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# How to produce a pure ozone sample?

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A home-made ozone generating system is described in this paper. A commercial ozone generator produces a gas mixture of 10% ozone and 90% of oxygen. A distillation process purified the mixture that achieves ozone samples with purity between 90 and 95%. A system consisting mainly of glass and PTFE components is used to produce and purify the ozone. The use of these inert materials is imperative to get the purification process and guarantee the non-degradation of the sample.

*Keywords:* Ozone; coincidence spectroscopy; instrumentation.

Un sistema casero de generación de ozono se describe en este documento. Un generador comercial de ozono produce una mezcla de gases del 10% del ozono y el 90% de oxígeno. Un proceso de destilación purifica la mezcla de ozono logrando alcanzar muestras de pureza entre el 90 y el 95%. Un sistema que consiste principalmente de vidrio y componentes PTFE se utiliza para producir y purificar el ozono. El uso de estas materiales inerte es imprescindible para la eficiencia del proceso de purificación y de la no degradación de la muestra.

*Descriptores:* Ozono; espectrometría de coincidencia; instrumentación.

PACS: 33.80.Gj; 82.37.Vb; 33.20.Ni

## 1. Introduction

The ozone molecule is composed by three oxygen atoms. These atoms are disposed in a V shape with a bond angle of 116.8° and the bond length of 1.27 Å in the ground state. The molecule is planar and belongs to the $C_{2v}$ symmetry. The three oxygen atoms are in different chemically environments. One site consists of the central oxygen atom ($O_C$), and it is in the center of the V. The other ones consist of two terminal oxygen atoms, $O_T$. The distinction between them can be observed in the XPS ( X-Ray Photoemission Spectroscopy) spectra by the energy separation of the O $1s^{-1}$ core orbital from $O_C$ and $O_T$ atoms of 4.6 eV [1,2]. The peak width of $O_C 1s^{-1}$ is larger than $O_T 1s^{-1}$, 0.75 and 0.63 eV, respectively.

The molecular electronic configuration on the ground state is written as: core: $1a_1^2$ $2a_1^2$ $1b_2^2$ valence: $3a_1^2$ $2b_2^2$ $4a_1^2 5a_1^2$ $3b_2^2$ $1b_1^2$ $4b_2^2$ $6a_1^2$ $1a_2^2$ empty orbital: $2b_1^0$ $7a_1^0$ $5b_2^0$ where the inner molecular orbital (MO) $1a_1$ corresponds to the 1s orbital from the $O_C$. And the degenerated MO orbital $2a_1$ and $1b_2$ are even and odd combinations of 1s orbital of $O_T$ atoms, respectively. The inner valence orbitals, $3a_1^2$ $2b_2^2$ $4a_1^2$, are O 2s like orbitals. The orbitals $1b_1$, $1a_2$ and $2b_1$ are out-of-plane, and the $5a_1$, $4b_2$ and $6a_1$ are in- plane $\pi$ orbitals, where $2b_1$ and $6a_1$ have $\pi$ anti-bonding character. The $3a_2$, $7a_1$ and $5b_2$ orbitals are $\sigma$ anti-bonding character [3-5].

## 2. The ozone production

The ozone gas is produced by an electric discharge of pure $O_2$ using a commercial ozonizer [6]. The $O_2$ gas enters the generator and goes through a high electric field, where some molecules can be broken. This reaction in $O_2$ produces the ozone, $O_3$. The yield of this process produces a mixture of 10% of ozone and 90% of oxygen. This amount of ozone is not sufficient to do good spectroscopy. Therefore, another stage to improve the $O_3$samples is necessary, and it is called “purification of ozone”. A sketch of the experimental set-up is shown in Fig. 1.

The high reactivity of ozone requires the use of neutral material to build the system and produce ozone, such as Pyrex, flexible tubes of PTFE, Viton, etc. To produce ozone it is necessary to use high-purity $O_2$, a commercial gas cylinder, which is joined to the ozone generator; a cooling system to separate the oxygen and ozone molecules, one reservoir to store the samples and one efficient vacuum system with a cooling trap system included for security. All the connections

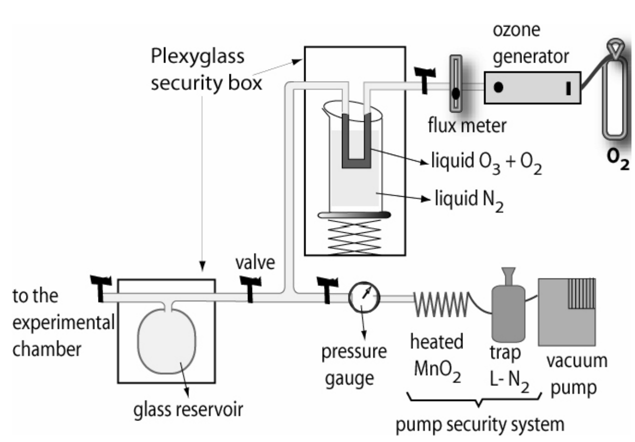


FIGURE 1. A schematic view of the ozone generation set-up.

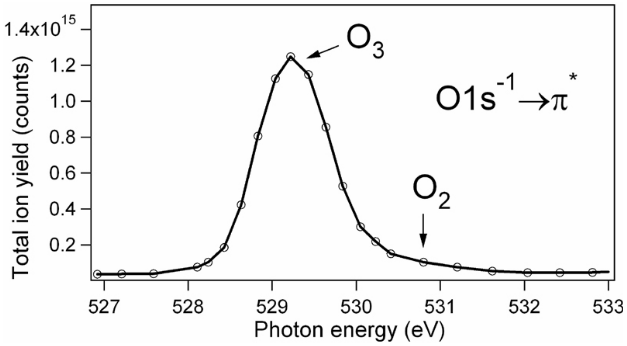


FIGURE 2. The $O_2$ contamination in the $O1s^{-1} \rightarrow \pi^*$ excitation in the total ion yield spectrum from ozone sample.

are made by heating the PTFE tubes and pushing them against valves, connectors, etc. This type of connection links the system to the primary vacuum ($\approx 10^{-3}$ m*bar*). The gas flux between the generator and the purification system is controlled by the flux meter (0.2-2.5 *lpm (liter per minute)*). The flux control is very important because the pressure inside the system can rise rapidly and increase the risk of explosion. The purification system consists of a Pyrex U-tube where the $O_2/O_3$ mixture will be trapped in liquid phase. A security procedure must be followed to avoid fire or explosion inside the vacuum pump. The pumps need to be protected by heated $MnO_2$ granules which act as a catalyst to break the ozone molecules and, in addition, liquid nitrogen traps.

The system is pumped continuously. The purification of ozone is realized by passing the oxygen/ozone mixture through a U-tube glass that can be cooled externally with liquid nitrogen. At the liquid nitrogen temperature (-196°C) both oxygen (boiling point 182.8°C) and ozone (boiling point –111.7°C) get trapped and can be seen as violet liquid inside the U-tube. Generally, about 12 minutes is enough time to produce ozone in the generator. This point is crucial because the production for a long time can increase the pressure of the system and can result in an explosion. There are other parameters that must be observed in order to avoid problems: the oxygen pressure inside the cylinder should be around 1 *atm*, higher pressure can damage the ozone generator; the gas flux must be 0.5 *lpm*, approximately, and the pressure inside the system can not be over 20 m*bar*. In resume, the most important precaution that must be taken in order to avoid explosions is to keep the pressure inside the system as low as possible.

When some amount of liquid is obtained in the ozonizer, it is turned off and the purification process will start. The separate process is done by cooling and heating the sample inside U-tube. It is used one platform that moves up and down to put in contact the sample hold with liquid nitrogen reservoir. When the sample reaches the boiling point of oxygen, the oxygen evaporates and can be pumped out. After that the reservoir that contains liquid nitrogen is moved up to freeze the sample again. This cooling and heating procedure is repeated three or more times in order to obtain a pure ozone sample.

The purified liquid ozone is warmed up and filled into a glass reservoir which is connected with the experimental chamber. In order to refill the glass reservoir the connection to the pumps is shut and the liquid is heated up, while monitoring the pressure in the system. Stainless steel proved to be sufficiently inert to prevent ozone from dissociating during the inlet into the experimental chamber. Some care must be shown concerning the diameter of the needle used to inlet the gas in the chamber (that needs to be bigger than usual). The experimental data revealed that following this procedure a gas mixture with more than 90% ozone could be trapped in the system [7,8]. In Fig. 2 the signal from the $O_2$ contamination can be compared to the $O_3$ signal. The spectrum of $O1s^{-1} \rightarrow \pi^*$ excitation in the total ion yield spectrum from the ozone sample is shown. The $O_2$ contamination is hard to see, it is appears like a small shoulder at 530.8 eV photon energy, the $O1s^{-1} \rightarrow \pi^*$ excitation from oxygen.

Explosions can never be excluded, so it is important to surround the glass U-tube containing the liquid ozone with a Plexyglass box to prevent pieces of glass from injuring anybody. Since ozone is sensitive to visible and UV-light, covering the whole inlet system with non-transparent foil increases the lifetime of the liquid and the gaseous sample.

## 3. Conclusion

It is very important in spectroscopic studies to have pure samples. In order to separate the contributions coming from ozone from those of the major contaminant, oxygen, which is also composed of oxygen atoms, it is necessary to have very pure ozone sample. With the home made system described above it is shown that is not easy but it is possible to produce a pure ozone sample.

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