

Residual Gas Analysis in Color Cathode Ray Tubes

Audrius GIEDRAITIS^{1*}, Sigitas TAMULEVIČIUS^{1,2}, Vytautas ZABARSKAS³,
Igoris PROSYČEVAS², Kęstutis ŠLAPIKAS², Rimas GUDAITIS²

¹Department of Physics, Kaunas University of Technology, Studentų 50, LT-51368 Kaunas, Lithuania

²Institute of Physical Electronics, Kaunas University of Technology, Savanorių 271, LT-50131 Kaunas, Lithuania

³AB "Ekranas", Elektronikos 1, LT-35116 Panevėžys, Lithuania

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Experimental equipment for registration of residual gas spectra in color cathode ray tubes (CCRT) and effective method of analysis of getter behavior is described. The construction of computerized facility for CCRT residual gas investigations and analysis of four types (A33EKC, A48 EKB and 51EKE(EJJ)) CCR tubes are presented. The quadrupole mass spectrometer (QMS) allows partial pressure measurements of the gases contained inside the tube. Outgassing process kinetics in the CCRT systems is described by residual gas dependence on time. These investigations allow predicting getter surface and volume changes in the different gas ambient, certificating properties of getters agents and to trawl of the new getters agents.

Keywords: residual gas analysis (RGA), mass spectrometry, color cathode ray tube (CCRT).

1. INTRODUCTION

The knowledge of the atmosphere composition inside TV tubes is a fundamental issue to investigate the characteristics of these devices and to determine the possible reasons of some lack of performances [1 – 9]. The term “residual gas” refers to those gases remaining in a vacuum system when the majority of the atmosphere previously occupying the vessel has been pumped out. It is often found that changes in the residual gases can dramatically affect the macro processes taking place in the vacuum system. The technology of any vacuum equipment is associated with the appropriate choice of highly outgassing substances for electrodes and usable structural details [1, 2]. Especially this problem is topical for CCRTs, computer displays that exploitation are more than thousands of hours. It is possible to improve the quality of materials or use getters, which allow to decrease the residual gases of equipment, in order to assure long-term vacuum and the stability of electrical and emission parameters. It's very important to evaluate outgassing phenomena in the vacuum equipment, that are associated with heating of cathode or structural details and etc.

Frequently encountered problematical residual gas species include oxygen, water vapour and hydrocarbons. Residual gas analysis in vacuum equipment is very well known. It is used for accelerated life test of cathodes, heaters and for materials used in vacuum systems (glass, steel) up to 1050 °C by quadrupole mass spectrometer (QMS) [4 – 5]. The main residual gas components in the high temperature were H₂O, H, CO and N [6], but at the lower temperatures only: H₂O, H₂, CO, N₂ and CO₂ [6–8].

The investigation and analysis of CCRT residual gas spectra in four types (14, 15, 20 and 21 inch) of TV tubes produced in the different technological regimes, and analysis of getter behavior is the aim of this work.

2. EXPERIMENTAL

2.1. Experimental set-up

A schematic diagram of computerized facility used for investigations of CCRT residual gases in accordance with SAES Getters experience [7, 8] is shown in Fig. 1.

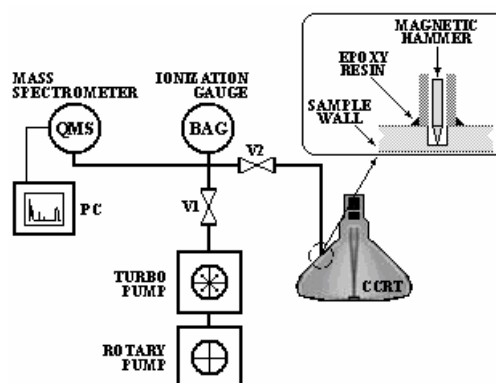


Fig. 1. Experimental set-up for RGA on CCRTs. PC – personal computer, V1 and V2 – valves, QMS – quadrupole mass spectrometer, BAG – Bayard-Alpert ionization gauge

The gas analyzer is a Quadrupole Mass Spectrometer (QMS), which allows partial pressure measurement of the gases contained inside the tube under test. Its operating range is comprised between 10⁻³ Pa and 10⁻⁹ Pa and it is calibrated for each gas. Ionization gauge (BAG) is placed in the manifold connecting the analytical area to the sample, to measure the total gas pressure within the tube, just after its opening. The metal valve (V1) connects the analytical system to the pumping system. Another bakeable metal valve (V2) divides the vacuum system into two parts, which are respectively called sample side and analyzer side.

A jointed steel manifold connects the vacuum system to the sample tube by a known “break in” technique [9].

*Corresponding author. Tel.: +370-37-313432; fax.: +370-37-314423.
E-mail address: audrius.giedraitis@stud.ktu.lt (A. Giedraitis)

The connection of the sample to the vacuum bench and the “break in” system are realized as follows, (see Fig. 1):

1. A window is made in the glass wall of the sample by ultrasonic drilling until a thin diaphragm (about $5 \cdot 10^{-5}$ m) is left;
2. The jointed steel manifold is placed onto the CCRT, after the introduction of a magnetic hammer carefully laid on the glass diaphragm;
3. A jointed steel tube is finally welded to the wall of the sample by means of an epoxy resin.

After the connection of a new sample, the bench is outgassed to restore the optimal background pressure. Valve (V2) is kept closed during the substitution of the sample: using this configuration, it is possible to expose to the air the sample side only, thus maintaining always under pumping the mass spectrometer.

The system is baked 8 hours at 250°C to reach a final pressure in the low range of 10^{-4} Pa or less. The pressure detected inside the tubes (typically in the range of 10^{-5} Pa or lower) is in general significantly lower than pressure of system, because the vacuum inside of tube is better than vacuum reached in our analytical system. The gas compositions for different TV tubes are very different. In any case, the rise of pressure due to the outgassing of the system walls is measured before each test; taking into account of this contribution it is possible to obtain results not affected by the background conditions.

2.2. Test procedure

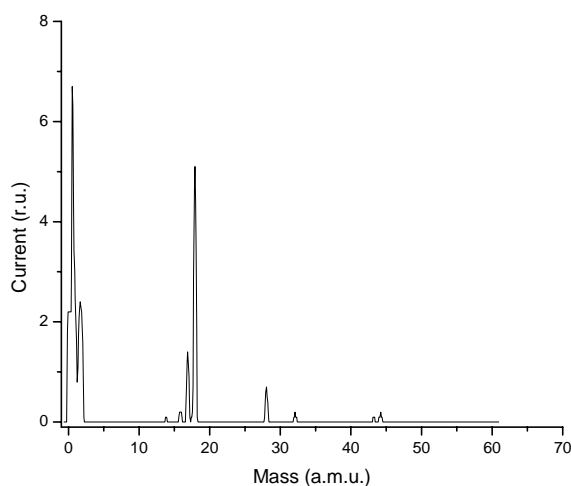
After the CCRT sample is connected to the manifold, baking and outgassing at 250°C takes place for 8 hours. Residual gas analysis measurements are carried out in static conditions, i.e. without any external pumping: therefore, valve (V1) is maintained closed for the complete duration of the tests (Fig. 1). At the end of the baking process, when the cooling of the vacuum system is completed, the valve (V1) is closed, (V2) is opened, and the rise of pressure is observed. The residual gases ($\text{H}_2 = 2$ a.m.u., $\text{He} = 4$ a.m.u., $\text{CH}_4 = 16$ a.m.u., $\text{H}_2\text{O} = 18$ a.m.u., CO and $\text{N}_2 = 28$ a.m.u., $\text{O}_2 = 32$ a.m.u., $\text{Ar} = 40$ a.m.u., $\text{CO}_2 = 44$ a.m.u.) currents due to the outgassing of the system walls is measured using the mass spectrometer QMS (Fig. 2). The term (a.m.u. = $= 1.66055 \cdot 10^{-27}$ kg) is atomic mass unit – the unit used in RGA to compare the mass of particles (atoms, fragments, molecules).

The outgassing evolution is recorded by QMS for about 30 minutes: this duration can in fact be considered sufficient to determine the outgassing trend as a function of time. After a short evacuation of the system, the glass diaphragm is broken by means of the metallic hammer. The partial pressures of residual gases is read by the ionization gauge BAG and the total pressure inside the tube can be approximately determined by summarizing these partial pressures.

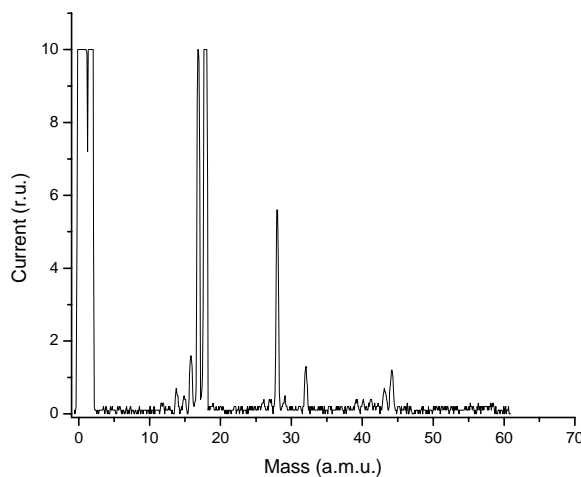
The standard test schedule of CCRT residual gas is as following [7, 8]:

1. Residual gas analysis, when CCRT switched on (duration is about 30 min.);
2. Evaluation of the pressure evolution during the CCRT cathode is heated (duration is about 1 hour).

3. Measurement of the pressure evolution after the cathode switching off (duration is about 1 hour).



a



b

Fig. 2. Typical CCRT residual gas mass spectra, measured for A33EKC class tubes. Sensitivity factor of a device is: (a) 10^{-12} and (b) 10^{-13}

Based on the SAES Getters experience, the duration of these tests should be considered sufficient to give a complete description of the gas evolution inside the CCRT. Measured ion currents, mass spectra, are characteristic of gas composition for each step of analysis and help to perform qualitative analysis. Typical CCRT residual gas mass spectra for the A33EKC (14 inch) class tube registered for two ranges of sensitivity factor are presented in Fig. 2.

2.3. Calculation method

At the end of RGA test procedure we have more than 30 mass spectra for each CCR tube. The currents recorded by the mass spectrometer should be transformed to the partial pressure values.

Partial pressures p_{parc} for different components were calculated as follows:

$$p_{\text{parc}} = \frac{k \cdot I_p}{J}, \quad (1)$$

where p_{parc} is the partial pressure, k is the relative sensitivity factor of residual gas, J is the sensitivity factor of the device ($J = 2 \cdot 10^{-3}$) and I_p is the residual gas ion current.

Sensitivity factors for different gases are shown in Table 1. The indicated partial pressure of a peak on mass spectrum should be divided by the relative sensitivity factor to obtain the “true” partial pressure i.e. that pressure which correctly indicates its actual abundance in the gas sample.

Table 1. Sensitivity factors for different gases registered in color cathode ray tube

Residual gas	Mass (a.m.u.)	Sensitivity factor	Residual gas	Mass (a.m.u.)	Sensitivity factor
H ₂	2	0.7	CO	28	1.09
He	4	0.23	N ₂	28	1.00
CH ₄	16	1.08	O ₂	32	0.62
H ₂ O	18	1.17	Ar	40	0.8
Ne	20	0.24	CO ₂	44	0.9

In the statistical analysis of experimental data we have used the Shapiro-Wilk test [10]. The Shapiro-Wilk test is a test for normality (for the fit of the normal distribution) and calculates a W statistic that tests whether a random sample, x_1, x_2, \dots, x_n comes from (specifically) a normal distribution. The test statistic is W , roughly a measure of the straightness of the plot. The closer W is to 1 the more normal the sample is.

The W statistic is calculated as follows:

$$W = \frac{\left(\sum_{i=1}^n a_i x_{(i)} \right)^2}{\sum_{i=1}^n (x_i - \bar{x})^2}, \quad (2)$$

where $a = (a_1, a_2, \dots, a_n) = m' V^{-1} [m' V^{-1} V^{-1} m']^{-1/2}$, $m' = (m_1, m_2, \dots, m_n)$ is the vector of expected values of standard normal order statistics, V is the n by n covariance matrix, $x' = (x_1, x_2, \dots, x_n)$ is a random sample, and $x_{(1)} < x_{(2)} < \dots < x_{(n)}$.

3. RESULTS AND DISCUSSIONS

The residual gas composition and variation during outgassing, cathode heating and etc. was checked experimentally for four types (A33EKC, A48 EKB and 51EKE(EJJ)) CCR tubes. Main investigations of residual gas were done with A33EKC color cathode ray tubes. Typically the residual gas partial pressure dependence on time consists of several parts (Fig. 3 – 5):

First point. Residual partial gas curves are started with registration of residual gas in after chamber heating and degassing process.

Other part of residual gas dependence on time is attributed to the system degassing process, when valve of pump is closed. The rise of pressure due to the outgassing of the system walls is measured experimentally (Fig. 3 – 5). One can see increase of amount of H₂, He, CH₄, H₂O, CO,

N₂, O₂, Ar and CO₂, but oxygen amount in this region is decreased. This is due to oxygen dissociation and extra amount of CO and CO₂ formation in ambient of ionisation chamber.

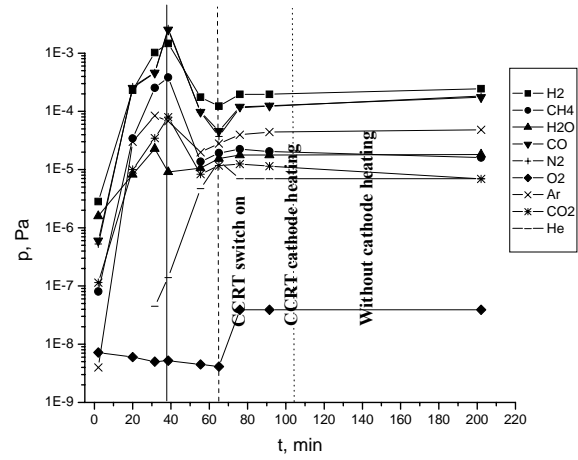


Fig. 3. Typical residual gas partial pressure dependence on time

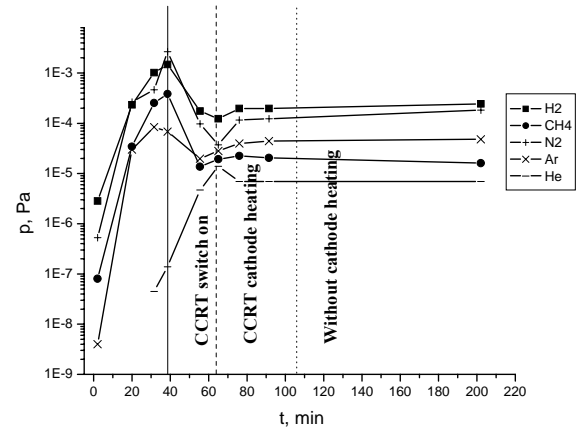


Fig. 4. Residual gases (H₂, CH₄, N₂, Ar, He) partial pressures dependence on time

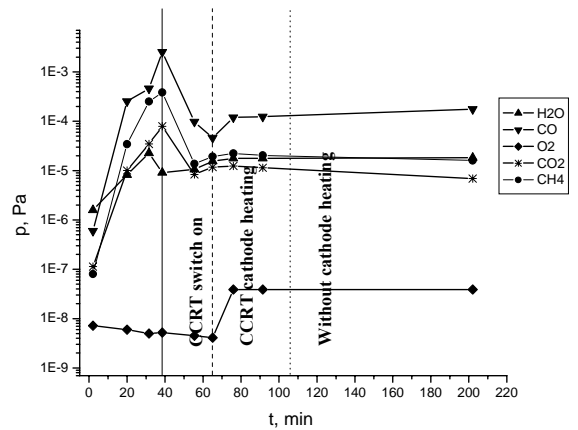


Fig. 5. Residual gases (H₂O, CO, CO₂, CH₄) partial pressures dependence on time

Solid vertical line (CCRT switched on) is attributed to CCRT connections to the system. Dynamic equilibrium between vacuum system and CCRT is established after

about 30 minutes due to residual gas absorption by CCRT getter. In this regime variation of residual gas pressure is dependent only on getter's sorption phenomena. Helium as residual gas component appears only in this region. Getter does not adsorb it and its pressure increases.

Dashed vertical line (CCRT cathode heating). It corresponds to the CCRT heating voltage switching on. When CCRT heating is switched on, partial pressures increase commonly up to 20% (except for helium and oxygen). They become stable after 10–15 min of degassing process. Extra amount of oxygen is a product of CCRT cathode and electronic optical system degassing process.

Dot vertical line (without CCRT cathode heating). This region is registered when CCRT cathode is switched off. This part of residual gas variation represents stable work of the getter by only weak variation of different gases.

An overall view of the RGA results shows that partial pressures of detected active gas as H_2 , CO , CO_2 and N_2 in the analysed CCRT were higher than 10^{-6} Pa. The noble Ar and He gases were detected in the most of investigated CCRT. The partial pressure for argon was about 10^{-8} Pa and helium – 10^{-7} Pa. For molecular oxygen it was about 10^{-9} Pa. These partial pressures are provided by the getter absorption within CCRT and from this point of view all the components of residual gas can be divided in three categories:

1. Active gases (H_2 , N_2 , O_2 , H_2O , CO , CO_2);
2. Noble gases (He , Ar);
3. Hybrid category (CH_4 and hydrocarbons).

The total pressures of fifteen analyzed A33EKC color cathode ray tubes in the range from $8.58 \cdot 10^{-5}$ Pa to $1.04 \cdot 10^{-3}$ Pa are shown in Fig. 6. Statistical analysis of experimental data was done by PC program "Business SPSS9". Experimental data were normalised by standard Shapiro-Wilk criteria.

Results of statistical analysis show that experimental data of 15 analysed CCR tubes are distributed by non-normal distribution law. The Shapiro-Wilk criteria $W = 0.32$. The minimum total pressure $p = 8.58 \cdot 10^{-5}$ Pa was observed for CCRT No.13 (after 3000 work hours). The maximum total pressure $p = 1.04 \cdot 10^{-3}$ Pa – in CCRT No.6 (that has passed small regeneration). Average total pressure of all investigated A33EKC CCRTs was $3.04 \cdot 10^{-4}$ Pa and its root mean square was $3.29 \cdot 10^{-4}$ Pa.

From the statistical data analysis we have found that only three CCRT of all 15 CCRT were with high total pressure. They represented critical cases of CCRT technology processes (as small regeneration of CCRT or emergency shutdown of pumping line at the technological cycle). In the following analysis we excluded these three CCRT and detailed analysis of experimental data was done only for 12 CCRT. From this data analysis we found that the minimum total pressure was observed in CCRT No. 13 (after 3000 work hours, $p = 8.58 \cdot 10^{-5}$ Pa) and the maximum – in CCR tube No.2 ($p = 2.94 \cdot 10^{-4}$ Pa). Average total pressure of 12 investigated CCRT was $1.49 \cdot 10^{-4}$ Pa and its root mean square was $6.44 \cdot 10^{-5}$ Pa. Fig. 7 shows a histogram of 12 analysed CCR tubes. The frequency shows how many CCR tubes passed in a particular range of pressure.

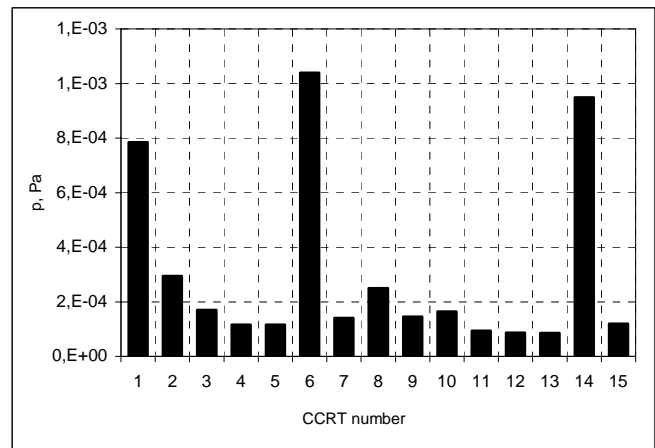


Fig. 6. The distribution of total pressures within A33EKC CCR tubes

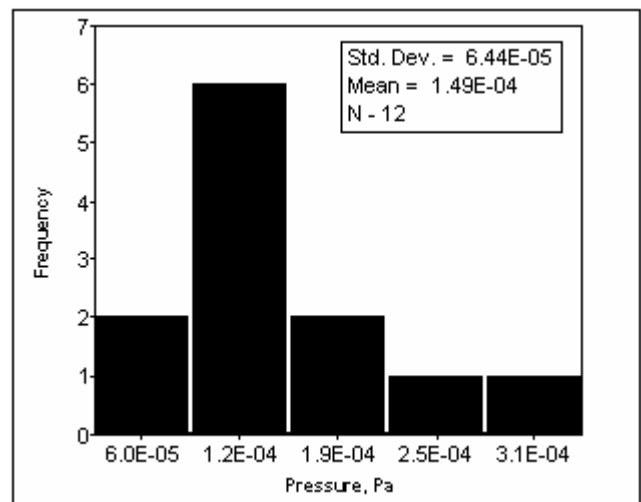


Fig. 7. Histogram of 12 A33EKC CCR tubes total pressures

One can see that according to the normal plot (Fig. 8) normal distribution law describes experimental data of these 12 CCRT. The Shapiro-Wilk criteria $W = 0.85$.

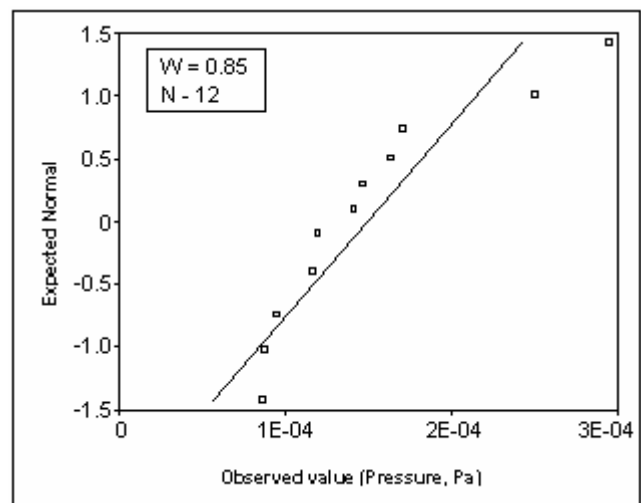


Fig. 8. Normal plot of 12 A33EKC CCR tubes total pressures

4. CONCLUSIONS

1. Residual gas composition of CCRT and variation with time could be investigated respectively using a quadrupole mass spectrometer (QMS).
2. The residual gas composition and variation was checked experimentally for four types (A33EKC, A48 EKB and 51EKE(EJJ)) CCR tubes. In the analysed CCRT partial pressures of detected active gases as H₂, H₂O, CO₂, CO, and N₂ were higher than 10⁻⁵ Pa. For molecular oxygen it was 10⁻⁸ Pa.
3. The noble Ar and He gases were detectable in the most of investigated CCRT. The partial pressure for argon was 10⁻⁵ Pa and helium – 10⁻⁶ Pa. The partial pressure for hybrid category gas CH₄ was 10⁻⁶ Pa.
4. Normal distribution law describes distribution of total gas pressure of A33EKC CCRT (except critical cases of CCRT technology). Total pressure values of CCRT varied from $p = 8.58018 \cdot 10^{-5}$ Pa to $p = 2.94 \cdot 10^{-4}$ Pa.
5. Average total pressure ($\langle p \rangle$) of 12 investigated A33EKC CCRT was $1.49 \cdot 10^{-4}$ Pa and root mean square σ was $6.44 \cdot 10^{-5}$ Pa.

Acknowledgments

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