

# The method of the research of residual gases in a tight case of quartz resonators

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**Abstract.** Mass spectrometric analysis of closed-volume gases of quartz resonators-thermostats emitted by the materials used in the installation of the device. A measuring complex with a vacuum of  $10^{-5}$ - $10^{-6}$  Pa has been developed. The mass spectra of the residual gases were obtained before the depressurization of the products in the DIL-14 housing. The temperature range of the study is 20÷160 °C.

## 1. Introduction

The increase of integration degree of modern piezoelectric products places high demands on the quality of the surface of crystals and the internal surfaces of the housings to limit negative surface processes leading to degradation of electrical parameters and corrosion of metal contacts and conductors. Destructive characteristics of the medium, including high vacuum (when operating in extreme space conditions), large temperature differences, mechanical or chemical factors can adversely affect the electrical parameters of the product [1]. The operation of microelectronic devices is adversely affected by adsorbates, moisture condensate, hydrogen, oxygen, hydrocarbons, ammonia, halides and other volatile substances [2, 3]. Mass spectrometric analysis of QRT confined gases emitted by the materials used in the installation of the device will determine the substances with the highest gas emission and, if possible, will eliminate or at least minimize their presence.

The aim of the work is to study the composition of the residual gases of the subcavity space of thermostatically controlled quartz resonators (QRT) with identified defects – displacement of the working frequency - by the mass spectrometric method.

## 2. Experimental technique

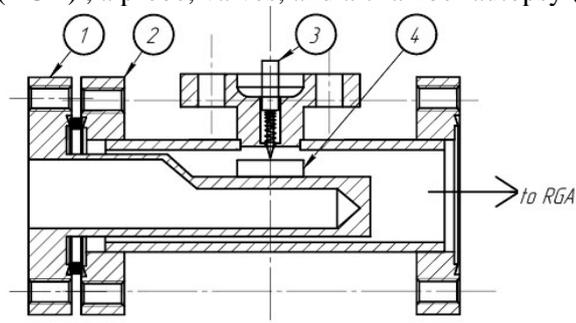
To study the composition of gases of the closed volume of QRT, two QRT samples were obtained. They contain a resonator and a control circuit (sample No. 219, 163), have malfunctions (sample No. 219 - offset from the operating frequency of 10 MHz by 137 Hz, sample No. 163 - lack of generation of the operating frequency).

One of the controlled parameters of QRT-based reference generators is the stability of the operating frequency, which is set with an accuracy of  $10^{-9}$ , over the entire life of the product, therefore, it is necessary to determine the reasons for the frequency deviation from the operating value. Possible causes of deviations may be gas products adsorbed on the surface of the QRT crystal from materials used in the installation of the resonator and during packaging. To determine the composition of adsorbates and possible chemically active particles, studies of the spectrum of residual gases of a closed volume QRT are carried out.

Measurement process: the product is placed in a vacuum system, after pumping to high vacuum, it is heated to 80°C (operating mode), then to 160°C (annealing mode). In the opening chamber is the ion source of the mass spectrometer. Upon reaching the required background level, the piercing device creates a micro-leak in the QRT housing. The vapor-gas mixture through the hole enters the ionization region of the mass spectrometer. After this, a control heating of the sample to 80°C and removal of the mass spectrum occurs.



The vacuum system consisted of a high-vacuum magnetron pump NMDO-0.25-1 (NORD 250), a PMM-32-1 magnetron sensor as part of a VMB-8 vacuum gauge, a 2NVR-5DM forevacuum pump, an XT-100 residual gas analyzer (RGA), a probe, valves, and a chamber autopsy (figure 1).

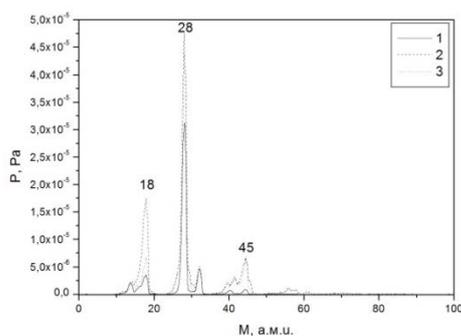


**Figure 1.** The scheme of the opening chamber: 1 – the probe with a heater and a thermocouple, 2 – the body of the opening chamber, 3 – the needle, 4 – the body of the product.

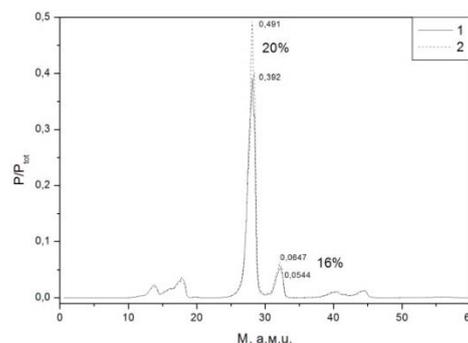
To study the samples, a probe (1) was mounted to the mass spectrometer (figure 2). The probe contains a heater, a thermocouple (T-type thermocouple) (not shown), an opening chamber body (2), a puncture needle (3), and QRT (4). The probe with the sample is placed in the opening chamber, after which evacuation to  $\sim 10^{-5}$  Pa occurs, then the needle, under the influence of a micrometer screw (not shown), punctures the sample, after which the mass spectra of the residual gases are taken.

### 3. The Results and discussion

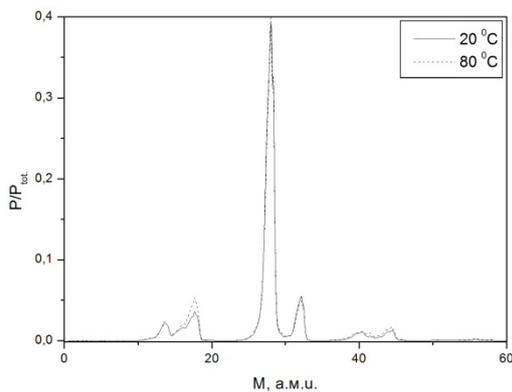
After placing the probe with the generator housing (No. 219) in the vacuum system and pumping it to  $\sim 10^{-5}$  Pa, the spectrum of the residual gases of the vacuum system was taken to puncture (background) at  $T = 20^{\circ}\text{C}$ ,  $80^{\circ}\text{C}$ ,  $160^{\circ}\text{C}$  (figure 2). Figure 2 shows that there are peaks of 18 masses of water ( $\text{OH}^+\text{-H}$ ), 28 masses of nitrogen and (carbon monoxide) ( $\text{N}_2^+(\text{CO})$ ), 32 ( $\text{O}_2^+$ ) and 45 masses, peaks heavier than 60 masses are absent, therefore, further measurements will only be carried out to this value. Heating the sample to  $80^{\circ}\text{C}$  leads to intensive evaporation of water vapor from the surface of the sample during continuous pumping, then the intensity of this mass decreases and at a temperature of  $160^{\circ}\text{C}$  the peak height approaches the background value. The intensity of the peak of 45 mass during heating becomes greater, which indicates a continuous flow of this compound from the surface of the housing of the chip. Figure 3 shows the reduced (to full pressure in the chamber) mass spectrum of residual gases, the background at  $T = 20^{\circ}\text{C}$  after the puncture. There was slight increase in the peaks of nitrogen (20%) and oxygen (16%), possibly due to the increased ( $10^{-2}$  Pa) pressure inside the body of the product, compared with the pressure in the chamber ( $10^{-5}$  Pa). Figure 4 shows the mass spectrum of the residual gases after a puncture at  $T = 20^{\circ}\text{C}$ ,  $80^{\circ}\text{C}$ . Slight increase in the water vapor in the spectrum occurred due to its desorption from the inner surface of the QRT casing.



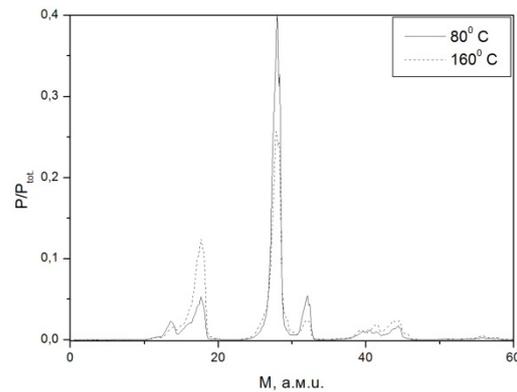
**Figure 2.** Range of residual gases before puncture at  $T = 20^{\circ}\text{C}$  (1),  $80^{\circ}\text{C}$  (2),  $160^{\circ}\text{C}$  (3).



**Figure 3.** Range of residual gases before and after the puncture at room temperature.



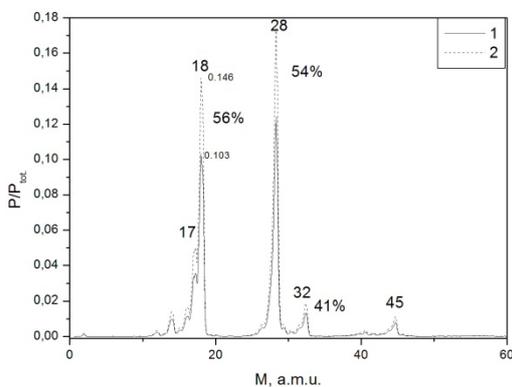
**Figure 4.** The spectrum of residual gases after a puncture at room temperature and 80°C.



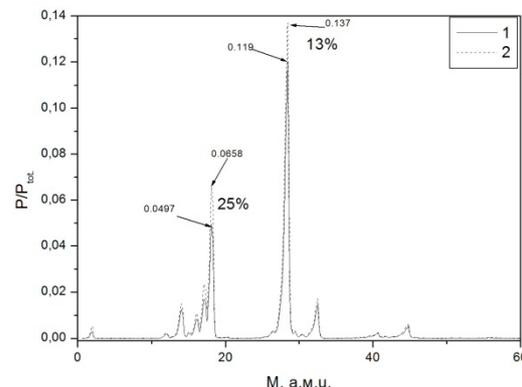
**Figure 5.** The spectrum of residual gases after a puncture at T = 80°C and 160°C.

Figure 5 shows the mass spectrum of the residual gases after a puncture at T = 80°C, 160°C. The graph shows the increase in the peak of water vapor ~2 times and peaks after 40 mass, which indicates the evaporation of water and substances from the internal volume of the sample upon heating.

Figure 6 shows the spectra of residual gases of sample No. 163 before and after the puncture at T = 20°C. There was increase in the peak of water by 56%, nitrogen by 54%, and oxygen by 41%, which indicates either the presence of contaminants in the sample or high pressure of residual gases inside the body of the product compared to sample No. 219. When the sample is heated to 80°C, the increase in the peaks of water and nitrogen occurs (figure 7).

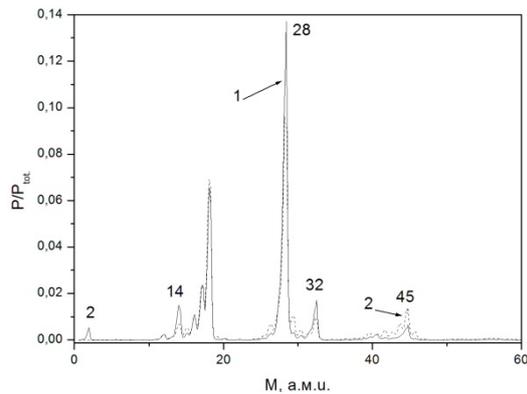


**Figure 6.** Range of residual gases before and after puncture at T = 20°C.

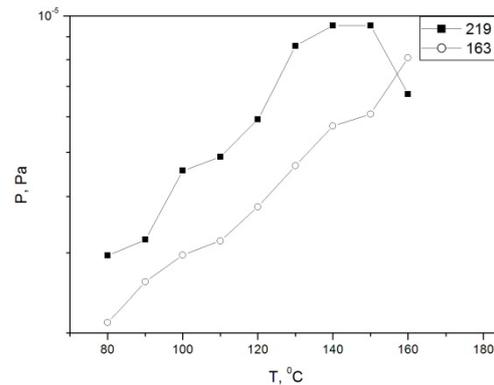


**Figure 7.** Range of residual gases after puncture at T = 20°C, 80°C.

Figure 8 shows the spectra of residual gases after a puncture at T = 80°C, 160°C. At T = 80°C, peaks of 2 and 14 masses, as well as nitrogen and oxygen molecules, are observed. With increasing temperature, the proportion of water vapor does not increase, but there is increase in the proportion of 45 mass in the total pressure. Figure 9 shows the dynamics of the partial pressure of water vapor after a puncture for arr. No. 163 and 219. It can be seen that the water vapor pressure for 219 samples increased with temperature, then, after 130°C, it started to decline due to desorption of contaminants from the walls of the QRT body and, apparently, from the surfaces of the QRT elements. A similar trend was observed in other experiments [4]. At the same time, the partial pressure of water vapor for 163 is constantly growing, which indicates high moisture content in this sample, perhaps this caused the product to malfunction.

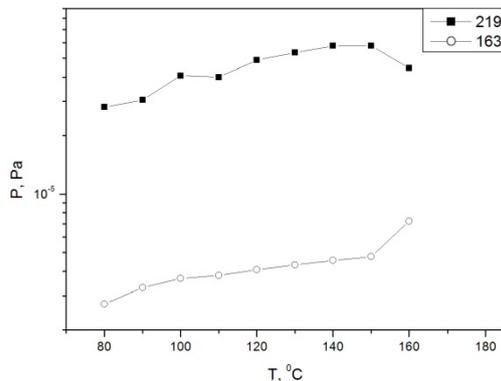


**Figure 8.** The spectrum of residual gases after a puncture at  $T = 80^{\circ}\text{C}$  (1),  $160^{\circ}\text{C}$  (2).

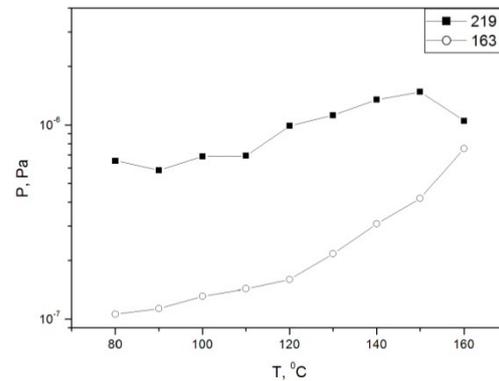


**Figure 9.** The dynamics of the partial pressure of water vapor in samples No. 219 and No. 163.

Figure 10 shows the dynamics of the partial pressure  $\text{N}_2^+(\text{CO})$  of samples No. 163 and 219. It is shown that at  $130 - 140^{\circ}\text{C}$  the pressure experiences a local maximum, after which it decreases, unlike sample No. 163, in which  $\text{N}_2^+(\text{CO})$ , although less by the order of magnitude, but the pressure is constantly growing. Figure 11 shows the dynamics of the partial pressure of a component with 45 mass, it is also seen here that the pressure for sample No. 163 is constantly growing, the source is adhesive and polymer structures used to fix elements in the housing. Comparative spectra of defective samples show the presence of various causes of malfunctions.



**Figure 10.** The dynamics of the partial pressure  $\text{N}_2^+(\text{CO})$  of samples No. 163, 219.



**Figure 11.** The dynamics of the partial pressure of 45 mass samples No. 163, 219.

A search for 45 masses on the basis of NIST2008 (National Institute of Standard and Technology) allowed us to identify several compounds that can get inside the case during the preparation and manufacture of QRT. This is  $\text{HCONH}_2$  (Formamide). Formamide is used as a raw material in the production of hydrocyanic acid (dehydration of formamide) and formic acid (by hydrolysis of formamide), it is also a part of some adhesives.  $\text{CH}_3\text{NO}$  (Nitrosomethane) – Nitromethane is a popular solvent in organic and electroanalytical chemistry.  $\text{C}_2\text{H}_5\text{NH}_2$  (Dimethylamine) – is used to obtain substances used in the manufacture of rubber. The surfactant dimethylamine oxide – lauryl is contained in soap and detergents [5]. The presence of such compounds is understandable, since the samples go through the stages of cleaning and etching, in the absence of annealing, they can still be inside the QRT case. Dimethylamine is used in the production of rubber, possibly its content inside the volume, due to the fact that adhesives and sealants are also used in the production of QRT.

## Conclusion

As a result of the analysis of the spectra, it was found out that the main pollutants are nitrogen-containing compounds and water vapor. The presence of water in the devices transfers the existing contaminants that cause corrosion and malfunctions. The corrosion process is enhanced by the presence of an electric current in the circuit of a working microcircuit. Apparently the corrosion of metal contacts in a closed QRT volume led to disruption of the operation of sample No. 163. To eliminate water vapor, it is enough to withstand QRT under vacuum at 120<sup>0</sup>C – 130<sup>0</sup>C for a long time, at least 2 hours. Removing nitrogen-containing compounds requires annealing of QRT under high vacuum at temperatures close to 160<sup>0</sup>C. It is shown that the mass spectra for various malfunctions of the generation of the operating frequency also differ. A specific answer can be given by an experiment, the purpose of which is to identify such pattern. To do this, it is necessary to divide the product groups by faults, measure each such fault for statistics, conduct measurements of the spectrum of residual gases of the sealed volume of serviceable QRTs group. Then conduct a comparative analysis of the results.

## References

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