Study of ozone generation

Contents

1 Measurement of ozone concentration

With the increasing number of water treatment facilities, and facilities for oxidation of gaseous and liquid exhalations, the process of ozone generation is becoming one of the most investigated plasmochemical reactions. recently the ozone is used in textile, paper and ceramics fabrication, replacing the past use of chlorine. In both ozone generation process and any applications in industry the determination of its concentration is fundamental.

There were many papers about the ozone concentration measurement published recently. These analytical methods involve chemical oxidation, absorption of the UV radiation, catalytic decomposition, chemiluminiscence, fluorescence or breaking the double bonds. Most of these techniques are not ozone specific and will generally determine the amount of any oxidation agents. They can be divided into two main subgroups:

- chemical methods
- photochemical methods

Among the ***chemical methods***, iodometric titration is one of the most widely used and the most refined with the main advantage being the absolute measurement of ozone concentration in oxygen. The tradeoff is, that it is not possible to provide continuous (in-situ) measurements.

In majority of recently published works, the ***photochemical method***, based on the UV radiation absorption, is used. This methods' main advantage is the possibility of continuous measurement of ozone concentration, which can be utilized for the automatic regulation of the ozone production by ozonizer.

It should be noted that for ozone concentration measurement, combining these two methods without further considerations or supplements is only possible when the ozone is generated from the pure oxygen. In different cases (e.g. ozone generated from air) however, contribution to the UV radiation absorption from other molecules has to be taken into account (mainly N_2, N_2O and NO). Fortunately, when the mercury lamp is used as the source of UV radiation, these contributions are negligible, as the it involves only excited metastables.

2 Chemical method

The principle of the iodometric titration (or iodometry) is the reaction of ozone with alcaline iodide solution

$$2\,\mathrm{KI} + \mathrm{O_3} + \mathrm{H_2O} \longrightarrow \mathrm{I_2} + 2\,\mathrm{KOH} + \mathrm{O_2} \tag{1}$$

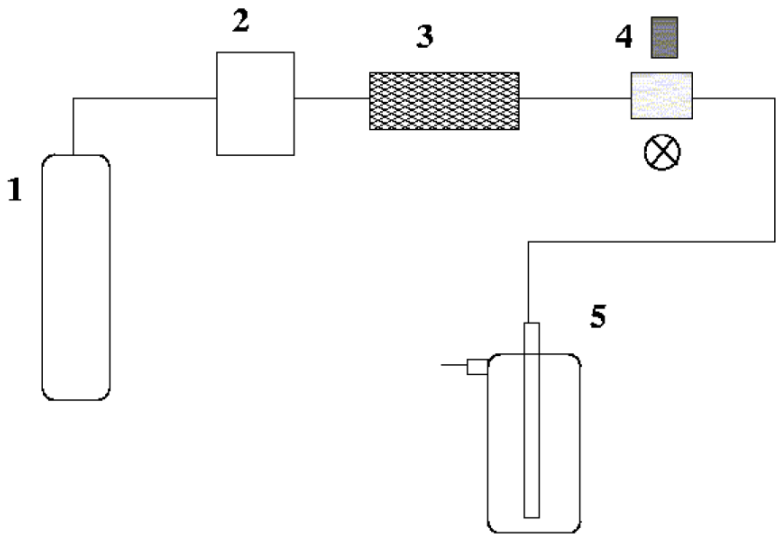

Figure 1: Experimental set-up: 1 – oxygen (or pressurized air), 2 - flow meter, 3 - ozonizer, 4 - UV radiation absorption measurement, 5 - washer with KI solution 0.2 M

during which iodine is extracted from the iodide. The solution then turns yellow or even brown. The amount of iodide is then determined via the sodium thiosulfate titration in the acidic environment.

$$I_2 + 2\,Na_2S_2O_3 \longleftrightarrow 2\,\Gamma + Na_2S_4O_6 \tag{2}$$

where the reduction of iodine to iodide dims the yellow tint in the liquid. For higher sensitivity of the method, a starch solution is added, at the point where the yellow tint has almost vanished. The diluted starch then reacts with the remaining traces of iodine coloring the solution into blue. The subsequent desaturation of blue tint is more apparent to human eye than the almost vanished level of the yellow tint.

The entire measurement will be as follows:

The gas is pumped from the discharge region (ozonizer) into the washer with 100 ml 0.2 M solution of KI (see Figure 1). The generated ozone reacts with the iodide, producing iodine. The reaction time suitable for sufficient amount of generated ozone is 5 minutes. Afterwards the solution with the extracted iodine is spilled over?? into titration flasks, acidified? with 10ml 2 M HCl and titrated using the 0.5 M solution of $Na_2S_2O_3$. The sensitivity of the measurement is then improved by adding the starch solution before the end of the titration. The content of ozone is calculated from the amount of used thiosulfate (1 ml of the 0.05 M solution $Na_2S_2O_3$ is equivalent to 1.2 mg of ozone).

3 Photochemical method

The most common photochemical method is based on the absorption of the UV radiation transmitting through the substance. The absorption of a species at the given wavelength can be characterized either by the absorption cross-section $\sigma(\nu)$ or the absorption coefficient $k(\nu)$. The absorption cross-section is defined as usually (Beer-Lambert law):

$$I(\nu) = I_0(\nu)e^{-\sigma(\nu)N} \tag{3}$$

where N is the number of absorbing species (molecules or atoms) in the cylinder, which has base area of 1cm^2, I_0 is the intensity of the radiation incident on the gas column, $I(\nu)$ is the intensity of the radiation transmitted through the gas and $\sigma(\nu)$ is the absorption cross-section. The absorption cross-section σ is often expressed in Megabarn (Mb) units, where $1\text{Mb} = 10^{-18}\,\text{cm}^2$. The Beer-Lambert law can also be written using the absorption coefficient $k(\nu)$:

$$I(\nu) = I_0(\nu)e^{-k(\nu)l} \tag{4}$$

where l is the distance traveled by the light in the gas. The relation between absorption cross-section $\sigma(\nu)$ and the absorption coefficient $k(\nu)$ can be determined using the Loschmidt constant $N_0 = 2,687 \cdot 10^{19}\,\text{molecules} \cdot \text{cm}^{-3}$, which is the number of molecules inside 1cm^3 at standard conditions (i.e. at the temperature $T_0 = 273,15\text{K}$ and the pressure $p_0 = 101325\text{Pa}$).

Should we measure the absorption in an environment under different conditions than T_0 and p_0, the real distance l in the Beer-Lambert formula has to be replaced with the reduced thickness x.

$$x = \frac{pT_O}{p_0 T} l \tag{5}$$

As for the absorption in gas mixtures, where the i-th species has the concentration c_i and $\sum_{i=1}^{n} c_i = 1$, the Beer-Lambert law must be used in the form:

$$I(\nu) = I_0(\nu)e^{-x\sum_{i=1}^{n} c_i k_i} \tag{6}$$

In case of ozone generated from oxygen using UV light with the wavelengths in the range 220-280 nm, the equation (6) reduces to:

$$I(\nu) = I_0(\nu)e^{-xc_{O_3}k(\nu)} \tag{7}$$

since the absorption coefficient for molecular and atomic oxygen is zero in this region.

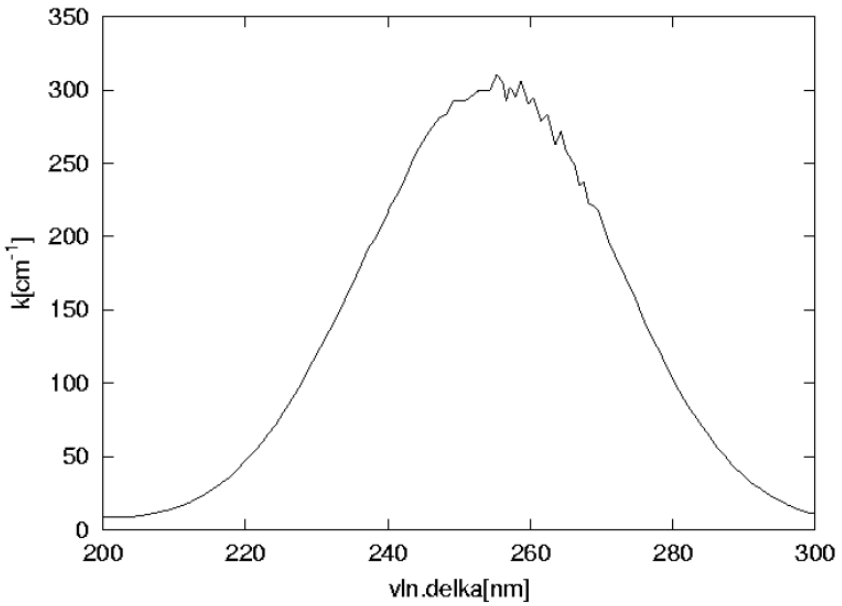

Figure 2: Absorption coefficient O_3 at 0 °C as a function of wavelength.

The ***absorption coefficient*** for ozone as a function of wavelength is shown in Figure 2. It is apparent that the mercury lamp and its 253.7 nm line can be used as a perfect source of the UV radiation. In this measurement this wavelength is picked using the interference filter, which is placed behind the absorbing environment.

4 Plasma characteristics

The Becker parameter is used for the expression of plasma efficiency. It is the amount of the discharge energy transferred from the discharge to the the volume of the flowing gas. It is calculated as:

$$\eta = \frac{I \cdot U}{Q} = \frac{P}{Q} \quad [\mathrm{W \cdot s \cdot dm^{-3}}] \tag{8}$$

where I is the total discharge current, U is the voltage across the electrodes, Q is the oxygen flow rate and P is the discharge power

5 Assignments

1. Perform the calibration of the float flow meter (rotameter) measuring the rate of gas filling up the known volume.

2. Calibrate the device for the measurement of ozone concentration from the UV radiation absorption using the iodometric titration. Use the appropriate absorption coefficient (reading from the Figure 2). Perform separate calibrations for technic oxgen and for air.

3. Measure the concentration of the generated ozone as functions of the air flow rate and the power supplied to the ozonizer.

4. Measure the concentration of the generated ozone as functions of the technic oxygen flow rate and the power supplied to the ozonizer.

5. Determine the Beck parameter for the plasma in ozonizer.