

***Measurement of High Ozone Concentrations in Gases by KI
Titration and Monitoring by UV-Absorption.
(Also: on the Design of Iodometric Washing Flasks).***

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1. Object of the Contribution.

Present contribution deals with the analytical following-up of the ozone production control at concentrations up to 200 g/m³ in the gas phase.

2. Introduction

Up to five years from now the large scale generators (i.e. more than 1 kg/h), of ozone from air could produce concentrations of 20 to 30 g/m³ (NTP). When using oxygen the concentration could be about doubled. By operating the generators out of the nominal design capacity up to 200 g/m³ were obtained (Franke, (1)). Actually 300 g/m³ in pure oxygen are on test for explosive conditions.

There is a considerable interest to produce ozone at the highest but safe concentration possible. Basically two technologies are existing in Europe (1997)

- The central-rod electrode type (Blankenfeld (2))
- The improved dielectrics in Welsbach-type generators (Lang et al. (3))

The analytical methods have to be adapted accordingly.

3. Iodometric Method for the Determination of Ozone in a Process Gas at Concentrations up to 200 g/m³

3.1 The KI-titration method

This method is the accepted reference method for calibrating of ozone monitoring methods. Different variants can exist (Rice & Netzer (4), Dimitriou (5), NIG-document)). The previous EAG standard (001/87) was also for the USA. An updated version (1997); is submitted for CEN approval (Pr EN 1278).

3.2 Range of Application

The method is directly applicable in the range of 1 to 200 g/m³ (NTP) of ozone in a process gas.

- 200 mL of the KI reagent solution are added to a "standard gas washing flask" to give a depth of liquid of 10-15 cm. For high concentrations an immersion depth of 30 cm. is recommended (Thieblin (6)). A second washing flask is connected in series for control.

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- The ozone containing process gas is bubbled at a flow rate of about 1L/min up to an estimated quantity of approx. 1 mMol ozone (0.048 g) has passed. All gas flows are measured by a totalizing flow meter with free exit to the atmosphere expressed at NTP conditions.

3.3 Precision and Accuracy:

Detection limit: 0.1 g/m³, Standard deviation: 1 mg/m³ or, 2% of the result.

(Remark: these data do not integrate potential errors on temperature, pressure and flow:(required precision: 1%).)

3.4 Interferences.

Other oxidants of iodide, if any present.

4. UV Monitoring of Ozone Process Gas (0-200 g/m³)

4.1: Hartley absorption band

The Hartley absorption band of ozone (200-300nm)is the present choice. The wavelength chosen is 253.7 nm (main emission of a low-pressure mercury lamp). The lamps used must be monokymatic, or the secondary emissions be cut-off (filters or monochromators). At that wavelength the molar absorption index considered now is 3000 L/mol.cm (IOA value of 1987 is confirmed by US-NIS)

The value as measured must be corrected for pressure and temperature of the gas, and eventual drift of the zero line.

The calibration method is the iodometric method.

4.2 Remark:

At a concentration of 194 g/m³ considering the absorption index and fixing a very maximum admissible optical density of 2.0 the necessary optical pathway of the cell becomes 0.167 cm. The problem of flow-through pattern and variable residence time remains. During a forum with the manufacturers, at the IOA-EAG symposium in Berlin 1997 these questions were addressed.

5. About the Design of "washing Flasks" for Iodometric Determination of Ozone in a Process Gas

5.1 Theoretical bases

- Fundamentally the reaction of ozone with iodide is of second order; but in the method(s) described, iodide always remains in excess and the reaction becomes pseudo-first order with $-k_1$ approximately 10⁸/s or a half reaction time of 6.9 x 10⁻⁹ seconds.
- The bubble rise velocity of ozone gas in laminar flow ranges 25-30 cm/s at a size of 4 to 6 mm diameter (7).
- At a depth of the liquid KI solution between 10 and 15 cm (avg. 12) and the flow rate at 1L/min., the theoretical contact time is 0.5 s or 2 x 10⁸ t_{1/2}

5.2 Mass transfer control of the reaction.

Two approaches (Masschelein (7)): symbols: k_L (R) and k_L respectively mass transfer coefficient with reaction and physical mass transfer coefficient without reaction ($k_L =$

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about $D(O_3)$ at Ph 7 and 20°C set at $1.74 \times 10^{-9} \text{ m}^2/\text{s}$ (value is under re-evaluation (Bin (7)))

(A calculated value for the diffusion coefficient of eventual OH-radical is $3.9 \times 10^{-9} \text{ m}^2/\text{s}$ (Roustan (8)).

5.2.1 Mass transfer coefficient acceleration coefficient (B), between ozone mass transfer with: $k_L(R)$ or without reaction:

$$k_L = 2 \times 10^{-4} \text{ m/s}$$

$$B = (1 + D_{O_3} \times k_1/k_L)^{1/2} = k_L(R)/k_L$$

Thus: $B = 24$; i.e. reaction is controlled by mass transfer

5.2.2 Approach based on the "Hatta number". It is considered that if the Hatta number is higher than 3 the reaction occurs essentially in the liquid film exchange layer of a bubble, $(Ha)^2 = (D_{O_3} \times k_2 \times \text{mol/l } O_3)/(k_L)^2$. Since $k_2 = 10^8 \text{ m}^{-1}\text{s}^{-1}$, Ha is higher than 3, thus the reaction is entirely mass transfer controlled.

As a consequence, mixing conditions are very important, and in the pseudo first order model, the reaction rate is about proportional to the velocity gradient.

5.3 The classical "open tube" washing flask

For high ozone concentrations in the gas phase it is recommended to operate with 530 mL of KI solution, the bubbling tube being immersed at a depth of 30 cm (Thieblin (6)). The gas expansion zone above the liquid reagent is usually small (10 cm). The diameter of the washing flask is 4.75 cm (2 inch). Flow of the gas bubbling is 0.25 L/min. The sampling tube plunges into the liquid reagent to reach 2.5 cm from the bottom, its diameter is between 2 and 5 mm (take 3). In such geometry the mixing conditions can be evaluated as follows:

The maximum velocity gradient in the bubble formation zone can be approached by the formula:

$$G(s-1) = g(\rho_l - \rho_g) \times d_b / 6 \mu;$$

with bubbles of 3mm diameter, and values taken as $\rho_l = 1.1 \times 10^3$; $\rho_g = 1.3$; $\mu = 1.2 \times 10^{-3}$; this ends by about 4500/s.

This value is independent of the immersion depth, the volume of the liquid and the gas flow rate.

The average velocity gradient is approached by:

$$G^2 = 10^5 \times (Q_{\text{gas}}) h / (\mu V (h/2 + 10.33)).$$

Usual washing flasks in Europe have an inside diameter between 6 and 8 cm. (take 7 as an example) and Q (gas) is 1L/min. In such conditions we have respectively for an immersion depth of 15 cm, and 30 cm: $G = 60/\text{s}$ and $120/\text{s}$.

5.4 "Washing flasks" with porous plate diffusers.

For classical bottles with inside diameter between 4.75 and 7.2 cm the diameter of the porous diffusers can range 3 to 5 cm. and the pore size 20 to 180 μm : 80 to 120 μm

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is the recommendable range for ozone transfer (Masschelein & Goossens (10)). In such conditions bubbles with size 1 to 2 mm diameter are generated. For 1.5 mm it results in a maximum velocity gradient in the range of 2000-2200/s, the average velocity gradient remaining unchanged compared to the examples in 5.3.

(REMARK: it has been reported that the porous elements can partially decompose ozone. We were not able to confirm this by just blowing (at + 0,5 bar) an ozone containing gas (concentration range 2 to 30 g/m³ in oxygen) through an empty washing flask or column. On regime, the concentration at inlet and outlet were identical. However the drawback of porous diffusers can be retention of iodine by adsorption in its structure, and, catalytic decomposition of I₂ cannot be excluded.

5.5 Bubbling flasks with aerodynamic amortized inlet: the so-called Muenke flasks.

5.5.1 In the classical German version for the determination of ozone in the gas phase (DIN Norm 19 627 (11)) as published, (applicable to max. 80 g/m³) (see also Maier (12)).

- Total volume: 500 mL; buffer volume capacity : 50 ml; bubble formation orifices: 5 in number one straight-on, four lateral on-side, one straight-on, diameter 1.2 mm each, the straight down orifice being located at the very bottom of the washing flask.
- Total KI reagent volume 200mL; i.e. 6 cm liquid or an average theoretical contact time of 0,25 seconds.

Consequently the "Muenke flask" technology is based on instant mixing conditions rather than on reaction time. Two flasks are mounted in series, for control.

Mixing conditions: bubble size at exit pores: 1 mm diameter, depending on the gas pressure at the inlet. In such assumptions the maximum velocity gradient equals about 2000/s which is convenient. The average velocity gradient becomes 200/s (Remark: the flask is equipped with "plain glass" tubes both at inlet and outlet of the gases, with an outside "male" glass connection to the washing flask and without security protection against "bumping" of the gas in case of instant excess-pressure.

5.5.2 The Belgian version of the Muenke flask: Inside diameter of 6cm; useful height of 13 cm: total useful volume 370 mL. Inlet buffer volume capacity: 35 mL; Outlet safety volume: 100 mL. Bubble formation orifices: same as for the German version but located at 1.2-2 cm above the bottom. Total KI reagent volume: 200mL; i.e. 7 cm liquid reagent or an average theoretical contact time of 0.3s; maximum velocity gradient at inlet (bubbles of 1.2 mm diameter) is again about 2000/s. The average velocity gradient becomes 220/s

(REMARK: The upper part of the flask is closed with a female grinded-close on the male end of the flask. This geometry makes the transfer to the titration vessel and subsequent cleaning of the flask easier. The upper parts are also equipped with hooks for fixing the upper part with springs to prevent hydraulic accidents in case of over-pressure. Ends of in- and outlet tubes are ribbed).

6. Conclusions:

- Expression of ozone concentrations in the gas phase is to be given at NTP (i.e. 0°C and 1 atm)
- Iodometric titration, properly performed is the selected calibration method.

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- UV-absorption photometry is, at present, the most practical monitoring method for ozone concentration in a process gas containing up to 200 mg/L ozone.
- New developments will be necessary for monitoring equipment dealing with higher concentrations of ozone in the process gas.
- Accurate standardization by the iodometric method supposes appropriate design of the ozone to iodide solution contacting systems.

References

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