The method of processing data of mass spectrometric analysis of vacuum medium of quartz resonator-thermostats

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Abstract. The theoretical and practical development of gas environmental analysis with the usage of a complex based on a residual gas analyzer is briefly presented. The data of technological search of annealing, degassing and sealing modes of quartz resonators and generators with participation of authors are summarized. The gas flow rate was estimated from the mass spectra. The method of measurement of working parameters of products, as well as estimation of operating time resource is proposed. Measurement of quartz resonator-thermostats (QRT) parameters is performed using serial technologies.

1. Introduction
The active development of miniature thermostatically controlled QRTs and generators in metal packages such as TO-8, DIP-14 and DIL-14 is currently in progress [1]. Inside the package, a ceramic plate is placed on thermally insulated stands and a quartz piezoelectric element (PE) is connected to the plate through holders. On the plate, a circuit of QRT or generator with units of voltage and temperature stabilization is formed. On the plate, they formed a power supply and temperature stabilization circuit. To connect and fasten QRT elements, glue mounting, soldering and spot welding of conductors are applied. In this design, there is no gas absorber (getter), therefore, severe thermal degassing of elements is required to obtain and maintain a vacuum in the product. In 16 hours via thermal vacuum annealing at a pressure of $10^{-5}$ torr and a temperature of 180°C there were obtained pressure-tight products with an internal gas release rate of $< 10^{-10}$ torr·cm³/s. The long-term frequency instability of generators in metal-glass cold-weld sealed TO-8 packages was studied [2]. The relative frequency instability per day after the technological run for 15 days did not exceed $\pm 5 \cdot 10^{-9}$. This value is comparable with a similar parameter for generators in glass packages. TO-8 packages were examined during the experimental development of of BT-cut (15/3 MHz) quartz resonators (QR) and TD-cut (10/3 MHz) quartz resonators [3]. The testing of annealing and vacuum sealing modes was also carried out on technological models. Instead of a micro plate, quartz PE was installed in the package, with a heater and a temperature sensor placed near the electrode. The absence of soldered joints allowed to conduct degassing at 200°C and 300°C for 6 hours in a vacuum of $10^{-5}$ torr. After vacuum sealing of the package by cold welding, the level of internal gas evolution has become significantly lower than $10^{-10}$ torr·cm³/s. No increase in pressure in the package after three days of exposure at 110°C was detected. It was established that long-term thermal trainings of resonators in a TO-8 package can be carried out at $\leq 120 \degree C$ after vacuum annealing at 200°C and sealing. The temperature of "training" can be raised to 140°C, if annealing is carried out at 300°C. As for the generators in DIL-14 cases, it should be noted that experimental and even serial designs of these products have serious drawbacks. Micro plates with
PE are placed on high glass racks, which did not allow to move the piezoelectric element and the plate to a distance of more than 0.1–0.2 mm for proper cleaning during assembly and annealing. In addition, a significant drawback is the presence of soldered joints on gilded pads. The shock resistance of such generators did not exceed 100g, and the reserve of stable frequency generation was 3–5 years.

Many problems have been eliminated in a new design [4] with original nichrome thermal insulators. However, circuit designs based on photolithography of thin-film structures with soldered pads complicate the process of stable generators manufacturing. It should be reminded that here the vacuum cleanliness of the assembly is ensured by annealing conducted in two stages: at first, in an open case with periodic frequency adjustment; then, after the resistance (seam) welding of the package, final annealing through the technological hole in the cover and sealing the hole in a vacuum. It was necessary to reduce the annealing temperature to 150–160 °C due to the following: the structure of the electrode coating (Ag + Au) on PE is destroyed; soldered contacts burn out on the circuit pads; there are frequent failures of semiconductor microcircuits in the blocks of stabilization of the supply voltage and temperature. We associate the last two points with the presence of aggressive compounds in the evacuated package (residues of fluxes, H₂O, OH, etc.)

The development of the latest Low Temperature Cofired Ceramic (LTCC) technologies for manufacturing of microplates and even packages for vacuum products has begun [5]. Design and technology solutions for QRT assembly in a DIL-14 package allow to refuse from soldered contacts with soft solders of POS-61 and PSRO 10-90 types. Moreover, labor-intensive photolithography operations with “aggressive chemicals” and UV radiation were replaced with vacuum deposition of conductive tracks on microplates [6, 7]. The use of LTCC micro plates allows to create designs that withstand impacts over 400g. In the process of microplates manufacturing there may appear holes, protrusions and cavities, which mean that a more rigid fixation of the elements of wall mounting in products should be performed. The vacuum properties of DuPont LTCC plates [5], together with the adhesive mounting of elements in a DIL-14 package, provide a 10⁻⁴ torr vacuum after technological annealing at 160°C. Comparison of the data on the gas evolution of H₂, H₂O, CₓHᵧ with the results of [8] shows that the composition of the medium is determined by the products of gas desorption from the adhesive. The gas release rates are close to the values obtained by the authors of [3], i.e. equilibrium temperature of the sorption-desorption process is at the level of 120°C.

As it was already noted above, a two-stage annealing before sealing is also used in DIL-14 packages for QRT. The package is fixed by laser welding along the perimeter only at the first stage of annealing. The first studies of generators based on the specified QRTs showed positive results. Frequency instability after a technological run did not exceed ± 5·10⁻⁹, which corresponds to the technical requirements [9].

In [6], the frequency instability of generators at 10 MHz was estimated. The large departures of the resonant frequency are due to the adsorption and chemisorption of atoms and molecules on QRT electrodes during thermal desorption of these particles from soft solders and adhesives. Possible compounds that deposit on PE in a gaseous state are qualitatively established. These include: SnH₄ ↑ (from soft solders), CO, H₂, H₂S, C₃H₁₀, C₂H₄OH and other compounds from CP-2 ((Conductive Adhesive-2)) and K-400 adhesives. With the elimination of SnH₄ ↑ formation mechanisms the daily aging of generators decreases by 20-40 times. When using adhesive installation, relative instability frequencies per day make up ~ 2·10⁻¹⁰, and after six months, this figure reaches (2.9–3.5) · 10⁻¹².

The problem of quantitative measurement of gas composition in the space under package of QRTs and generators has been set and is being solved. A mass spectrometric complex was developed to control the modes of technological annealing and sealing of products in metal-glass packages [10].

A qualitative analysis of gas composition in sealed rejected QRTs (DIL-14 package) was carried out at temperatures from 20°C to 160°C. The established connections can be the cause of short- and long-term aging of resonators, uncontrolled frequency departures and stalls. These are, as a rule, H₂O, OH, and hydrocarbon components, such as propargyl, chloroethane, propargyl alcohol, etc. For products in a DIL-14 package, the dynamics of the relative content of water vapor with increasing temperature was studied. The pressure of water vapor after 130°C decreases as a result of interaction of H₂O
molecules with impurity molecules when an equilibrium composition is established. There is a possibility of formation of nitrogen-containing surfactants, such as dimethylamine, formamide and nitromethane. The measurements are based on EXtorr X-100 residual gas analyzer [10]. The samples are installed on a heat probe, which is placed in a package-opener chamber (ionization) of a mass spectrometer. After pumping vacuum out of the chamber at a preset temperature, a micro-leak is formed in the package by means of a piercing device and mass spectrum of gas flow from samples is fixed.

The purpose of work is to evaluate the capabilities of a mass spectrometric method for monitoring the gas environment at the stages of development and production of piezoelectric products.

The tasks of work
1. To evaluate the level of residual vacuum in models and working samples of quartz resonator-thermostats in a metal-glass package.
2. To evaluate the rate of gas fraction evolution from the elements of micro-assemblies in sealed packages of products at operating temperatures.
3. To define the acceptable period of functioning of the products in the specified modes.

2. Sample preparation and measurements

Products in working condition and rejected for various reasons are marked as follows. Quartz resonators are thermostats in a DIL-14 package: QRTs 163, 215, 219, 315, 343, 435. Micro-assemblies are assembled on a lucalox (99.9% \( \text{Al}_2\text{O}_3 \) and 0.3–0.2% \( \text{MgO} \)) plate with a TD-cut quartz piezoelectric element at a frequency of 10/3 MHz. Laser welding along the perimeter of the package and final sealing of the hole in a package cover with a diameter of 0.4 mm after vacuum annealing at 160°C were used. Preliminary degassing of QRT was carried out in a vacuum furnace also at 160°C for 24–40 hours with periodic frequency adjustment. Only QRT 215 has rated values. In QRT 163 and 343, frequency generation schemes failed, and in QRT 219, 315, 435 the frequency is much lower or higher than the nominal value. In addition, QRT 215 was re-sealed with a short final annealing, and QRT 219 was moved to another building after repair. All products were subjected to mechanical tests and thermal cycling operations, as well as underwent runs of various durations as parts of generators.

The sealed QR is marked as C-1, assembled in a cold-welded TO-8 package with an AT-cut quartz, at a frequency of 11.3/3 MHz. The final annealing of the resonator was carried out in an oil-free environment of the cold welding installation at a temperature of 160°C during one shift. Technological models in a DIL-14 package are assembled on LTCC micro plates with a temperature stabilization circuit within the range of 40-150°C. In models D-1, D-3, D-5 was used ceramic by DuPont company. D-1 model passed monthly tests with internal and external heating up to 150°C. In a D-3 model, the heating transistor burned down after internal heating above 120°C. D-5 model withstood heating up to 100°C for 40 hours. Istok models, I-1 and I-2, are assembled in a DIL-14 package and contain LTCC plates produced in Russia by JSC "RPC "Istok" named after Shokin". Inside the packages there is QRT circuits assembled using spot welding and mounting with CD-2 and K-400 adhesives; circuits are not connected to the external terminals of the package. I-1 sample was not subject to vacuum annealing and was not sealed (polymerization of adhesives at 120°C). I-2 sample was annealed in a vacuum at 160°C during 3 shifts, followed by final annealing and sealing. It should be noted that the QR C-1 has an internal volume of 0.5 cm³, not occupied by mounting elements. All other products have an internal volume of 0.7 cm³. The volume of the package-opener chamber with an ionization source is 28 cm³.  

At the first stage, the entire spectrum of chemical elements and compounds in the samples was recorded after long-term heating and cooling at 15 min intervals. On the first day, background spectra from QRT and D-1, 3, 5 models were recorded during heating at every 20°C for 3 hours. Further, the samples were cooled with evacuation of vacuum for about 20 hours; and after puncture of the package cover, the spectra of gas components were taken from the micro-leak upon repeated heating to 160°C. C-1 sample was measured immediately after exposure to ~ 10^{-7} torr in a vacuum and the formation of a micro-leak. It should be noted that all experiments began after a 3-day pumping of the package-opener chamber under vacuum in an ion source, better than 10^{-5} torr. The spectra of the open I-1 sam-
ple were taken after a 5-day evacuation in the package-opener chamber. I-2 sample was measured starting at a temperature of 80°C with holding for one hour at this temperature and subsequent heating to 160°C. After cooling to 80°C, the spectra were again recorded for an hour at this temperature at 15 min intervals.

3. Estimation of residual gas partial pressures by mass spectra

Permissible comparative pressure units are 1 torr = 133 Pa. A residual gas analyzer (RGA) provides registration of atomic mass units (a.m.u.) of elements and chemical compounds in the vapor-gas phase with a resolution of 0.1 a.m.u. Obviously, in order to measure the gas composition inside the sealed enclosure, there are at first recorded the background spectra in a RGA camera (empty chamber), or the spectra of the chamber with the sample mounted on the probe in a given temperature range T. After a micro-leak is formed in the sample package (puncture), peak and total mass spectra in the chamber \( \sum P_{pi} = f(T, t) \) and in the sample in units of pressure \( \sum P_{oi} = f(T, t) \) are recorded. For example, spectra for QRT can be constructed using formula (1) for different T or t:

\[
\sum P_{pi}(QRT) \equiv \sum P_{fi} + \sum P_{oi},
\]

where \( \sum P_{fi} \) is denotes background spectra. There is used an approximately equal symbol (\( \cong \)), because the pumping speed of the vacuum system \( \nu_{VS} \) is not taken into account. Plots \( P_i \) for individual mass numbers \( M \) in sample, show that in order to get the value of the total pressure \( P_0 \) in QRT 435 sample after a puncture at any temperature, you need to take \( \sum P_i \) of all 100 \( M \) and subtract the same amount of 100 \( M \) of the background spectrum and the contribution of the \( P_{bc} \) pumping system with a certain sign:

\[
P_0 = \sum P_i(QRT) - \sum P_{fi} \pm P_{VS}.
\]

By definition, the rate of leak or leak \( \nu \) from a constant volume \( V \) [11] is:

\[
|\nu| = \frac{\Delta P \cdot V}{t}, \quad \text{(torr·cm}^3/\text{s})
\]

where \( \Delta P \) is the change in pressure over time \( t \).

The evaluation of \( P_0 \) by formula (2) requires a complex theoretical and experimental preparation. Here, it is necessary to take into account several factors: attenuation of the flow from a sample as a result of possible absorption of part of molecules by the chamber walls; dissociation of complex compounds in the ion source, as well as losses to the pumping system during the spectrum recording time (100 s). At a minimum, not only calibrated micro-leaks are needed, but also a large number of standard samples with a known gas composition.

Under our conditions, the parameters of the mass spectrometry complex (geometry and mode of operation of the vacuum system, geometry of the thermal probe and the size of a micro-leak in the package of the products) are selected for simple estimation of the partial pressure in vacuum samples. In practice, it is sufficient to sum the partial pressures of gas components recorded by a RGA detector for 100 seconds at intervals of every 0.1 seconds.

The procedure was worked out, firstly, by means of a comparative analysis of data in the table and in [12, figure 1], as well as calculations of heat radiation losses in the author's QRT [13]. The author of the last work indicates the value of these losses within 25% –36% of the total power consumed by the QRT. Thus, the heat loss through the residual air in the QRT (molar mass 29·10^3 kg/mol) is 2-3 mW. This corresponds to pressures from 3·10^{-5} to 4·10^{-4} torr [12]. For most QRTs, the measured pressures are within the reference range (average molar masses of the gas medium in them are 28.7·10^3 kg/mol).

Secondly, the pressure calculated from the mass spectra of the open model was compared with the pressure in I-1 model by means of Bayard-Alpert sensor, equipped with RGA. Numerical values are 3.03·10^{-7} torr and 3.09·10^{-7} torr, respectively.
In literature, calibrated and estimated values of vacuum parameters in mass spectrometry have variation within 10% [14]. Given the similarity rules, i.e. the repeatability of the conditions of manufacture and measurement of the samples, this is sufficient for their comparative analysis.

Figures 1 and 2 show the total pressures of gas components from QRT 163 and QRT 219. These pressures are recorded in the ionization source with increasing probe temperature from 80°C at 15 min. intervals.

To go to pressures inside the samples, it is enough to multiply the numerical values of $P$ in the graphs by a factor of 40, which is equal to the ratio of the volume of the package-opener chamber to the volume of the sample (28:0.7 = 40). According to the diagram, the pressure in the package of QRT 163 at 80°C is $2.36 \times 10^{-4}$ torr; while in QRT 219 it is $2.76 \times 10^{-4}$ torr. Figure 3 shows comparative graphs of recorded QRT 163 pressures and pressures from the background spectra of an empty chamber. At 80°C, the pressure values differ by two orders of magnitude. A similar conclusion can be made for QRT 215 in the graphs in figure 4, which shows the total pressure in the package-opener chamber before the puncture and after the puncture in the sample. In this case, the pressure values at 80°C differ by a factor of 50.

Another group of products was examined in the same mode: heating of sealed samples to 160°C with step-by-step removal of mass spectra, cooling to the next day for ~ 20 hours, the formation of micro-leaks and repeated heating to 160°C with analysis of the spectra. Figure 5 shows the graphs of...
the total pressures for the mass spectra for QRT 215, 315, 343 and 435 after puncture at 200°C and heating for 3 hours to 160°C.

According to the graphs, the estimated pressures in the samples at 80°C, torr are as follows: QRT 215- $4.28 \times 10^{-4}$; QRT 315- $3.36 \times 10^{-4}$; QRT 343- $4.324 \times 10^{-4}$; QRT 435- $2.63 \times 10^{-4}$. These values change a little to 120°C, and during the last hour of heating they increase by 1.5 times. Products are made using the same technology, as indicated by the similarity of their parameters. However, the "nuances" of assembly operations are also visible. Sealing of QRT 215 at the final sealing operation of the technological hole was carried out twice, with filling the package with air before the second sealing. In mass spectra of QRT 435, there is an increased content of hydrocarbons [9], for example, compounds with a mass number of 55. For these reasons, an increase in pressure in the first minutes of heating is observed in the graphs for the indicated spectra (figure 5). Under sustained technological conditions, we observe a smooth change (decrease) in pressure in the QRT 315, 345 for the first 2 hours of heating to 120°C. It is also observed in figure 3 for QRT 163. One can distinguish QRT 219, which is rearranged in another metal-glass package. Additional soldered and adhesive joints did not pass a long-term vacuum annealing. Figure 2 shows fractures in the graph, probably associated with structural transitions in polymer adhesives upon heating.

Attention should be paid to the numerical values of pressure in the considered products at 80°C. Obviously, these parameters are overestimated in relation to the initial ones before recording the mass spectra, because QRT in a sealed state was heated for a long time to 160°C on the first day of measurements. A scheme for adjusting pressure to its real values can be suggested here. According to Figure 1 for QRT 163 it can be seen that the main gas evolution occurs in the range of 120–160°C. The pressure increase here is $1.92 \times 10^{-4}$ torr. The same pressure increase is also probable when the samples are cooled to 120°C, i.e. you can apply the factor 2 ($1.92 \times 10^{-4} \times 2 = 3.84 \times 10^{-4}$). On the other hand, during thermal vacuum degassing of resonator-thermostats after sealing the package, a sorption threshold of about 105°C was detected [1]. Above this temperature, active gas evolution from the elements of micro-assemblies is observed, and below 105°C reverse absorption occurs. The average rate of reverse sorption of gas in the range of 40-100°C is $\approx 5 \times 10^{-9}$ torr·cm$^3$/s. If we accept, for our case, that the adsorption process lasts 10 hours, then by equality (3) we find the pressure drop by $2.26 \times 10^{-4}$ torr. The total pressure increase in the sealed package is $1.58 \times 10^{-4}$ torr ($3.84 \times 10^{-4} - 2.26 \times 10^{-4}$). By this value, the previously found pressure value in QRT 163 at 80°C should be reduced, i.e. the initial vacuum had a level of $7.8 \times 10^{-5}$ torr ($2.36 \times 10^{-5} - 1.58 \times 10^{-4}$). This value is three times less than the measured pressure value. Mass spectra of the gas composition in the C-1 quartz resonator were measured after puncture of the package at 20°C and 3 hours of heating to 160°C. Immediately, we note that the vacuum in QR C-1 at 80°C is by an order of magnitude better than in QRT. The total pressure inside the package is $2.32 \times 10^{-4}$ torr. This is due to the design and technological differences of the products. The C-1 spectra
are characterized by linear increase in the partial pressures of all atoms and molecules in the range of 60-140°C. For all gas components, their partial pressure increases sharply by 3 times when heated from 140°C to 160°C.

4. Experiments with technical models

The internal design of D-1, 3, 5 models has significantly fewer assembly elements, conductive tracks and contact pads, than the QRT in DIL-14 packages. Probably, therefore, the total pressures in these samples at 80°C are of a different order. When calculated by mass spectra, pressure values of $1.07 \times 10^{-5}$ torr were obtained; $4.8 \times 10^{-5}$ torr and $1.0 \times 10^{-5}$ torr, respectively.

Another characteristic feature which can be noted is the high content of molecular hydrogen in D-1 and D-5 models at operating temperature. This was stated in [5], where a hypothesis about the accumulation of H2 and its compounds in pores on the surface of ceramic microplates was out forward.

I-1 and I-2 models with domestic microplates (LTCC) were measured using another method. Since before the sample is punctured the pressure in the ion source is recorded by Bayard-Alpert sensor in RGA at a level of up to $10^{-7}$ torr, the micro-leak is formed at the beginning of heating at 20°C. I-1 sample was heated to 180°C with regular monitoring of the mass spectrum and then cooled to the initial temperature. Figure 6 below shows graphs of the total pressure in the sample for a continuous heating-cooling cycle. The graphs show that at 80°C the pressure is $3 \times 10^{-7}$ torr (heating) and $6 \times 10^{-7}$ torr (cooling), and at 180°C it is $1 \times 10^{-6}$ torr.

There is observed a sharp increase in the total pressure from 120°C to 140°C and the same sharp decline to 160°C, with a further increase in the area of up to 180°C. The glass transition process of unannealed polymer adhesives with a temperature $T_d = 140^\circ C$ [15,16], where $T_d$ is the glass transition temperature, was recorded. Structural transformations of polymer chains in the adhesive mass occur; thus, solid glue becomes soft or rubbery with a sharp release of gaseous components.

In addition, significant resistance to gas flow (Z) in a micro-leak hole was found [11]: $Z = \frac{1}{c}$, is c hole conductivity, l/s. On the graph of figure 6 it is clearly seen that the vacuum system does not have time to pump out the gas evolution products in the sample.

The dynamics of total pressure inside I-2 package after puncture is shown in figure 7. The glass transition effect of adhesives is not clearly visible. It is possible that as a result of thermal vacuum annealing, the structure of an epoxy polymer goes into a stable phase.

The measurement cycle was carried out in the sequence provided below.

The spectrum was recorded before a puncture in the package (point 1 on the bottom graph) at 80°C, then after a puncture (point 2) and after holding for 1 hour (point 3), figure 7. Then, the spectra were
measured after the model was heated to 160°C and after cooling to 80°C. At this temperature, 4 measurements were taken every 15 minutes (points 1-4 on the upper graph).

It is clearly seen that the gas flow is limited by the conductivity of the hole. The pressure at the cooling stage, figure 7, is 3 times higher than at the heating stage. After a needle pierces the cover, the hole has the shape of a channel with a diameter of 1 mm and depth of 0.5 mm.

According to [17, 18], during molecular outflow of gas through the hole, the conductivity of this hole is determined by the formula:

$$ c = \frac{Q}{P_2 - P_1} = 12.1 \cdot \frac{d^2}{L} \cdot a, \text{ l/s}, $$

where $Q$ is the gas flow, l-torr/s; $P_1$ and $P_2$ are pressures in the package-opener chamber and in the product, respectively; $L$ is the length of the canal of a technological hole, cm; $a$ – is tabular coefficient, depending on the ratio $L/d$. In our case, we choose the following values: for $d = 0.01$ cm and $L = 0.05$ cm a - values are not given by the authors, so we use formulas to estimate the conductivity of the hole [11]:

$$ c = \sqrt{\frac{m}{kT}} \cdot d \text{ and } c = 0.256 \cdot d, $$

where $m$ is the molar weight of the gas; $k = 1.38 \cdot 10^{-16}$ erg/K; $T$ is the temperature in degrees Kelvin; $d$ – is hole diameter, cm. The second equality in (5) corresponds to the air flow at the temperature of 293 K. From the equation (5) we find the conductivity of the hole with diameter of 1 mm for air at 353 K: $2.33 \cdot 10^{-2}$ l/s.

Gas desorbing surfaces are divided into categories according to their purity: low, medium and high purity. The corresponding values of specific gas evolution are $10^{-2}$ – $10^{-3}$; $10^{-3}$ – $10^{-4}$; $10^{-4}$ – $10^{-5}$ l·torr/(s·m²). According to our estimates, the geometric area of inner surfaces of I-1 and I-2 models is $S_g = 12$ cm² models. Due to roughness and porosity of the material, the true surface increases by 100–1,000 times [17], $S_i = 100$, $S_g = 1.2 \cdot 10^{-1}$ m². If we denote the specific gas evolution by $q$, then from (5) we can find:

$$ q = \frac{(P_2 - P_1) \cdot c}{S_i}, $$

Let us evaluate the degree of surface cleanliness in I-2 model after a puncture from the graph in Figure 7.

$$ q = \frac{0.1045 \cdot 10^{-5} \cdot 2.33 \cdot 10^{-2}}{0.12} = 2.03 \cdot 10^{-6} \text{ l/torr} \cdot \frac{s}{m^2} $$

Using the resulting $q$ values, a tabular coefficient $a = 0.01$ for formula (4) can be found. In the future research we will calculate the purity of internal surfaces for all products.

An even more interesting and promising technique is the measurement of time dependences of pressure in the space under package at a selected temperature. Figure 8 shows a graph of this dependence at 80°C at the end of cooling. According to the rule of similarity, a similar graph is constructed on Figure 9 for I-2 model at the beginning of heating.

The change in the total pressure over time is approximated by an exponential function:

$$ P = P_H \cdot e^{-\frac{c \Delta t}{B}}, $$

where $P_H$ is initial measurement pressure, torr; $c$ is hole conductivity, in l/s; $B$ is a constant, liter; $\Delta t$ is a time step of measurements, minute.

Figures 8, 9 are supplemented by graphs $Ln(p) = f(\Delta t)$ according to formula (7). The analysis of the graphs shows that a sharp drop in pressure during the first 30 minutes does not determine the gas evolution inside, but is a consequence of establishing an equilibrium flow through the hole due to the pressure difference $P_2 - P_1$. Gas emission levels are set only at the end of the first hour, when the ratios $P (45\text{min})/P(60\text{min})$ approach the same value of 0.985 for both graphs. It is obvious that further the
pressure will decrease, following rather complex laws of diffusion of gas molecules from adhesives [19]. Therefore, we again choose a simple approximation in the form of an n-degree parabola for estimating the parameters of physical processes in a vacuum [20].

\[ P_{n+1} = P_n \ast K^n, \]  

(8),

where \( n = 1, 2, 3 \ldots \) are measurement numbers after establishing a quasi-uniform gas flow; \( K \) is transformation coefficient or virtual time coordinate, in our case \( K = 0.985 \). On the right-hand side of formula (8), the second term, for example, \( K_0 \) is missing, which in practice should limit pressure reductions. Firstly, a mass spectrometer has a sensitivity limit, and on the other hand, the pressure period is retained during vacuum evacuation through a micro-leak.

\[ P_{n+1} = P_n K^n + K_0 \]  

(9)

This refers to the dynamics of measurements, and we are interested in the dynamics of gas evolution in the space under package. According to formula (8) in 48 hours the pressure in I-2 package decreases to the level of \( 4.64 \times 10^{-6} \) torr, and the average rate of gas desorption in the next 15 minutes – to \( 5.4 \times 10^{-12} \) torr cm\(^3\)/s.

**Conclusions**

Measurement data according to the considered procedures are given in tables 1 and 2. In addition, the tables include the requirements for the vacuum density of the package as a value of average rate of gas filling of the products through the walls and welds, as well as a result of desorption of the gas fraction from internal surfaces during tests. Data on the amount of moisture and hydroxyl group OH in sealed packages of products at the operating temperature of 80 °C are provided.

It should be noted that the average gas-filling rate is only partially equivalent to the vacuum density of the packages. The real values of the last parameter are probably by an order of magnitude better. By definition, a compound through which leak does not exceed a predetermined level is considered to be vacuum. For QRT this level shall not exceed \( 5.0 \times 10^{-3} \) torr during operation [12]. With this in mind, the operating times of serial products are predicted. C-1 resonator does not contain internal heating elements and is sealed in vacuum with bladed pumping. Process models have been used to prove that LTCC plates can be used. Only the storage time of I-2 prior to mass spectrum analysis (3 months) is known. However, until present several working QRTs have been obtained using LTCC technology (e.g. I-1 and I-2). Relative daily instability of generator circuits based on these QRTs is better than \( 1 \times 10^{-13} \) after annual tests.

The projected operation time of QRT is 11.6–19.0 years (table 1) which is the minimum time reserve. Pressure in the packages according to the text [18] is measured after a long-term heating up to
160 °C and subsequent cooling. The terms of operation of the QRT in operating modes are probably 2−3 times more. However, the forecast does not take into account “degradation of electrical parameters as a result of corrosion of metal contacts and conductors” [18]. The authors attribute this to the presence of moisture and the hydroxyl group of OH in the space under package: “according to the standard OST 11073.013-2008 used in microelectronics, the moisture content inside integrated circuit (IC) package should be no more than 0.5 volume percent at a temperature of 100 °C. The measurements indicated the presence of OH groups in the amount of 0.1% to 0.35% in the IC (“Micro-assembly”, the city of Zelenograd), regardless of the number of H₂O molecules. The main source of OH groups are adhesive and polymer structures used to fix elements in the package. The chemical activity of OH hydroxyl group exceeds the activity of water molecules; therefore, when performing tests for moisture content, it is necessary to control the concentration of OH molecules.

**Table 1.** Parameters of QRT, QR C-1, made by serial technologies.

| Parameters                        | QRT215 | QRT315 | QRT343 | QRT435 | QR C-1 |
|-----------------------------------|--------|--------|--------|--------|--------|
| Package pressure at 80°C, torr    | 4.28·10⁻⁴ | 3.36·10⁻⁴ | 4.32·10⁻⁴ | 2.63·10⁻⁴ | 2.32·10⁻⁵ |
| Vacuum cleanliness of internal surfaces, l·torr/(s·m²) | 8.31·10⁻⁵ | 6.52·10⁻⁵ | 8.38·10⁻⁵ | 5.1·10⁻⁵ | 6.75·10⁻⁶ |
| Average speed of gas-filling of the tight package, torr·cm³/s | 9.66·10⁻¹² | 7.58·10⁻¹² | 9.94·10⁻¹² | 5.94·10⁻¹² | 1.66·10⁻¹² |
| Predicted product function time, years | 11.6 | 14.9 | 11.58 | 19 | 48.6 |
| Moisture content, in volume %     | 2.5 | 2.97 | 2.59 | 4.65 | 0.78 |
| Content of hydroxyl group OH, vol.% | 4.04 | 1.79 | 1.61 | 3.25 | 0.95 |

**Table 2.** Parameters of QRT at the stage of checking LTCC microplates.

| Parameters                        | D1      | D3      | D5      | I-1     | I-2     |
|-----------------------------------|---------|---------|---------|---------|---------|
| Package pressure at 80°C, torr    | 1.07·10⁻⁵ | 4.8·10⁻⁵ | 1.0·10⁻⁵ | 3.03·10⁻⁷ | 1.04·10⁻⁵ |
| Vacuum cleanliness of internal surfaces, l·torr/(s·m²) | 3.12·10⁻⁶ | 1.68·10⁻⁵ | 2.91·10⁻⁶ | open | 2.03·10⁻⁶ |
| Average speed of gas-filling of the tight package, torr·cm³/s | 2.42·10⁻¹³ | 1.08·10⁻¹² | 2.26·10⁻¹³ | - | 5.4·10⁻¹² |
| Moisture content, vol.%           | 7.18    | 2.75    | 12.1    | 1.18    | 1.89    |
| Content of hydroxyl group OH, vol.% | 3.24    | 4.57    | 5.5     | 0.57    | 0.85    |

1. It has been established that design and technology solutions of the QRT assembly in DIP-14 and DIL-14 packages (annealing at 160°C in vacuum for 40 hours) provide pressure of (2.63-4.28)·10⁻⁴ torr inside the packages. Even under critical test conditions, a high degree of vacuum purity is maintained within the products.

2. The moisture and hydroxyl levels of OH, ranging from 0.57% to 12.1%, were surprisingly high. This is probably due to overheating of serial products during mass spectrum measurement processes, as well as weakening of model annealing modes.

3. Vacuum parameters of C-1 quartz resonator are by an order of magnitude better than for QRT. The process model parameters are close to this level. It is worth mentioning that there was identified the pressure of one order in the models with LTCC plates of DuPont and JSC RPC "Istok" companies. For example, the I-2 model life by approximation formulas (8, 9) is 48.6 years.

4. As shown in figures 1, 2, 3, 5 it can be concluded that external heating of QRT in the range of 80-120 °C is the optimal mode of accelerated ageing. In addition, the upper temperature limit provides greater time savings during final sealing operations of the package.

The set objectives are solved. The most difficult tasks which are set for the future research are as follows: the development of methods of calculation of energy of chemical reactions activation in
evacuated packages, as well as processes of adsorption, desorption and diffusion of gas components on internal elements of structures.

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