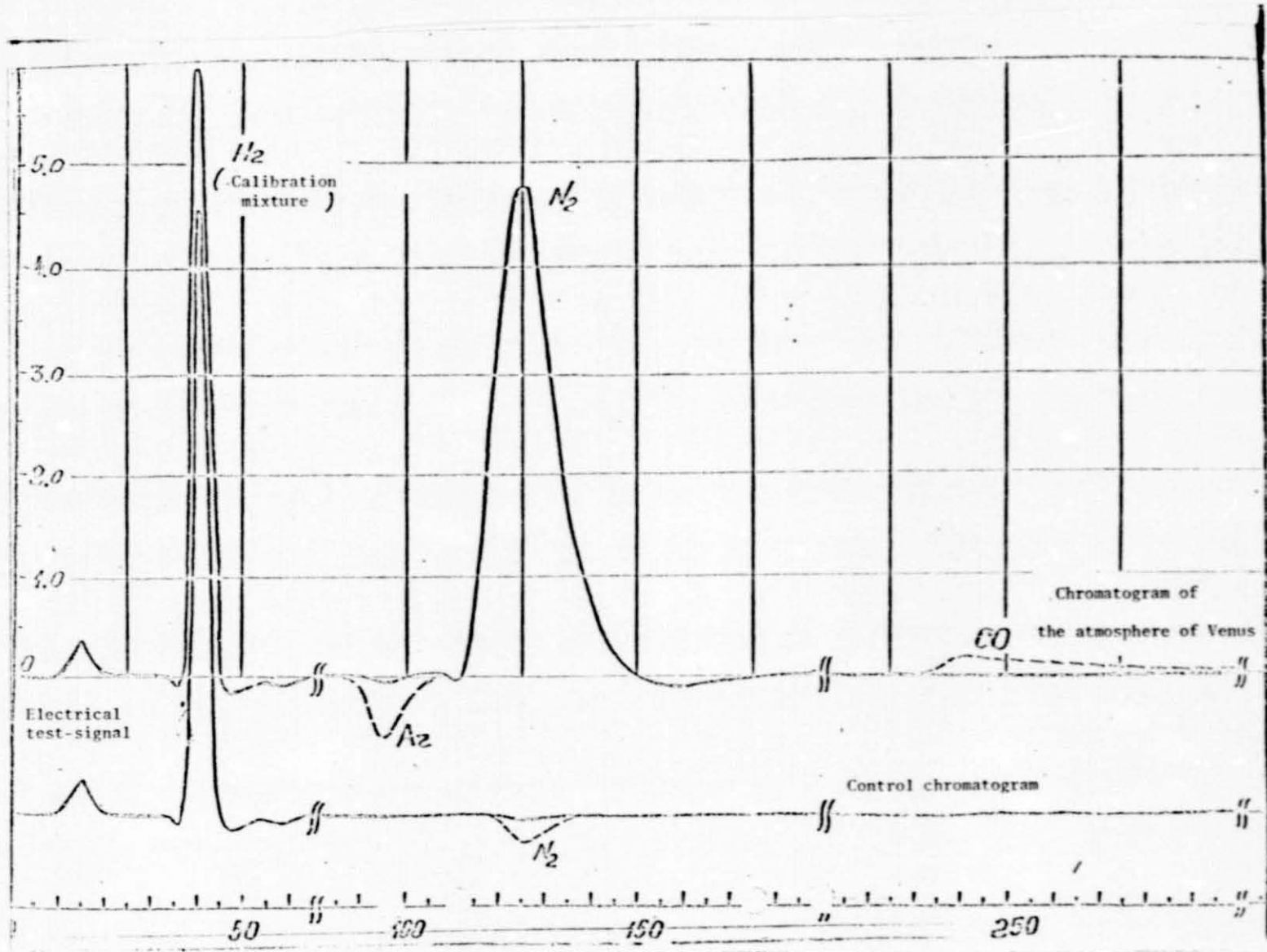
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Figure 2

were separated in the second column which is 2.5 m long with molecular screens (Kiselev et al., 1967).

Three columns--a reactor 1 m long with reduced manganese was used for determining the content of argon.

The threshold of sensitivity of all three detectors for   /2 pure neon in a state of saturation by a current was found at a level of 10^{-5} volumetric % which guaranteed sensitivity of the analysis at a level of 10^{-4} volumetric % with the volume of the working charge less than 1 cm^3 (Okhotnikov et al., 1978).

The design of the sampling device precluded the entry of gases filtered from the sheathing of the spacecraft into the chromatograph. All of the columns of the detector, and also the input reductor of the sampling block were placed in a special thermostat whose temperature on standard procedure was 70±1°C. Electrometric amplifiers and voltage-frequency converters which together with the direct current voltage source made up the measuring system of the ionization detectors were also placed in this same thermostat.

Due to the high sensitivity of the ionization detectors to the admixture in the gas carrier, certain units of the chromatograph, after the cycle of ground calibration was completed, were hermetically sealed to prevent leakage of extraneous gases in the period of storage, testing and flight.

The operating program of the Sigma chromatograph on the descent vehicle of the AMS Venera-11-12 included the following operations.

For approximately 4 hours before entry into the atmosphere of the Venus planet, the stop devices on the cylinder with

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the gas carrier and the ejection lines were opened, the thermostat for the columns were switched on and the chromatograph was **blown** with the gas carrier for a period of 4 hours. After entry into the dense layers of the atmosphere during descent from 65 to 54 km from the surface of the planet, the following were accomplished: depressurization of the instrument for sampling, opening of the stop device on the calibration mixture line and preparation of the control cycle for analysis.

At these altitudes, absolute pressure in the atmosphere $/\underline{3}$ of Venus is less than 1 kg/cm^2 and therefore a sample was not taken from the atmosphere for control analysis, but the gas carrier with contaminants present in the instrument was analyzed.

During descent from an altitude of 42 km to the landing moment of the descent vehicle, 8 analyses of the atmosphere of the planet were made. Fifty-four chromatograms were obtained of which 18 corresponded to the readings on detector 1 (determination of sulfur compounds of water) and 27 analyses of constant gases.

Information on the results of chromatograph analysis in similar form were transmitted on a telemetric panel and simultaneously chromatograms of the first three cycles of analysis were recorded in the memory of the instrument. The typical form of the chromatogram is presented in Figure 2.

An analysis of the control chromatogram and the chromatogram of the atmosphere of Venus reliably indicated the presence in the samples studied, besides the main component, **carbon dioxide, of** admixtures of N_2, Ar, CO, SO_2. The components indicated were identified according to holding time. Identification of argon was accomplished according to the sign of the signal of the neon detector in the form of partial
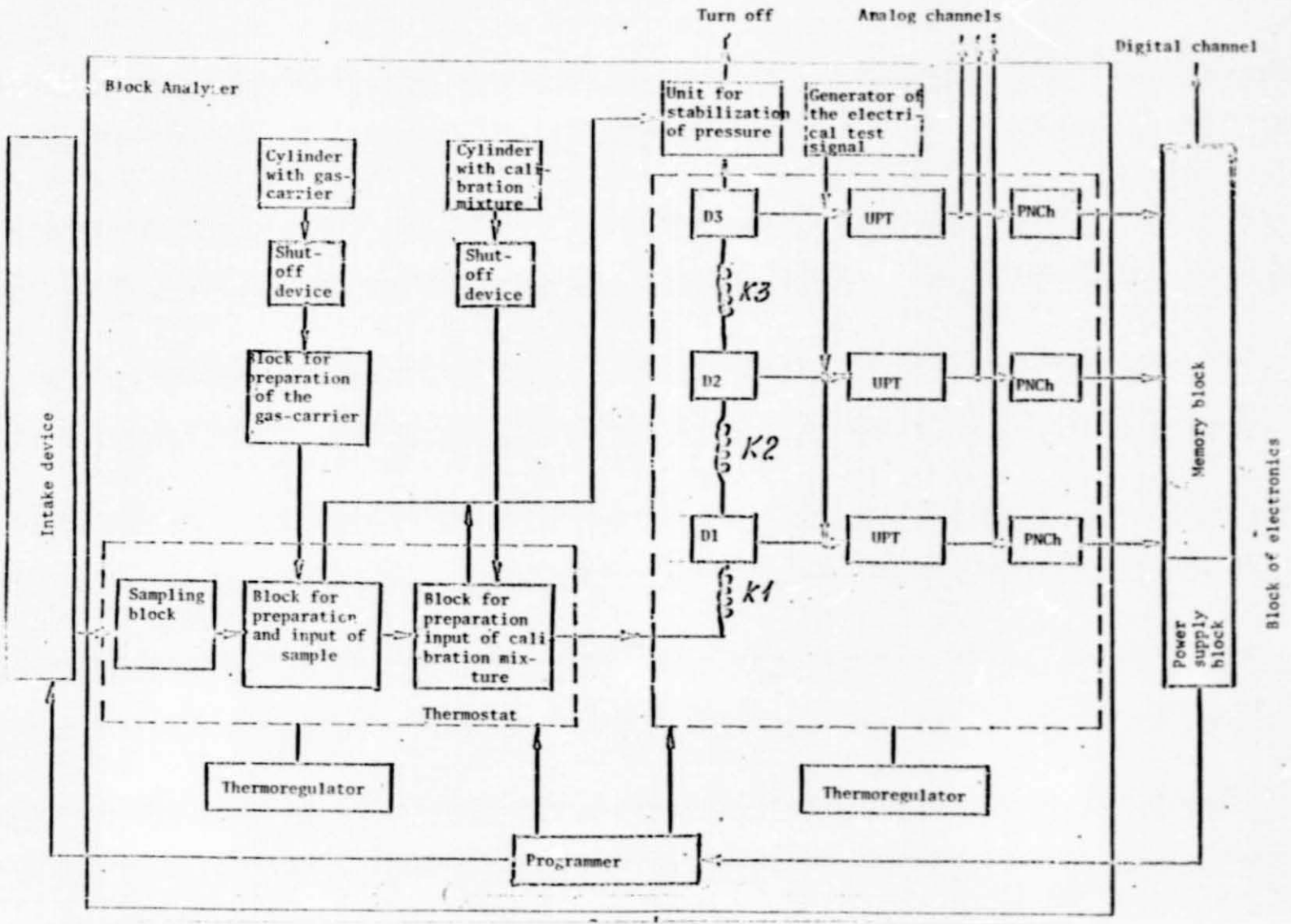
Figure 1

oxidation of the manganese reactor.

A quantitative interpretation of the chromatograms obtained made it possible to calculate the change in frequency of the gas-carrier and contamination of gas communications of the chromatogram in the storage period and during flight to the planet. The studies of operation of the neon detector in the saturation current condition, with different stages of contamination of the gas-carrier, indicated the possibility of distortion of the calibrated curves in the prethreshold field of concentrations resulting in negative signals for substances with high ionization potentials: argon, /4 hydrogen, nitrogen and sulfur dioxide. This characteristic made it possible not only to identify the A peak but also to reproduce the calibrated characteristics of the chromatogram **during the** contamination conditions under which the instrument operated.

The calibrated characteristics were recreated with standard values of pressure, temperature and consumption of the gas carrier. In order to exclude the effect of the activity of β-sources on the characteristics of the calibrated curve, the heights of the peaks of the substances analyzed were standardized for a value of a maximum signal of a detector according to the hydrogen in the calibration mixture, CO_2 and N_2.

During analysis of low-boiling gases, the second and third detectors duplicated the ratings although they had β-sources of different activity and operating in different contamination conditions. This circumstance made it possible to make independent calculations of the concentrations of components studied.

The heights of the peaks of nitrogen on the chromatograms of the atmosphere of Venus amounted to 40% and 32% of the

maximum signal for the second and third detector, respectively. In spite of such a significant difference, the measured values of the concentrations of nitrogen, according to an independent calibrated curve, coincide well. A similar method was used for reproducing calibrated curves for the remaining components.

The content of oxygen was not reliably established due to partial oxidation of the manganese reactor. However, laboratory testing of the characteristics of the neon detector **when** the **Sigma** instrument was operating showed that a negative signal for argon is reproduced /5 only in a case when the concentration of oxygen in the mixture is noticeably smaller than the concentration of argon. It is just this circumstance that is the basis for considering that a concentration of oxygen in the atmosphere of Venus is at least smaller by $2 \cdot 10^{-3}\%$ of the volume.

Due to the strong overload of the first detector, the sulfur compounds must lag behind the chromatograph peak of carbon dioxide. Therefore, for a quantitative calculation of concentrations of the sulfur dioxide detected, a standardized calibrated curve was determined from analysis of the model mixtures made up on a base of carbon dioxide.

The results of analysis of the atmosphere of Venus, using the Sigma gas chromatograph, are presented in Table 1.

An evaluation of the concentration of water vapors in the atmosphere of the planet **causes** definite difficulties inasmuch as the control analysis showed the presence of moisture itself in the instrument. As a result of this, a detailed analysis of the chromatograms makes it possible to indicate only the upper limit of concentrations of water vapors. According to preliminary evaluation, the content of

TABLE 1

Components	Concentrations in volumetric %
N_2	2.5 ± 0.5
Ar	$(4 \pm 2) \cdot 10^{-3}$
CO	$(2.8 \pm 1.4) \cdot 10^{-3}$
SO_2	$(1.3 \pm 0.6) \cdot 10^{-2}$

moisture in the atmosphere of Venus at all altitudes when measurements were made was less than 0.01% by volume.

Making the results of analysis more precise as to moisture and oxygen, and also identification of the peaks of those hypothetically corresponding to the presence of hydrogen, COS, H_2S, require computer processing of the chromatograms and additional laboratory modelling with the Sigma instrument operating. These studies are being done at the present time. /6

There is interest in compilation of the results of the Sigma instrument and the Pioneer-Venus gas chromatograph (Oyama et al., 1979). On the whole, coincidence of the results is good although there are two components for which there are significant differences in the measured concentrations. These are oxygen and water vapor. The characteristics of the neon Sigma detector are such that in the range of concentrations of Ar ≤ 60 ppm, its chromatograph peak is inverted. This peak for oxygen, for the entire range of concentratio s measured, is always positive. Therefore, if the oxygen had
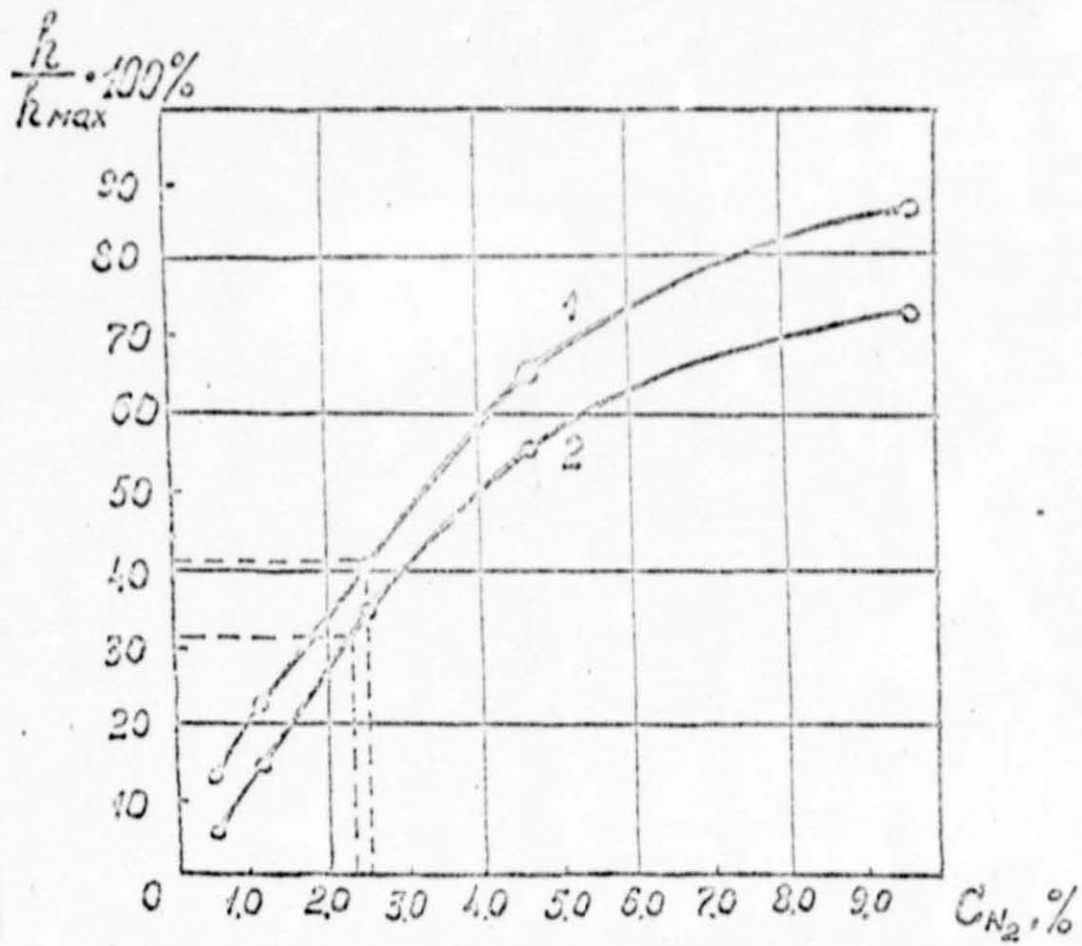
Figure 3: Calibration curves of the second and third detectors

been present in a quantity of 60 ppm, then on the Sigma chromatogram one would not have obtained the negative peak of argon. This fact was established in laboratory tests.

The content of water vapor obtained by the gas chromatograph on the Pioneer-Venus (less than 0.5%) is clearly high because similar quantities of gas vapor on the Sigma instrument would cer**tainly** have had to have been recorded.

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