Theoretical and experimental studies of molecular (atomic) exchange at the installation for measuring and analyzing the residual gas medium UID-2

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\textbf{Abstract.} The paper presents the results of studies of mass transfer in the measuring circuit of the UID-2 installation (installation of pressure measurement and analysis of the residual gas medium in the electro-vacuum devices), which consists of two parallel vacuum paths, in the volumes of which are placed a total pressure transducer and a monopolar mass spectrometric sensor, limited by pairs of inlet and outlet diaphragms. Using the Monte-Carlo method, estimates of the average density of the distribution of the number of collisions of the latter with surfaces of characteristic dimensions of these volumes are obtained. The experimental results obtained within the accuracy of the experiment are consistent with the calculated data on the protective properties of diaphragms that prevent the negative influence of the heated cathode of the gauge transducer on the gas composition of the analytical sample during the quantitative and qualitative analysis of the residual gas medium in the electro-vacuum devices based on the implementation of the destructive method.

When developing the measuring vacuum system of the UID-2 installation (installation of pressure measurement and analysis of the residual gas medium in the electro-vacuum devices (EVD)) \cite{1} to solve the problem of reducing the mutual influence of the manometric (PMI-27) and mass spectrometric (MX-7304A) sensors during their simultaneous operation, as well as ensuring normal operating conditions with access to the established the maximum achievable parameters required a theoretical and experimental analysis in the selection of the most acceptable values of the values of the conductivity of the diaphragms and their ratios that satisfy the tasks.

The selection of the conductivities of the diaphragms of the required size was in many respects controversial and based on the possibility of their multifunctional use:

1) installation of pairs of diaphragms on the path of movement of the gaseous medium outflowing from the product, divided into two parallel independent flows with the values of conductivity at the level of $10^{-7}...10^{-8}$ m\textsuperscript{3}/s at its inlet (quantitative estimates of the values of the conductivities of the inlet diaphragms were determined taking into account the accepted values of the correction for the pumping out action of pressure transducers $\approx 0.01$–0.001) and $10^{-4}...10^{-5}$ m\textsuperscript{3}/s at the outlet (follows from the condition that the inequality between the conductivity of the outlet diaphragm and the effective pumping speed $S_e$ in the section behind it – $10^{-4}...10^{-5} \ll S_e$) is fulfilled, respectively,
should have abruptly reduce the pressure behind the outlet diaphragms and in front of them. This made it possible for the pressure transducers of both chambers and, especially the mass analyzer, with an upper limiting pressure of $10^{3}$ Pa in the opening chamber, to operate in a regulated range of operating pressures, at which electron emission from the cathode is still permissible and there is a linear dependence of the ion current on the ion collector on the concentration of the test gas. In this case, however, it was required to ensure the maintenance of a relatively low level of background residual pressure, which was extremely difficult at small values of the outlet diaphragms, and, consequently, a low pumping speed of the chambers;

2) the ratio of the conductivities of a pair of diaphragms to be installed, differing from each other by three orders of magnitude, according to the preliminary opinion, should have had a similar proportional dependence in the probability ratio, i.e. the probability of the number of molecules removed from the volume of one of the measuring chambers through the outlet aperture and the probability of the number of molecules returning to the volume of the recipient (opening chamber) through the inlet diaphragms;

3) the difference between the outlet diaphragm of the ionization gauge transducer chamber from the diaphragm of the analyzer sensor chamber, which has one order of magnitude lower conductivity, and also, having more than 10 times the effective pumping rate of the path connecting them in comparison with the conductivity value the effective speed of pumping out the measurement chamber, gave hope that the effect of the vacuum gauge sensor would not have any noticeable effect on the composition of the gas under study from the product in the analysis chamber. The same circumstance, but to a lesser extent, applied to the sensor of the gas analyzer, which in turn could influence the measurements of the total pressure of the gauge transducer of the vacuum meter;

4) the value of the conductivity of the outlet diaphragm of the measurement chamber was also chosen on the basis that the evacuating effect of the ion source of the manometric transducer would be approximately 100 times less than the effective pumping rate of the chamber itself, thereby achieving leveling the phenomenon of the reverse gas flow from the high-vacuum pump.

On the basis of preliminary estimates, a pair of diaphragms was selected, the ratio of conductivity, which theoretically provided an output to the specified limiting parameters.

From the number of calibrated diaphragms purchased from NPO "VNIIM named after D I Mendeleev" [2], taking into account the obtained preliminary ratios, the following pairs of diaphragms were selected: $D_{1.1} = 3.0\times10^{-5}$; $D_{1.2} = 3.13\times10^{-8}$; $D_{1.3} = 6.86\times10^{-4}$; $D_{1.4} = 2.91\times10^{-7}$ m$^3$/s.

However, i immediately had to face a number of difficulties:

1) the conductivity of the diaphragm $D_{1.2}$ turned out to be noticeably variable, which manifested itself in a change in its value after several warm-ups of the high-vacuum opening chamber. Apparently, the reason was the contamination of a very small ($\approx 6.0\times10^{-3}$ mm) through hole of the diaphragm with particles of fine dust, which is always present in an insignificant amount in the vacuum system;

2) in addition, the value of the conductivity of the outlet diaphragm $D_{1.1}$ caused an increased background pressure to the measurement chamber $A_{1.1}$, which prevented the fulfillment of the condition of the accepted assumption in the form of the inequality: $P_{pa} << P_{kvs}$;

3) in turn, the conductivity value $D_{1.3}$ provided an acceptable level of the background of partial pressures, but at the same time, due to constant pumping out equal to $\approx 1.5$ s, led to irrational consumption of the investigated portion of the gas.

Due to the combination of these circumstances, it was necessary to replace the indicated diaphragms with diaphragms of higher conductivity for $D_{1.1}$, $D_{1.2}$ and a lower value for $D_{1.3}$. Based on the possibilities available with the diaphragms, as a result of the choice, a new line of conductivity values was organized, namely:

$D_{1.1} = 1.0\times10^{-4}$ m$^3$/s; $D_{1.2} = 5.75\times10^{-7}$ m$^3$/s; $D_{1.3} = 9.14\times10^{-5}$ m$^3$/s; $D_{1.4} = 2.91\times10^{-7}$ m$^3$/s.

In this case, for $S_k = 1\times10^{-3}$ m$^3/$s, the estimates of the probabilities obtained from the calculated dependences had the following values:
\[ A_{2-4} = 2.91 \times 10^{-3}; \ A_{4-2} = 6.29 \times 10^{-3}; \ A_{4-3} = 1 \times 10^{-1}; \ A_{3-1} = 9.14 \times 10^{-2}. \]

In addition to this, a more in-depth theoretical study of issues related to mass transfer was also required, while it was necessary to clarify a number of important points: first, under the conditions of the molecular regime, as the most probable, it was required to determine what is the probability of reverse migration of molecules, who have already been in the measuring chambers, and also how likely is the fact of their presence in the chambers where they have not been before. Here we take into account the cases of interpenetration of molecules, both from the side of inlet and outlet diaphragms; secondly, it was required to determine what are the probabilities of direct flight of molecules from the side of the holes of the inlet diaphragms to the side of the outlet and in the opposite directions; thirdly, it was required to determine how effective the joint pumping of gas by pumping means was.

In this regard, relying on the existing powerful base of methods for modeling and imitation of processes occurring in a discharged space, the method of statistical tests, the so-called Monte-Carlo method [3, 4], was used as an effective tool.

Based on this method, four simplified flat geometric models of various sections of the measuring vacuum system were developed with a correction for their linear dimensions, as required by the law of cosines taken as a basis.

The algorithm for constructing each such model was software implemented using the high-level algorithmic language Borland Pascal 7.0.

In order to ensure a high degree of reliability of the results obtained, the value of the confidence level was taken equal to \( P = 0.95. \)

In figure 1 shows the geometry of the profiles for each of the four models; the dimensions shown in table 1 are in mm.

| Table 1. Flat collector models dimensions. |
|------------------------------------------|
|   | d  | D1 | D2 | L  | H1 | H2 | h  | S  |
|---|----|----|----|----|----|----|----|----|
| 10| 50 | 45 | 175| 550| 310| 129| 300|

Below are the probabilistic values of a possible event with a characteristic error for each calculation model separately.

The performed calculations showed convergence with the obtained preliminary estimates. For the case with the interchange of molecular flows between adjacent chambers from the side of the outlet diaphragms \( D1.1 \) and \( D1.3 \), the calculations showed that, in general, the data obtained reflect the correctness of the chosen approach to this issue. Indeed, the percentage ratio between the number of molecules that have penetrated from the side of the measuring chamber into the analysis chamber and vice versa confirms the expected distribution pattern. Of the 10000 traced molecules launched through the cross section of the \( D1.1 \) diaphragm, only 502 will end up in the analysis chamber through the \( D1.3 \) diaphragm, which is a 5 \% probability \( A_{1-3} \) instead of the expected 10 \%. A similar result was obtained for the analysis chamber: 471 molecules out of 10000 launched through section \( D1.3 \) will enter the measurement chamber through the diaphragm \( D1.1 \), which is 4.7 \% of the exchange probability instead of 10 \%, based on the estimate. The relative error of the results at a given level of confidence was about 1 \%. Figures 2 and 3 show the curves of the statistical distribution of the observation results in the form of a polygon (histogram) of frequencies and the relative total frequency from the number of possible collisions with walls.

It was also found that part of the molecules returning from the chambers with the placed manometric and mass spectrometric converters, despite the small values of the conductivity of the inlet diaphragms \( 5.75 \times 10^{-7}, \ 2.91 \times 10^{-7} \ \text{m}^3/\text{s}, \) respectively, can migrate from the measurement chamber to the chamber analysis and, conversely, in the following proportions: for the inlet diaphragm \( D1.2 \), the number of molecules that have returned and found themselves in the section of the diaphragm \( D1.4 \) will be 101 \((N = 10000)\), for the inlet diaphragm \( D1.4 \), the number of molecules that will be in section \( D1.2 \) is 89 \((N = 10000)\). The relative calculation error does not exceed 0.5 \%.
Bringing these values to the values of the corresponding probabilities, it can be stated that the probability of migration to the side of the analysis chamber of a molecule that has escaped from the measurement chamber into the opening chamber is 0.0051, and the probability of migration of a molecule to the side of the measurement chamber from among those returning from the analysis chamber is 0.0044, which is the whole is unimportant.

Speaking about the "direct flight" of molecules, it should be concluded that in the A1.1 collector out of every 106 molecules that have flown through the section of the diaphragm D1.2 into the measurement chamber, only 93 will leave the chamber unhindered, and in the A1.6 collector only 91 molecules from million will remain "unnoticed", being without a single collision with the walls, in the section of the outlet diaphragm D1.3, which, in turn, suggests a low degree of "transparency" of sections D1.2-D1.1 and D1.4-D1.3 for the "direct flight" of molecules.

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It only remains to add that the estimates obtained for the "forward flight" of molecules are in full agreement with the data obtained at the stage of preliminary development of the setup even before the appearance of the above-considered flat models using the method of slopes.

Analyzing and generalizing the available positive results on the whole, one of the most painful questions, as experimental studies later confirmed, was the question of the relatively high percentage of "insecurity" of the chambers from the interpenetration of "processed" molecular flows from the outlet diaphragms. The obtained quantitative characteristics of such an exchange could not be considered satisfactory.
In this regard, steps were taken to search for measures to limit the unimpeded access of a significant portion of molecules into the chambers from the side of the outlet diaphragms. As a barrier to the movement of molecules in the A1.3 collector model, a partition was installed with such a linear dimension that it allowed to completely block the cross-section of pipelines suitable for the collector and the spatial arrangement of which divided the common channel of the collector tract into two equal sections with the simultaneous possibility of pumping to a cryopump (see figure 1 - section NM). In other words, the counter streams were deprived of the possibility of direct interdiffusion.

The results of installing such a barrier showed that out of 10000 molecules, the starting points of which lay in the plane of the exit diaphragm D1.1, only 184 will pass through the section of the

**Figure 2.** a) – frequency polygon (histogram) of the statistical distribution of collisions of molecules with walls for collector A1.3 when considering the mass transfer scheme D1.1 → D1.3. b) – curve of the total (cumulative) frequency for collector A1.3 when considering the mass transfer scheme D1.1 → D1.3 (in percent).

**Figure 3.** a) – frequency polygon (histogram) of the statistical distribution of collisions of molecules with the walls for the A1.1 measurement chamber when considering the D1.2 → D1.1 mass transfer scheme, b) – the total (cumulative) frequency curve for the A1.1 measurement chamber when considering the mass transfer scheme D1.2 → D1.1 (in percent).
diaphragm D1.3. Accordingly, when molecules are fired from the side of diaphragm D1.3, the cross section D1.1 will be crossed by 187 molecules. Proceeding from this, the coefficients of interpenetration in the measurement and analysis chambers decreased approximately three times for them.

Based on this, an addition was made to the design of the measuring vacuum system in the form of a thin nickel plate, fixed by means of contact welding to the bottom of the blanking flange and installed directly on the A1.3 manifold, which thereby limited the optical transparency of the connecting path between the inlet diaphragms D1.1 ... and D1.3 in a cut plane dividing it into two mirror halves. Experimental studies with the installed partition have confirmed the correctness of the calculated data on the decrease in the interpenetration of molecules into the transducer chambers.

Simultaneously with the verification of the protective properties of the diaphragms, an analysis was carried out on the efficiency of joint pumping of the connecting chamber (behind the outlet diaphragms) of the connecting duct of the A1.3 collector.

Thus, when using two pumping devices - cross sections NM and NR (see figure 1) - when tracing 50000 molecules "emitted" by the diaphragm D1.1 with the partition installed on the A1.3 manifold, it turned out that only 755 molecules constituting 1.5% of the total number of molecules considered, where the indicated percentage is about 25% less than the same value when using one pumping agent (NM).

In general, it should be noted that the data obtained on the efficiency of joint pumping by two pumps [TMH 01AB-450-003 (NR), 010-VK600-013 (NM)] show no tangible advantages over pumping to one cryogenic pump 010-VK600-013.

Thus, using the elements of valves with a low throughput, and applying an improvement insignificant from the point of view of design, installing a dividing wall, it was possible to reduce the values of the probabilistic exchange between the chambers through the outlet diaphragms to almost 1 ... 2% instead of 10% predicted.

As additional information, it will not be superfluous to note that, thanks to the method of statistical tests, the estimate of the time spent by a molecule (atom) to move from the opening chamber to the measurement and analysis chamber, based on the data on the number of collisions with the wall with the sticking coefficient equal to zero, is not serious, difficulties. According to the available data, when molecules are evacuated from A1.5 through aperture D1.2 for M/e - 4 (arithmetic mean velocity 1256 m^3/s at T = 293 K), the time for molecules to reach volume Vpa (characteristic size 0.01 m) will be 3.0 % from the total number of molecules - 0.4 s; for 0.72 % - 0.08 s; for 20 M/e (arithmetic mean velocity 559 m^3/s) - the time for molecules to reach the volume Vpa will be 0.9 s for 3.0 %; for 0.72 % - 0.18 s; for 44 M/e (arithmetic mean velocity of 378 m^3/s), the time for molecules to reach from the volume VkvS will be 1.32 s for 3.0%; for 0.72% - 0.26 s.

When molecules are evacuated from A1.5 through aperture D1.4 for 4 M/e (the arithmetic mean velocity is 1256 m^3/s), the time for molecules to reach from the volume VkvS will be 0.4 s for 1.9%; for 0.27 % - 0.04 s; for 20 M/e (arithmetic mean velocity 559 m^3/s), the time for reaching molecules from the volume VkvS will be 0.9 s for 1.9%; for 0.27 % - 0.09 s; for 44 M/e (the arithmetic mean velocity is 378 m^3/s), the time for reaching molecules from the volume VkvS will be 1.32 s for 1.9%; for 0.27 % - 0.13 s.

Experimental studies were carried out to assess the effect of the PMI-27 gauge transducer on the composition of the residual gas and the values of the partial pressures of its components in the on and off mode of the cathode in the presence and absence of low conductivity elements in order to analyze the protective properties of the diaphragms used. The change in the gas composition was recorded by a mass spectrometer in the range of mass numbers 1–45 M/e with a scanning frequency of ≈1.4 s.

The studies were carried out in two series. In the first – the volumes of the manometric and mass spectrometric chambers were combined by means of two open valves (not shown schematically in figure 1; see [1]). After preliminary degassing of the transducers with simultaneous high-vacuum evacuation of the combined volume by turbomolecular and magnetic discharge pumps, evacuation of volumes A1.1 and A1.6 was transferred through diaphragm D1.3 to a helium priming pump.
Having reached the establishment of a new dynamic equilibrium pressure, an analyzer sweep was started in the system, recording mass spectra, first with the cathode of the manometric ionization converter turned on (state - ON), after which it was turned off for about 5.5 min, and then voltage was applied to it again.

Figure 4 shows a histogram reflecting the nature of the effect of turning off the cathode of the manometric transducer, which is exerted on the partial pressures of individual gas components, which, within the background error, were subjected to a certain influence during the research.

The experiments were carried out at a pressure of $3 \cdot 10^{-5}$ Pa. The first column of the pair in the histogram, colored in monochrome red, corresponds to the switched on cathode; the shaded column next to it refers to the switched off cathode. The resulting residual background of the system was characterized, as is usually the case for high and ultrahigh vacuum, with a dominant hydrogen component of 96.1 % (by volume). In addition, the system contained insignificant amounts of gases of the CnHm group, as well as $N_2$, CO, Ar and CO$_2$. The results show that when the cathode is turned off, the amount of hydrogen decreases by 3 %, while the decrease in the partial pressure of H$_2$O is 9 %, for CO$_2$ - 26.6 %, and for CO the decrease was almost 82 %. The increases in the partial constituents CH$_4$ and Ar did not exceed +24.1 % and +13.7 %, respectively.

Figure 5 shows the dynamics of changes in the ion current intensities of a number of mass numbers that have undergone changes when the heated cathode of the total pressure sensor is turned off and on. As can be seen from the graphs, when the cathode is turned off, a decrease in the ion current is characterized by mass numbers 2, 18, 28, 44, and, conversely, an increase in the ion current is observed with mass numbers 16 and 40. It can be seen from the graphs presented that when the cathode is turned on, the most intense burst appears for masses 2, 28 and 44, followed by an exponential decrease, approaching the asymptote from the initial values in a time of $\approx 15$ min. In this case, for H$_2$, its relative value reaches 265.5 %, for CH$_4$, the relative increment was 155.3 %. The maximum obtained increment relates to carbon dioxide, its value was $11.71E + 3$ %, while for CO this value is slightly less and reaches $5.01E + 3$ %.

The second series of experiments was carried out while pumping volumes $A_1.1$ and $A_1.6$ separated from each other, respectively, through diaphragms $D_1.1$ and $D_1.3$ with a baffle installed on the collector $A_1.3$; the transducers, as in the case of the 1st series of experiments, were pre-degassed.
Figure 5. Dynamics of changes in mass numbers 2.12 – (a), 15.16 – (b), 28.44 – (c) in the combined volume from collectors A1.1, A1.4 and A1.6 with pumping through a diaphragm D1.3 when turning off (OFF) and turning on (ON) the PMI-27 cathode.
Figure 6. Dynamics of changes in mass numbers 2.12 – (a), 15.16 – (b), 28.44 – (c) with divided volumes of collectors A1.1, A1.6 and pumping through diaphragms D1.1, D1.3 when you turn on (ON) the cathode PMI-27.
The pumping was carried out to the cryogenic pump 010-VK-600-013 as in the case of pumping to the diaphragm D1.3. Figure 6 shows the dynamics of changes in the ion current for the previously listed mass numbers, while, as can be seen, the expected changes when the cathode is turned on in a given time interval of 5 min. practically not detected.

In contrast to the first series of experiments, the sweep of the mass spectrometer was started when the manometric transducer was already turned off for a while (5 min), since it was assumed that the corresponding responses through the diaphragms when turned off would be less pronounced and therefore their registration by the mass spectrometric the system is unlikely, in contrast to the significant bursts typical when the converter cathode filament current is turned on.

For the conditions of the molecular regime, the probabilities of mass exchange between the chambers of the measuring system are theoretically determined using the Monte-Carlo method. In this regard, it should be noted that the probability of migration of molecules returning from the measurement and analysis chambers through inlet diaphragms D1.2 and D1.4 for the accepted ratios of pairs of inlet and outlet diaphragms is less than 0.005. In this case, the value of the probability characterizing the "direct flight" of molecules, the starting point of which is the cross section of the inlet diaphragms leaving the limits of the above-mentioned chambers, being enclosed, inside the solid angles, the base of which are the cross sections of the outlet diaphragms, is less than 0.0001.

The conditions under which the probability of migration of gas molecules from the side of the outlet diaphragms between the measurement and analysis chambers can be reduced by a factor of 3 are theoretically determined. By making an improvement in the design of the A1.3 collector - by installing a separating baffle - it was possible to reduce the values of molecular exchange between the chambers through the outlet diaphragms to practically 1...2 %. The experimental studies carried out confirmed the calculated data: when the volumes A1.1 and A1.6 were separated from each other with pumping through the diaphragms D1.1 and D1.3, the expected changes in the gas composition when the cathode of the manometric sensor was turned on in a given time interval and with an accuracy within the experiment were not found.

The form of distribution functions in the form of a polygon of frequencies and the relative total frequency of the number of possible collisions of molecules with the walls of the opening, measurement and analysis chambers, as well as an estimate of the average distribution density of the number of molecules within the specified intervals, has been determined.

References
[1] Bushin S A and Papko V M 1997 J Vac. techn. and technol. 7 3 22
[2] Calibration results of diaphragms with nitrogen at 290-295 K for molecular flow 1990 Svidetelstvo №1657,1678; (L.: NPO “VNIIM im D I Mendeleeva”)
[3] Nesterov S B, Vasilev Yu K and Androsov A V 2001 Calculation of complex vacuum systems (Moskva MEI) p 180
[4] Nesterov S B, Vasilev Yu K and Androsov A V 2004 Calculation of complex vacuum systems (Moskva MEI) p 220