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Ozone concentration measurements. State of the art.

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Abstract

There is a wide interest regarding how to accurately measure the ozone concentration in agas mixture. Concerns are even more relevant regarding ozone medical applications because outcomes greatly depend on the correct administered dosages.

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Introduction

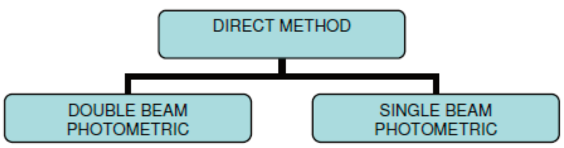
The usefulness of ozone for medical applications, namely Ozone Therapy, has being explored by many physicians for several decades gaining experience and knowledge on its indications as well as its therapeutic dosage ranges. An important fact and a milestone in the Ozone Therapy practice was the "Madrid Declaration on Ozone Therapy" (1) produced in the framework of the International Meeting of Ozone Therapy Schools, Madrid June 2010 organized by A.E.P.R.O.M.O association (2). This Declaration, among other important issues, defines therapeutic protocols and therapeutic ranges considering ozone concentrations. This factor has never been considered as playing an important role in the success of therapies as it is today.

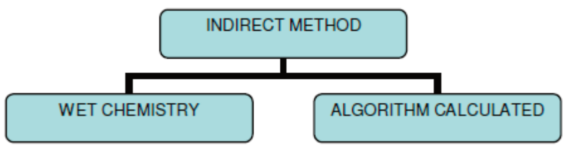
For ambient ozone, UV photometry is a worldwide standard. The National Institute of Standardisation and Technology, NIST (3) plays a leading role in providing national standards to many nations. Unfortunately, there is no such national standard available for high ozone concentrations as commonly used in Ozone Therapy.

However, the International Ozone Association, IO3A (4) regulation 002/87 (F), gives a recommendation for ozone extinction coefficient of about 3000 ltr/mol cm (1atm / 0ºC).

1. Measuring methods

Ozone concentrations can be measured mainly in two different ways, directly and indirectly which in turn, can be divided into two other methods.





2. Photometric method

Sometimes called spectrophotometric, is a quantitative analysis based on the Beer-Lambert law consisting in the assessment of the absorption of a light radiation with specific wavelenght. The light energy amount absorbed by the sample is directly related with its concentration. Ozone has a peak absorption in the ultraviolet spectrum at 254nm wavelength so a monochromatic UV light must be used.

Operation of an ozone standard photometer is as follows:

- The light beam is sent through a cuvette and its intensity measured for zeroing.
- The gas mixture O3/O2 enters the cuvette.
- Depending on the O3 concentration, some amount of the light is absorbed.
- The light beam outing the cuvette is detected by a sensing device such as a photodetector.
- The intensities for input and output light beam are compared for measuring.

While relatively simple in concept, determining the transmittance involves careful consideration of the geometrical and spectral conditions of the measurement. The method of UV photometry, if performed in the right way, is accurate and reliable for ozone concentration measurement being the election method for ozone researching. Nevertheless this method is very sensitive to dust, contaminants and condensation on the measuring cuvette and these items must be considered in the design. Also, zeroing and frequent calibration is needed. As an UV source, a low pressure mercury lamp is used to produce the 254nm wavelength and these devices are not linear and have a limited lifespan. In addition, the devices using mercury lamps are not RoHS (5) compliant being obsolete since 1st July 2006 when the directive entered in force within EU. This directive is well known by the medical community as it obliges to remove all the mercury clinical thermometers removing all of them from their original use in the hospitals within the EU. Further considerations must be taken using UV wavelengths because same energy radiation, by hitting oxygen in an O2/O3 mixture, produces as well ozone thus increasing the ozone concentration in the sample measured.

There are two major classes of devices: single beam and double beam photometers. A double beam spectrophotometer compares the light intensity between two light paths, one path containing a reference sample and the other the test sample. A single beam spectrophotometer measures the relative light intensity of the beam before and after a test sample is inserted. Many medical ozone generators include a single beam calibration system as described before.

Regardless if a single or double beam device is used, an important issue is the calibration method used for the photometric device because depending on it, measurements done with the same photometer may result in concentrations with a margin of error of 10%. For instance, those calibrated with the chemical method give 10% higher values than those calibrated with UV photometers which consider the ambient pressure and temperature for correction. These systems usually show the concentration values as µg/Nml, i.e. normalized “N” millilitres (1atm and 0ºC).

2.2 Sources of error in an photometric Ozone Analyzer

One of the most important factors to achieve accurate measurements on a photometric device is the stability. Stability of a UV device based on a UV lamp is highly compromised by the emission lamp and sensor drift due to its normal wear, mainly of the lamp. Also soiling of the cuvette due to humidity, dirt, NOx and hydrocarbons compromises the accuracy of the analyzer. Because of this, periodic zeroing and/or calibrations of the instrument are needed.

Humidity on the cuvette will appear when the dew point temperature of the water contained in the gas is higher than the temperature of the cuvette windows triggering water condensation on the windows.

Dirt will appear on the cuvette by several reasons such as using polluted oxygen supply from the cylinder or wall supplies, or the use of oxygen concentrators from PSA (7) systems being the latter one of the worst cases, because some lubricating hydrocarbons from the air compressor may reach the cuvette. Then the high energy UV light could burn it creating a gas that glues in the cuvette windows as a thin layer. This effect completely destroys accuracy and even the cuvette must be discarded. Also contamination of NO has to be considered as PSA systems delivers oxygen at concentrations of up to 95% and balanced with 5% nitrogen. This nitrogen is modified to different nitrous oxides when passing through the core of generator receiving high voltage discharge.

3. Indirect method

Two main procedures are used as indirect methods. One is the called iodometric “wet chemistry” (6), and the other is a calculated algorithm. We will deal only with the latter because the chemical method is based on the oxidation of a potassium iodide solution according to the reaction 2KI + 03 + H2O 2KOH + O2 + I. This method is a calibration reference for some photometric devices, as mentioned before, but it is impractical to use by a medical ozone generator into a clinical environment because readings are not in real time and procedure is not convenient.

Algorithm calculated measuring (ACM) procedure is an indirect method because there are no sensors or cuvettes involved in the measurement process. The ozone gas mixture does not touch any sensor or detector thus no flow restriction is produced. It is well known that the output ozone concentration produced by any ozone generator is inversely proportional to the flow passing through; therefore, this method requires a constant flow to be accurate so a well designed gas management system is mandatory. Another important issue for an accurate ACM is the high voltage production and control that involves complicated designs for high frequency voltage generators and sophisticated transformers. The high voltage must be stable and constant. Therefore for concentration settings the generator must modify the PWM (Pulse Width Modulation). Furthermore resonant or quasi-resonant circuits must be considered for high performance generators.

All the required data, pulse width, high voltage, timing, triggering angle and some other are sent to a CPU (central processing unit) that with a proprietary algorithm calculates the ozone concentration. At this point, some advanced and improved devices, considers temperature and pressure to calculate the normalized volume of the O3/O2 gas mixture giving the units in terms of µg/Nml (micrograms per normalized "N" millilitre). These units are the recognized one by the IO3A (4) association. Regardless of the measuring method (photometric or ACM) a serious measure device intended for gas, must consider temperature and pressure to avoid further errors (some times up to 7%).

3.3 Sources of error in an ACM measuring device

Since neither detectors nor cuvettes are used on this method, humidity, dirt and other pollutants do not affect the measurement accuracy. Nevertheless, this method is "blind" to the oxygen supply gas purity or kind of gas, so if a gas different than oxygen is used as gas supply, the ACM method still will show concentration readings. This is a highly unlikely situation because pipelines and cylinder valves have international standards for each every gas in order to avoid mistakes by the operator. For instance, it is almost impossible to fit by mistake an oxygen breathing mask & flow system to a CO2 cylinder also commonly available within hospital environment. The same happens with wall supply sources which are standardized by dedicated plugs avoiding fitting vacuum plug or N2O instead of oxygen.

Another source of measuring error is the use of oxygen concentrators. As said before, ACM method is non sensitive to the feeding gas because it considers it as 100% pure oxygen while actually some percentage of nitrogen is on the mixture. Real concentration on this case will be lower than showed by the readings and must be considered according the application. While this procedure must be absolutely avoided for systemic route application, it is a choice for oil or other liquids ozonation where high oxygen consumption is involved. On the other hand, no damage will be produced to the ACM measuring device due to the lack of UV sensors or cuvettes are in the process.

Summary

The use of one method or another is not inherently better compared to each other. As many other things in the field of technology, if a poor design of the device and / or wrong procedure is involved, poor results will be obtained regardless the used method. Instead to focus the method that must be used, the manufacturers must be requested to advice about the accuracy of their measuring devices as well as its linearity and maintenance requirements.

Many aspects are involved in the medical ozone generators manufacturing that are impossible to be covered by regulations so it is highly desirable that the manufacturers joined the "Good Manufacturing Practices" which is covered by the ISO 13485:2003 regulation that grants the design will be even better and beyond the standard regulations. Then, manufacturers having ISO 13485:2003 certificate will be a good clue about how much care they put into their designs. Needless to say that all medical ozone generators should have CE certification for the directive 93/42EEC Anex II which is the one that regulates medical devices into the European Community.

References

1. Declaration of Madrid can be downloaded from ISCO3 web page.

2. A.E.P.R.O.M.O (Asociación Española de Profesionales Médicos en Ozonoterapia. www.aepromo.org

3. NIST. National Institute of Standardisation and Technology. www.nist.gov

4. INTERNATIONAL OZONE ASSOCIATION, STANDARDISATION COMMITTEE-EUROPE: "Ozone Concentration Measurement in a Process Gas by UV Absorption", 002/87 (Paris, France: Intl. Ozone-Assoc., European-African Group, 1987). IOA3. International Ozone Association. www.io3a.org

5. RoHS. Restriction of Use Hazardous Substances. www.rohs.eu

6. INTERNATIONAL OZONE ASSOCIATION, STANDARDISATION COMMITTEE-EUROPE: "Iodometric Method for the Determination of Ozone in a Process Gas", 001/87 (Paris, France: Intl. Ozone Assoc., European-African Group, 1987)

7. PSA; Pressure Swift Absorption. Oxygen concentrators for oxygen breathing therapy. K. RAKNESS et al., "Guideline for Measurement of Ozone Concentration in the Process Gas from an Ozone Generator", Ozone: Science & Engineering, Vol.18 (1996), pp. 209-229