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STUDY ON THE FORMATION OF OZONE GAS IN INDUSTRIAL IRRADIATION PROCESS

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ABSTRACT

In industrial irradiators, the generated electromagnetic radiation or particles, such as gamma or X rays and electrons interact with air during the irradiation of products. In this gas layer, these effects cause the radiolysis in the constituent atoms, affecting mainly the oxygen atoms. This interaction is similar to what occurs in the stratosphere, when the diatomic molecule of oxygen (O_2) absorbs ultraviolet radiation from the sun, breaking the connection and separating it into two highly reactive atoms, which combined with another molecule of oxygen produce ozone (O_3). Ozone, at high altitudes, is beneficial and protects us from ultraviolet radiation. At low altitudes, it is a highly oxidizing gas and harmful to living beings. Aiming to study the formation and behavior of this gas in gamma irradiators, the measurements were made at a Multipurpose Gamma Facility from IPEN / CNEN-SP, which has cobalt-60 sources with a total activity of 5.22 PBq.

1. INTRODUCTION

Commercial use of radiation in industry is present in many products such as food, medical disposables, electrical cables, gemstones and other products. This process aims to improve the properties or sterilize and sanitize these products.

In industrial irradiators, electromagnetic radiation (gamma and X-rays) or electrons, before interacting with the products under processing, find a layer of air. When the radiation interacts with this layer, it produces radiolysis effects in the atoms present in the ambient atmosphere; the main interaction is with the oxygen atoms. This interaction is similar to what occurs in the stratosphere, according to the Chapman Cycle [4], when the diatomic molecule of oxygen (O_2) absorbs the sun ultraviolet radiation with wavelengths less than 240 nanometers, breaking the connection and separating it into two highly reactive atoms that, when combined with another oxygen molecule, produce ozone (O_3). In the troposphere, ozone acts as a protective layer, shielding the earth surface from ultraviolet rays of high energy from the sun [5].

Because it is highly reactive, ozone on the earth's surface is harmful to plants, animals and humans [7]. Chronic exposure to ozone can cause morphological, immunological, biochemical and functional effects in the lung and contribute to tumor formation [8]. Even at low concentrations (from 0.01 to 0.05 ppm) this gas can be perceived by a characteristic odor [6]. In facilities with gamma irradiation, X-rays or electron accelerators, the ozone produced interacts with the surface of treated products and structural elements of the radiators. Hence, the high concentration of this harmful gas is a job security issue inside the irradiation chamber, especially when the access is required from operators to perform maintenance work or product positioning. Consequently, it is necessary to install a ventilation system to reduce the concentration and subsequent release, within permitted levels of this gas in the environment.

In Brazil, both the National Council for the Environment (CONAMA) of the Ministry of Environment, through the Resolution CONAMA 03/90 [9], as the Labor Ministry, through the regulatory norm NR No. 15 [10], set as the maximum concentration value of the pollutant ozone in the air 0.08 ppm or 0.16 mg / m³. Only as a second reference, the American Environmental Protection Agency (EPA), in 2008, established a new national limit for the concentration of ozone (0.075 ppm), after an extensive socio-economic study [11].

2. EXPERIMENTAL METHODS

The equipment used to measure the concentration of O_3 was a 49C monitor that is an O_3 analyzer from Thermo Environmental Instruments Company. It has an internal pump that collects air through the hose at the point to be evaluated. The principle of operation is based on optical absorption. O_3 molecules absorb ultraviolet light at a wavelength of 254 nm and the O_3 monitor associates this measurement to the attenuation of light, by the Lambert-Beer's law.

The industrial facility used for the tests was the Multipurpose Irradiator from IPEN / CNEN-SP. Its irradiation chamber allows the entry of external air only from gaps in the doors for products and service. The irradiation chamber volume is 64 m³ and the exhaust system was designed for extracting 3850 m³ / h of air or about 60 air exchanges per hour.

The Multipurpose Irradiator from IPEN / CNEN-SP, Figure 1, uses radioactive sources of cobalt-60 distributed in two racks, with source activities of 0.87 PBq, in rack 1, and 4.35 PBq, in rack 2, allowing a variation in the dose rate inside the chamber irradiation according to the source rack position.

Figure 1: Compact Multipurpose Irradiator from IPEN / CNEN-SP.

The procedures for measurements were as it follows:

1) As a standard procedure, a previous measurement of the O_3 concentration in the environment has always been carried out, considering it as the background value (BG), discounted from measures at the facility considering their respective uncertainties.

2) A Teflon hose with 6 m in length and 4 mm in diameter was used to collect the gas, within the limits of use for the O_3 analyzer, according to the manufacturer. In order to verify some loss occurred by insertion of the hose length, a comparative measurement was performed between a 3 m length hose and a 15 m length hose, collecting samples of the exhaust system during normal operation (sources exposed and exhaust system on).

3) The equilibrium concentration of O_3 with the irradiation time and collected from the exhaust pipe, in normal operation, was measured.

4) The ozone decay time, after the O_3 concentration reached the region of equilibrium, inside of irradiation chamber, with the exhaust system off and after gathering the sources of cobalt-60, was measured. Samples were collected with different volumes of product being irradiated.

5) The decay curves of O_3 concentration, after gathering sources with the data collected from the exhaust pipe in normal working conditions, were measured.

3. RESULTS

There were no significant differences in the measured O_3 concentration due to different hose lengths tested. With the 3 m hose, it was obtained a value of the ozone concentration of 119.6 ± 0.9 ppb and with a 15 m long, it was obtained the value of 120.5 ± 1.5 ppb. Since the two measurements were similar, this showed that the O_3 analyzer can adapt to the possible pressure variations the length of hose and that no significant adsorption, due to hose length, was observed.

Figure 2 shows the temporal evolution of the O_3 concentration, as time function, for different activities. It was observed that the systems tend to show a region of O_3 equilibrium concentration and Table 1 shows the obtained values for these regions. Measurements were taken from the exhaust pipe, in normal operation.

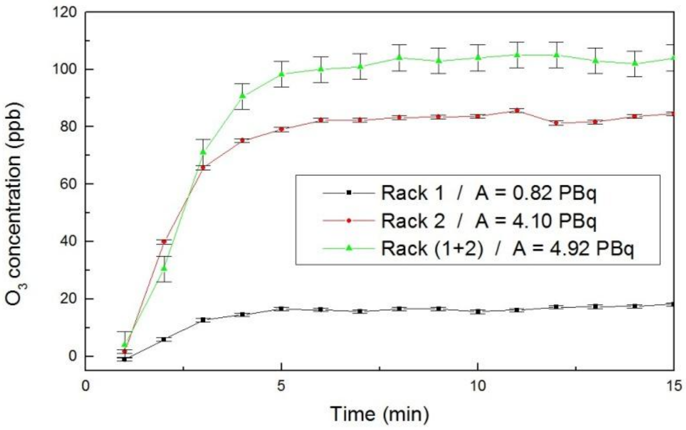

Figure 2: Measurements of O_3 concentration, taken in the exhaust system pipe for different activities, until equilibrium condition.

Table 1: Values of maximum concentration of O_3 in the exhaust system pipe, obtained from Figure 2.

Rack	**Activity (PBq)**	**Maximum concentration (ppb)**
1	0.82	17 ± 1
2	4.10	82 ± 2
1+2	4.92	104 ± 5

With the exhaust system off and after the O_3 concentration reached equilibrium, the O_3 decay times were measured within the chamber for different irradiation volumes occupied and using the maximum activity available in the irradiator. Measurements were made at floor level, due to the tendency of O_3 precipitation; an air circulator inside the chamber was used for better mixing. Figure 3 shows O_3 decay curves for different occupied volumes inside the chamber. The volumes occupied in the irradiation chamber are in the following proportion: Empty <V1 <V2 <V3.

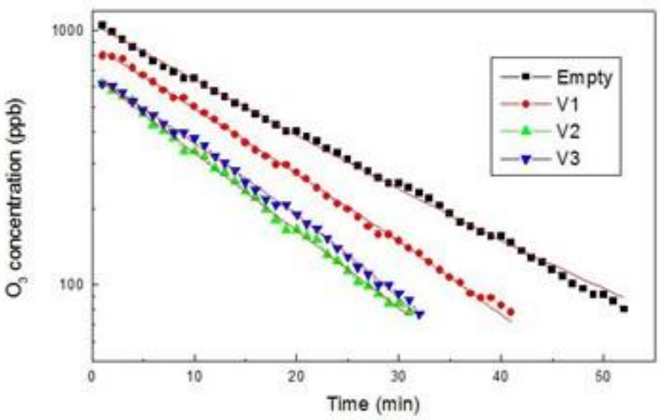

Figure 3: Decay Curves of O_3 concentrations, at the internal floor level of the Multipurpose Irradiator, for different volumes occupied and with the maximum activity available in the irradiation chamber.

The differences in the maximum ozone concentrations were found and were in accordance with the expectations: when more gamma radiation energy is deposited on a product, less energy is available to produce reactions in the air. These values tend to stabilize due to the free minimum volume that can not be occupied by products, allowing the reaction of O_3 production.

The curves shown in Figure 3, in this case, straight lines at a logarithmic scale for the O_3 concentration values, demonstrate the behavior of the first order exponential decay to the concentration of this gas. With these data, O_3 half-life time was calculated for each volume occupied; these results are presented in Table 2.

Table 2: Times of half-life for the decay of O_3, for different volumes occupied.

Volume	**Maximum concentration (ppb)**	**$T_{1/2}$ (min)**
empty	1052	13.9 ± 0.3
V1	793	12.3 ± 0.5
V2	616	9.4 ± 0.5
V3	617	9.9 ± 0.5

From the four measurements at Table 2, the average time for the decay of O_3 in the installation was obtained: $T_{1/2} = 11.4 \pm 2.1$ min.

With the aid of an equation from "Technical Reports Series No. 188", published by the IAEA [14], which was published covering aspects of radiological protection in the operation of linear accelerators of electrons This paper has the purpose of applying an equation to obtain the equilibrium concentration for O_3, as it is a similar phenomenon to the equation mentioned in the reference, where it could be inferred that the O_3 concentration, C (t) may be obtained by the equation:

$$C(t) = \frac{p\overline{T}}{V}[1 - e^{\frac{-t}{\overline{T}}}] \tag{1}$$

where,

t = irradiation time (min);
p = O_3 production rate (ppb.m^3/min);
V = irradiation chamber volume (64 m^3);
$T_{1/2}$ = 11.4 ± 2.1 min;
With an extraction rate of air through the exhaust, Flow = (64.17 m^3/min);

and,

$$\overline{T} = \frac{T(vent) \cdot T_{1/2}}{T(vent) + T_{1/2}} \tag{2}$$

$$T(vent) = \frac{V}{Flow} \tag{3}$$

Considering a steady state, where the concentration of O_3 is homogeneous and equal throughout the irradiation chamber and the exhaust pipe, it was obtained p = production rate of O_3 (ppb.m³ / min), assuming C(t), taking t as long enough, which makes the value inside the brackets equal to 1. With a longer time t, the value of C(t) is already in equilibrium, then p = 7258 ± 954 ppb.m³ / min. This value was found using the Multipurpose Irradiator, with the two sources exposed (Activity = 4.92 PBq), and the corresponding equilibrium concentration for this activity, C (equilibrium) = 104 ± 5 ppb.

Figure 4 shows the concentration values measured in the multipurpose irradiator (black) and the curve obtained using equation 1 (red). The similarity between them showed an adequate behavior, for the proposed equation, to describe the production of ozone in this irradiator.

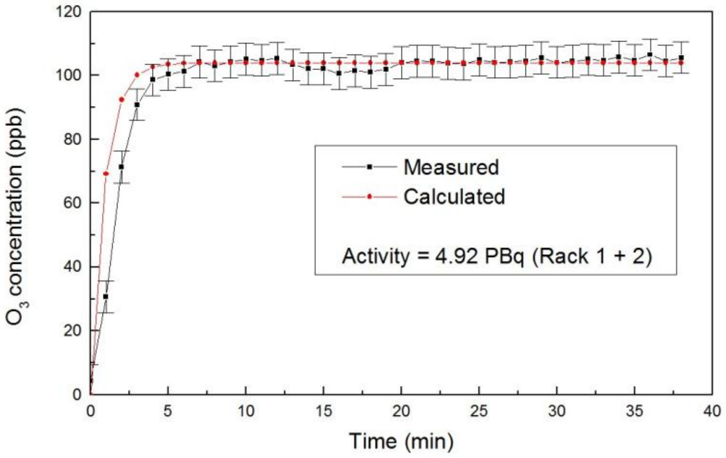

Figure 4: O_3 concentration versus time in the exhaust pipe and with the exhaust system on. The black curve is the measured values and the red, the curve calculated using the proposed equation.

The above adjustment took into account only the results with the irradiator operating at maximum activity. For activities under this, it was proposed for p, the O_3 production rate as a function of the activity of the sources, as shown in the following expression:

$$p = A \cdot k \tag{4}$$

where,
p = O_3 production rate (m³/min);
A = exposed activity source (PBq);
k = proportionality constant (m³/PBq.min).

From p = 7258 ± 954 ppb.m³ / min, obtained from the equilibrium with the maximum activity, it was calculated the value 1476 ± 194 ppb.m³ / PBq.min for the proportionality constant k. Table 3 shows the values of the activity for each irradiator source rack and its respective O_3 production rate, calculated using equation (4).

Table 3: Values of O_3 production rate calculated and the rack's activity, for the Multipurpose Irradiator from IPEN / CNEN-SP.

Rack	Activity (PBq)	O_3 production rate (ppb.m³/min)
1	0.82	1210 ± 159
2	4.10	6048 ± 795

Combining expressions (1) and (4), it was obtained expression (5) that allows the concentration of O_3, from the irradiation beginning until the condition of equilibrium, to be calculated:

$$C(t) = \frac{Ak\overline{T}}{V}[1 - e^{\frac{-t}{\overline{T}}}] \tag{5}$$

Using the expression (5), the O_3 concentrations at the exhaust pipe were calculated, using racks 1 and 2 independently. Figure 5 shows the calculated and measured concentration curves in the exhaust pipe, with the exhaust system on and with rack 1 source exposed.

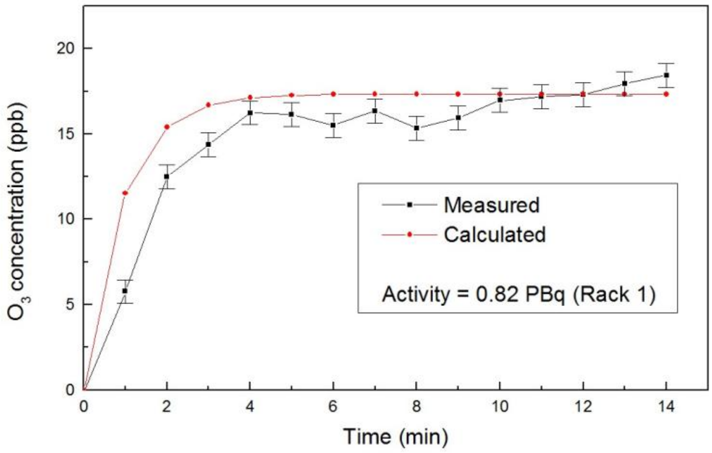

Figure 5: Values of O_3 concentration in the exhaust pipe with rack 1 source exposed. The black curve refers to the measured values; the red curve was calculated using equation (5), proposed.

Figure 6 shows the O_3 concentration curves calculated and measured at the exhaust pipe, with the exhaust system on and rack 2 exposed.

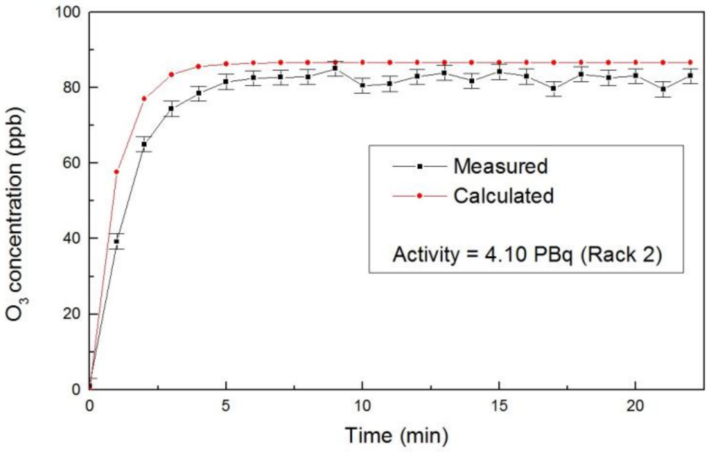

Figure 6: Values of O_3 concentration in the exhaust pipe with rack 2 source exposed. The black curve refers to the measured values and the red curve was calculated using equation (5), proposed.

For a sufficiently long irradiation time, the concentration of O_3 at equilibrium condition (6) can be derived from expression (5) as:

$$C_{equilíbrium} = \frac{Ak\overline{T}}{V} \tag{6}$$

Table 4 shows the O_3 concentration values, at equilibrium condition, obtained from the measurements and calculated values using expression (6).

Table 4: O_3 concentration values measured and calculated, at equilibrium condition.

Activity (PBq)	**Measured concentration (ppb)**	**Calculated concentration (ppb)**
0.82	17 ± 1	17 ± 2
4.10	82 ± 2	87 ± 11
4.92	104 ± 5	104 ± 14

Using the values at table 4, Figure 7 shows that the O_3 equilibrium concentration is a linear function, with the activity for the values available in the Multipurpose Irradiator.

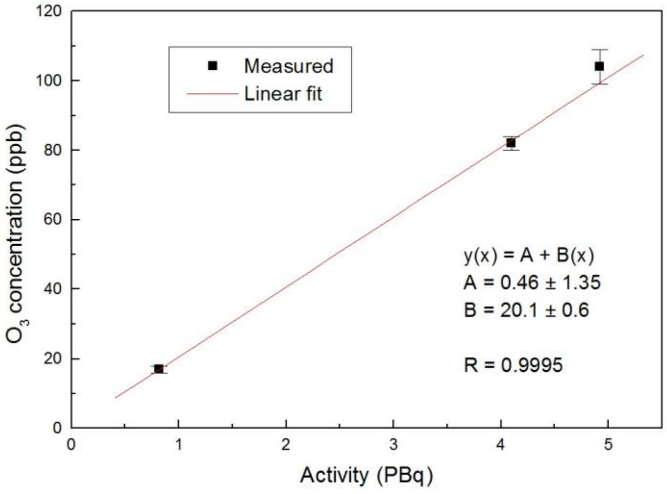

Figure 7: O_3 equilibrium concentration as a function of the activity. The linear fit shows that the equilibrium concentration is a linear function with the activity for the values available in the Multipurpose Irradiator.

Figure 8 shows the O_3 decay curve in the exhaust pipe, with the exhaust system on, and after gathering sources of cobalt-60. It could be seen that after 1.3 min, the O_3 concentration is already lower than the limit for workers.

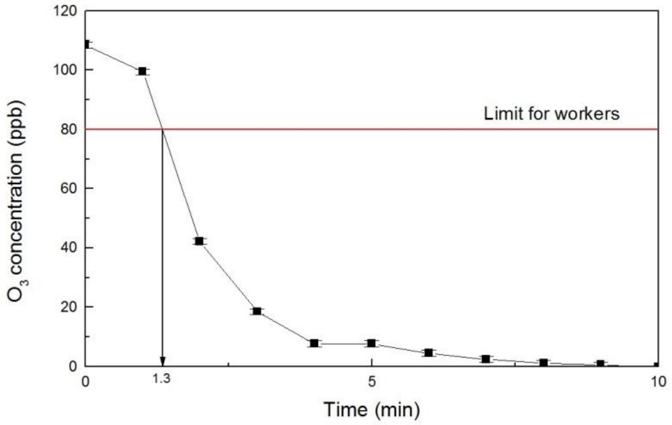

Figure 8: O_3 decay curve in the exhaust pipe, with the exhaust system working, and after gathering sources of cobalt-60 in the Multipurpose Irradiator.

4. CONCLUSIONS

The BG varies greatly throughout the day, reaching maximum values after the solar radiance peak and because this, in all measurements, it is imperative to remove the BG from the values to evaluate the results correctly. The measurements were not performed at night since there are also nocturnal peaks, with different explanations [7] [15].

O_3 concentration reaches an equilibrium value after a processing time, with the exhaust system on or off. This equilibrium value was linearly proportional to the source activity used for the measurements. These results suggest further studies, with facilities with higher activities, because there are at the literature papers suggesting that this value does not grow linearly with the dose rate because the own radiation destroys the gas molecules [16] [17].

As expected, the ideal situation would be operating the facility with maximum occupancy of the useful volume, so there will be less energy available for the production of O_3.

At the facility used to carry out the measurements, O_3 decays as a function of first order and shows $T_{1/2} = 11.4 \pm 2.1$ min.

The O_3 rate production as a function of time and activity was obtained. The equations describe well the phenomenon of O_3 formation for the activity values available in the Multipurpose Irradiator, from IPEN / CNEN-SP. Measurements on devices with higher activities are necessary for the verification of this phenomenon behavior.

The high ozone concentration obtained without circulation of the atmosphere inside the irradiator suggests that, for products fully enclosed and without vacuum or special gas, high concentrations of O_3 can be achieved in these packages. O_3 is a powerful germicide, but at high concentrations it can attack the processed product, especially fruits and works of art [17] [18]. Equipment components, also, deserve attention.

For this facility, a 1.3 min waiting time is enough to permit access to the installation, avoiding high O_3 concentrations. This time does not take into account possible concentration points at existing dead zones or a potential high value of background environment.

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