



## New Data Processing Equation to Improve the Response Time of an Electrochemical Concentration Cell (ECC) Ozonesonde

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### ABSTRACT

Ozone concentrations of an electrochemical concentration cell (ECC) ozonesonde determined using a data processing equation typically lag changes in the concentrations of ozone sampled into an ECC by 20–40 s. This work develops a new equation for determining ozone concentrations of an ECC ozonesonde so that the determined ozone concentrations can respond relatively quickly to changes in the concentrations of the ozone sampled into the ECC. The new equation is derived by examining the chemical reaction rates and transport limits of related species and electrons in an ECC. To demonstrate the power of the new equation, an ECC is exposed to prescribed variations of ozone concentrations. The variations of the ozone concentrations of an ECC that are determined using both the new and the old equations are compared to the prescribed ozone variations. The results demonstrate that the ozone concentrations that are determined using the new equation responds approximately 50% faster to the prescribed ozone variations than do those obtained using the old equation.

**Keywords:** Ozone; Ozonesonde; Response time; ECC; Vertical.

### INTRODUCTION

Since the 1970s, the ozonesonde has been the most important instrument that is used to measure vertical distributions of ozone from the surface to 35–40 km above the ground (Komhyr, 1969; Logan, 1994; Oltmans *et al.*, 2001; Lin *et al.*, 2010). The three common types of ozonesonde are the Brewer-Mast, the carbon iodine cell and the electrochemical concentration cell (ECC), which were initially developed by Brewer and Millford (1960), Kobayashi and Toyama (1966) and Komhyr (1969), respectively. Currently, most users favor the ECC ozonesonde owing to its relative stability (Smit *et al.*, 2007). In this study, we focus on the ECC ozonesonde, but our results can be easily extended to the other two types of ozonesonde.

Fig. 1 shows comparison between the ozone concentrations determined from an ECC ozonesonde and prescribed ozone concentrations. The later was produced from an ozone calibrator. The calibrator provided ozone free air at the start and continued for 10 minutes. Subsequently, it abruptly provided 100 ppb of ozone and continued for another 10

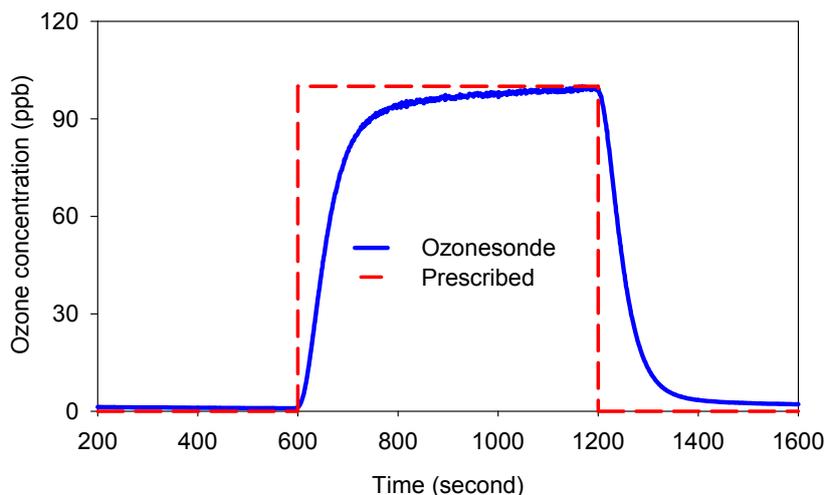
minutes. Finally, it abruptly provided ozone free air again and continued for another 10 minutes. This kind of experiment is a standard process in a preparation of an ECC ozonesonde (Komhyr *et al.*, 1995; SPC, 1999). Obviously, the ECC ozonesonde need some times to respond to the prescribed ozone variations (Fig. 1). The slow response of an ECC ozonesonde is likely caused by some limitations, such as chemical reactions and transportation of related species and electrons in the ECC (Thornton and Niazy, 1982; Thornton and Niazy, 1983; Komhyr *et al.*, 1995; Vomel and Diaz, 2010). A slow response of an ECC ozonesonde can make it underestimate or overestimate the real ozone concentrations when they are increasing or decreasing, respectively. Notably, ozone concentrations typically increase with altitude from the high troposphere to the middle ozone layer (within the low stratosphere) and decrease with altitude beyond the middle ozone layer (Komhyr *et al.*, 1995). This feature suggests that an ozonesonde may underestimate ozone concentrations at the altitudes in the lower part of the ozone layer and overestimate at the altitudes in the upper part of the ozone layer, respectively.

This work develops a new equation for determining ozone concentrations of an ECC ozonesonde so that the determined ozone concentrations can respond relatively quickly to changes in the concentrations of the ozone sampled into the ECC. As a result, the new equation can enable an ozonesonde to diminish underestimation and overestimation

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**Fig. 1.** Comparison between ozone concentrations determined by an ECC ozonesonde using Eq. (1) and prescribed concentrations of ozone sampled into the ECC.

of ozone concentrations in a vertical sounding while the ambient ozone concentration is increasing with altitude and decreasing with altitude, respectively.

## METHODOLOGY

### Typical Data Processing Equation

Fig. 2 shows the ECC of an ozonesonde. The details of its structure can be found elsewhere (Komhyr *et al.*, 1995; SPC, 1999). An ozonesonde contains a cathodic half-cell and an anodic half-cell. Typically, one of the two half-cells is filled with 1% potassium iodide (KI) solution and the other is filled with saturated KI solution. An ion bridge between the two solutions provides an ion pathway while preventing the mixing of the two solutions. One platinum electrode is immersed in each of the two solutions, and these electrodes are connected to each other by an external circuit. The external circuit provides the pathway for the transfer of electrons from the anode to the cathode. When ozone is sampled into the cathode solution, it reacts with KI, triggering a tri-iodide/iodide redox reaction (Komhyr *et al.*, 1995). When the redox reaction occurs, a current can be measured through the external circuit. This external current was used to determine the ozone concentration of an ECC ozonesonde (Komhyr *et al.*, 1995).

The typical data processing equation, hereafter the old equation, to determine ozone concentration measured by an ECC ozonesonde (Komhyr *et al.*, 1995; Smit *et al.*, 2007; Vomel and Diaz, 2010) is,

$$[O_3] = \frac{RT\zeta\eta_p(i - i_b)}{2FQ} \quad (1)$$

where  $[O_3]$  is the determined ozone concentration in mPa;  $Q$  is the flow rate of air that is sampled in the ECC in liter/s;  $R$  is the universal gas constant, 8.314 J/K-mol;  $T$  is the absolute temperature of the sampled air;  $\eta_p$  is the pump sampling efficiency, which is used to correct for leakage

from the air pump at high altitude;  $\zeta$  is the correction coefficient of the reaction stoichiometry;  $i$  is the current that is measured at the external circuit in  $\mu\text{A}$ ;  $i_b$  is the background current, and  $F$  is the Faraday constant, 96485 C/mol. The term  $i_b$  represents the blank current in an ECC, and is generally measured when an ECC is exposed to ozone-free air for a period of around 10 minutes. Many researchers have investigated the interference of a background current on the accuracy of an ECC ozonesonde (Thornton and Niazy, 1982; Barnes *et al.*, 1985; Komhyr *et al.*, 1995; Reid *et al.*, 1996; Boyd *et al.*, 1998; Smit *et al.*, 2007; Vomel and Diaz, 2010). Pump sampling efficiencies can become important at low pressure environment (Johnson *et al.*, 2002). The stoichiometry is designed to correct for the effects of some possible side reactions in the ECC solution (Vomel and Diaz, 2010). The stoichiometry is slightly influenced by pH. When the pH is close to neutral, it is  $1.00 \pm 0.03$  (Dietz *et al.*, 1973). Most users neglect the effect of the stoichiometry and set it to unity (Oltmans *et al.*, 1996; Bodeker *et al.*, 1998; Newchurch *et al.*, 2003; Thompson *et al.*, 2007; Takashima *et al.*, 2008). Theoretically, all parameters in Eq. (1) influence the accuracy of an ECC ozonesonde. The typical accuracy of an ECC ozonesonde is  $\pm 5$  to  $\pm 15\%$  (Barnes *et al.*, 1985; Komhyr *et al.*, 1995; Boyd *et al.*, 1998; Smit *et al.*, 2007). As mentioned, the ozone concentrations of an ECC ozonesonde determined using Eq. (1) lag actual changes in the concentrations of ozone sampled into an ECC by 20–40 s. This drawback will be improved in this work.

### New Data Processing Equation

#### Chemical Reactions and Transport Processes in an ECC

When ozone is sampled into an ECC, various chemical reactions may occur within the solutions of both the cathode and anode of the ECC. And species and electrons may be transported in the cathode and anode solutions, in the ion bridge, in the external circuit and at the surfaces of the electrodes that are immersed in the solutions. However, large resistances, which control the overall rate of the redox

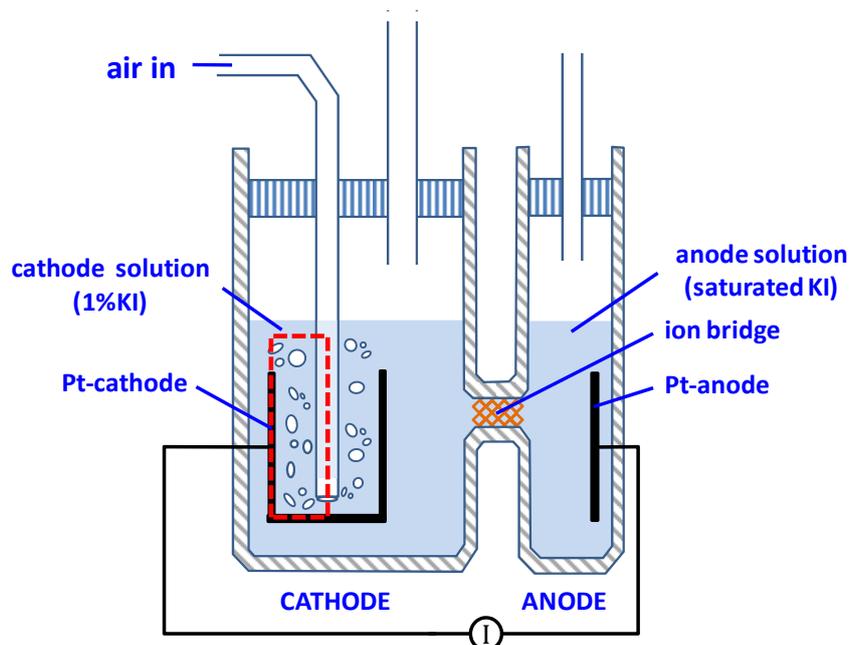


Fig. 2. Structure of an ECC; region enclosed by the dashed boundary is scaled up in Fig. 3.

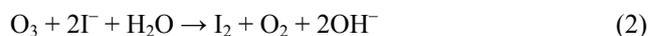
reaction of the system or the magnitude of the external current are expected to present in the cathode solution because major chemical reactions and changes in the concentrations of related species occur there. Therefore, the following will focus only on reactions and transport processes in the cathode solution.

The ability of a chemical species to be transported in a cathode solution is determined by the turbulence of that solution. Simply, the cathode solution in an ECC consists of a turbulent region and a non-turbulent region. Most of the solution is turbulent owing to the turbulence that is produced by air bubbles that are formed when the air is sampled into the solution (Fig. 3). The transport of a species in such a turbulent region is fast, and turbulent mixing causes the species in the turbulent region to be uniformly distributed. The turbulent region in the cathode solution is expected to be present in the core region of the solution, as indicated in Fig. 3. The non-turbulent region in the solution, hereafter called the diffusion region, is very close to the wall of the cathode cell and the electrode. In this region, also known as the wall region, turbulence is low owing to fluid viscosity (Hinze, 1975). The transport of a chemical species in the diffusion region, which proceeds only by molecular diffusion, is, therefore, limited. Accordingly, a concentration gradient of chemical species in the diffusion layer is expected. The diffusion layer in the cathode solution of concern herein is the one around the electrode, as indicated in Fig. 3.

Six steps between the dissolution of ozone that is sampled in the cathode solution of an ECC and the triggering of the flow of electrons in the external circuit are proposed and shown in Fig. 3. These steps are (I) a chemical reaction between  $O_3$  and  $I^-$  to form  $I_2$  (iodine) in the cathodic turbulent region, (II) a chemical reaction between  $I_2$  and  $I^-$  to form  $I_3^-$  in the same cathodic turbulent region, (III) the

diffusion transport of  $I_3^-$  from the turbulent region to the vicinity of the cathode electrode within the diffusion layer, (IV) the reduction reaction of  $I_3^-$  to  $I^-$  in the vicinity of the cathode electrode, (V) the transport of electrons from the surface of the cathode electrode to the surrounding cathode solution, and (VI) the transport of electrons in the external circuit. Notably, steps (I)–(III) are expected to take place in sequence but steps (IV)–(VI) occur at the same time.

The outlet of the sampling tube of an ECC is specially designed to be located at the bottom of the cathode cell, and to be surrounded by the cathode. This arrangement ensures that the air bubbles that are produced by the sampling air are small and uniform, allowing  $O_3$  molecules within the bubbles to dissolve immediately and completely into the cathode solution (Komhyr, 1969; Komhyr *et al.*, 1995). After an ozone molecule dissolves into the cathodic turbulent solution, the  $O_3$  immediately reacts with  $I^-$  in the region, as in step I in Fig. 3:



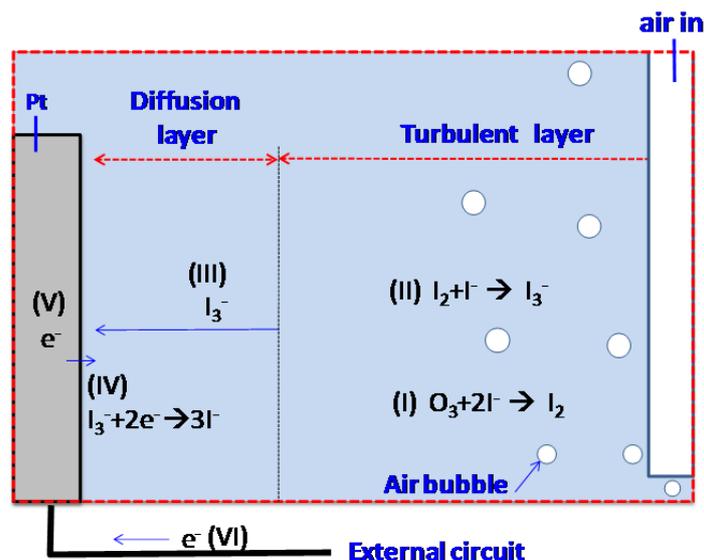
This reaction is believed to proceed rapidly (Komhyr *et al.*, 1995). Therefore, the rate of production of  $I_2$  in the turbulent region,  $[P_{I_2}]_c$ , equals the mass flow rate of the ozone that dissolves into the cathode solution,  $\dot{M}_{O_3}$ :

$$[P_{I_2}]_c = \dot{M}_{O_3} = \frac{[O_3]Q}{RT} \quad (3)$$

where the lower index c refers to the cathodic turbulent region.

The produced  $I_2$  in Eq. (2) is expected to combine rapidly with  $I^-$  to form  $I_3^-$ , as in step II in Fig. 3:





**Fig. 3.** Chemical reactions and transport processes in the cathode solution of an ECC during ozone measurement. Notably, the depth of the diffusion layer is scaled up greatly.

This reaction is also expected to be fast since the reaction constant for the formation of  $I_3^-$  in Eq. (4) is large,  $710 \text{ M}^{-1}$  (Lingane, 1970; Thornton and Niazy, 1982), and the concentration of  $I^-$  in the solution is as high as 1%. Therefore, the  $I_2$  that is generated according to Eq. (2) will be immediately eliminated according to Eq. (4). As a result, the rates of production and loss of  $I_2$  in the cathodic turbulent region equal each other,  $[P_{I_2}]_c = [L_{I_2}]_c$ . Consequently, the rate of production of  $I_3^-$  in the cathodic turbulent region,  $[P_{I_3}]_c$ , in Eq. (4), equals the mass flow rate of the ozone:

$$[P_{I_3}]_c = [L_{I_2}]_c = [P_{I_2}]_c = \frac{[O_3]Q}{RT} \quad (5)$$

In summary, the process and chemical reactions that form  $I_3^-$ , triggered by the ozone that is sampled in the cathodic turbulent region proceed rapidly. Therefore, neither step I nor step II is responsible for the time lag of an ECC.

Once enough  $I_3^-$  is produced in the cathodic turbulent region, the concentration of  $I_3^-$  in that region will exceed that in the vicinity of the cathode electrode, which is a sink of  $I_3^-$  owing to the reduction reaction. As a result, a concentration gradient of  $I_3^-$  is formed or enhanced in the diffusion layer, causing the transport of  $I_3^-$  from the cathodic turbulent region to the vicinity of the cathode electrode by molecular diffusion, shown as step III in Fig. 3. This step is proposed to be the step that dominates the overall rate of the system since mass transfer determined by the molecular diffusion of  $I_3^-$  in the diffusion layer is expected to be quite slow. The rate of diffusion of  $I_3^-$  from the turbulent region to the vicinity of the cathode,  $J_{I_3}$ , is expressed using Fick's law,

$$J_{I_3} = A \cdot D \frac{d[I_3^-]_d}{dx} \quad (6)$$

where the lower index d refers to the diffusion region;  $A$  is

the total surface area of the electrode;  $D$  is the molecular diffusivity of  $I_3^-$ , and  $x$  is the distance to the diffusion layer from the electrode surface. For simplicity, the variation in concentration of  $I_3^-$  in the diffusion layer is assumed to be linear, and the diffusion rate in Eq. (6) then becomes,

$$\begin{aligned} J_{I_3} &= A \cdot D \frac{[I_3^-]_c - [I_3^-]_0}{\delta} \\ &= A \cdot \left(\frac{D}{\delta}\right) \cdot ([I_3^-]_c - [I_3^-]_0) \\ &= A \cdot k_d \cdot ([I_3^-]_c - [I_3^-]_0) \end{aligned} \quad (7)$$

where the lower 0 refers to the vicinity of the electrode, and  $\delta$  represents the thickness of the diffusion layer. The ratio  $D/\delta$  is defined as the mass transfer constant of  $I_3^-$  in the diffusion layer,  $k_d$  (Thornton and Niazy, 1983).

The  $I_3^-$  in the vicinity of the cathode electrode is expected to undergo a reduction reaction, as indicated in step IV in Fig. 3:



Actually, the electrons in Eq. (8) are originally generated in the oxidation of  $I^-$  in the anode solution,



The reduction reaction of  $I_3^-$  in Eq. (8) and the oxidation of  $I^-$  in Eq. (9) together constitute a redox reaction and occur simultaneously. The electrons that are generated in Eq. (9) are delivered via external circuit (step VI in Fig. 3) to the cathode and then pass through the surface of the cathode (step V in Fig. 3), before finally participating in the reaction in Eq. (8) (step IV in Fig. 3). Owing to the reduction of  $I_3^-$  in Eq. (8), electrons are transferred from the surface of the cathode to the surrounding cathode solution (step V

in Fig. 3). The external circuit (step VI in Fig. 3) is caused simultaneously and stoichiometrically to the reduction of  $I_3^-$  in Eq. (8),

$$\frac{i}{2F} = \frac{J_c}{2} = [L_{I_3}]_0 \quad (10)$$

where  $[L_{I_3}]_0$  is the rate of reduction of  $I_3^-$  in Eq. (8);  $J_c$  is the rate of transfer of electrons from the surface of the cathode to the surrounding cathode solution, and  $i$  is the magnitude of the current.

The rate of reduction of  $I_3^-$  or the rate of the redox reaction of  $I_3^-/I^-$  depends strongly on the electromotive potential between the cathode and the anode,  $E$ , which can be determined from the Nernst equation (Lingane, 1970; Vassos and Ewing, 1983):

$$E = \frac{RT}{nF} \ln \left( \frac{[I_3^-]_0 [I^-]_a^3}{[I^-]_0^3 [I_3^-]_a} \right) \quad (11)$$

where the lower index  $a$  refers to the vicinity of the anode in the anode solution. Notably, the concentrations of the species in Eq. (11) should be expressed as activities. Were they expressed as concentrations, the estimated  $E$  would have an uncertainty of around 10% (Thornton and Niazy, 1982).

Clearly, when the electromotive potential becomes small, steps IV–VI become the dominant steps of the system. The transfer of electrons from the surface of the cathode to the surrounding cathode solution is proposed herein to dominate the overall resistance in steps of IV–VI, as suggested by Thornton and Niazy (1982). The electromotive potential is difficult to simulate. However,  $[I_3^-]_0$  is expected to dominate the variation of  $E$  because the concentrations of other three species are stable in Eq. (11). The transfer rate of electrons,  $J_c$ , is then simulated as,

$$J_c/2 = A \cdot k_h \cdot [I_3^-]_0 \quad (12)$$

where  $k_h$  is the heterogeneous transfer constant of electrons. The use of  $[I_3^-]_0$  in Eq. (12) is simply to simulate the effect of the electromotive potential,  $E$ . The effects of  $[I_3^-]_a$ ,  $[I^-]_a$  and  $[I^-]_0$  on  $E$  are accounted for by the constant  $k_h$ . Theoretically,  $k_h$  is also related to temperature because the electromotive potential is proportional to temperature, according to Eq. (11). Fortunately, the temperature of the cathode solution is expected to be maintained by the sampled air. The sampled air is heated by the air pump, and the temperature falls by roughly 10°K during a typical vertical measurement of ozone from the surface to 35–40 km above the ground (Smit *et al.*, 2007). Therefore, the possible decrease in the  $k_h$  is about 3% when the sampled air on the ground is 300°K. Eqs. (10) and (12) yield the relationship between the current magnitude  $i$  and  $[I_3^-]_0$ ,

$$\frac{i}{2F} = \frac{J_c}{2} = [L_{I_3}]_0 = A \cdot k_h \cdot [I_3^-]_0 \quad (13)$$

Finally, the hetero-transfer rate of electrons,  $k_h$ , in Eqs.

(12) or (13) implicitly accounts for the effects of the overall resistances on the transport of electrons from the anode solution to the cathode solution because all of these electronic transport processes are coupled together and referred to simply as the transport of electrons from the surface of the cathode to the surrounding cathode solution, as in step V in Fig. 3. As a result, the hetero-transfer constant,  $k_h$ , can also be regarded as the overall mass transfer constant of the electrons from the anode solution to the cathode solution.

Based on the six steps that were listed in the previous section, the response lag of an ECC is assumed to be caused by the low diffusion rate of  $I_3^-$  from the cathodic turbulent region to the vicinity of the cathode and by the low heterogeneous transfer rate of electrons from the surface of the cathode to the surrounding cathode solution when the electronic potential between the anode and cathode becomes small. The heterogeneous transfer rate of electrons is expected to be proportional to the concentration of  $I_3^-$ , according to Eqs. (12) or (13). Therefore, when the concentrations of  $I_3^-$  in the cathode solution are relatively high, the magnitude of the external current is expected to be limited by the diffusion rate of  $I_3^-$ . Conversely, when the concentrations of  $I_3^-$  become low, the magnitude of the external current is expected to be limited by the heterogeneous transfer rate of electrons. The latter situation can arise when no ozone enters the cathode solution and the concentration of the residual  $I_3^-$  in the cathode solution decreases significantly.

#### *New Equation Development under the Diffusion Limit of Tri-iodide Transport*

When the overall rate of the system or the current magnitude at the external circuit is determined by the rate of diffusion of  $I_3^-$  from the cathodic turbulent region to the vicinity of the cathode, the subsequent reduction rate of  $I_3^-$  and transfer rate of electrons, as expressed in Eq. (13), equal the diffusion rate of  $I_3^-$ ,  $J_{I_3}$ . Therefore, the following relationship is obtained,

$$J_{I_3} = A \cdot k_d \cdot [I_3^-]_c = [L_{I_3}]_0 = \frac{J_c}{2} = \frac{i}{2F} \quad (14)$$

Notably, in Eq. (14), the concentration of  $I_3^-$  in the vicinity of the cathode  $[I_3^-]_0$  is neglected because it is much smaller than that in the turbulent region,  $[I_3^-]_c$ . Rearranging of Eq. (14) yields the relationship between the concentration of  $I_3^-$  in the turbulent region of the cathode solution and the external current,

$$[I_3^-]_c = \frac{i}{A \cdot k_d \cdot 2F} \quad (15)$$

The relationship between the concentration of the ozone that was sampled into the cathode solution,  $[O_3]$ , and  $[I_3^-]_c$  can be derived by applying the principle of mass balance to  $I_3^-$  in the cathodic turbulent region. Notably, the variation of the  $I_3^-$  concentration in the cathodic turbulent region is determined by the rate of production of  $I_3^-$  in Eq. (5) and its rate of loss by diffusion into the vicinity of the cathode in Eq. (14):

$$V \frac{d[I_3^-]_c}{dt} = [P_{I_3}]_c - J_{I_3} = \frac{[O_3]Q}{RT} - A \cdot k_d \cdot [I_3^-]_c \quad (16)$$

where  $V$  is the volume of the cathode solution. Notably,  $V$  is almost equal to the volume of the cathodic turbulent region because the diffusion region is a very small proportion of  $V$ . Eqs. (15) and 16 yield the relationship between the concentration of ozone sampled into the ECC and the external current:

$$\left(\frac{V}{A \cdot k_d \cdot 2F}\right) \frac{di}{dt} = \frac{[O_3]Q}{RT} - \frac{i}{2F} \quad (17)$$

For simplicity, the response time of an ECC,  $\tau^d$ , is defined as the diffusion time scale of tri-iodide in the diffusion layer,

$$\tau_d = \frac{V}{A \cdot k_d} \quad (18)$$

A unit transfer coefficient,  $\alpha$ , is defined as,

$$\alpha = \frac{RT}{2FQ} \quad (19)$$

The unit transfer coefficient is the required ozone concentration in mPa that can yield a non-varying external current of 1  $\mu$ A in the ECC. Eqs. (18) and (19) reduce Eq. (17) as,

$$\frac{di}{dt} + \left(\frac{1}{\tau_d}\right)i = \left(\frac{1}{\alpha \cdot \tau_d}\right)[O_3] \quad (20)$$

#### *New Equation Development under Hetero-transfer Limit of Electron Transport*

When the overall rate of the system is limited by the heterogeneous transfer rate of electrons from the surface of the cathode electrode to the surrounding cathode solution, the rate of removal of  $I_3^-$  by its reduction in the vicinity of the cathode is also limited owing to the lack of available electrons. Then,  $I_3^-$  accumulates in the vicinity of the cathode. As a result, the difference between  $[I_3^-]_c$  and  $[I_3^-]_0$  is expected to be small and  $[I_3^-]_c$  can be assumed to equal  $[I_3^-]_0$ . Based on this assumption, the relationship between the concentration of  $I_3^-$  in the turbulent region and the external current is obtained from Eq. (13) as,

$$[I_3^-]_c = [I_3^-]_0 = \frac{i}{A \cdot k_h \cdot 2F} \quad (21)$$

As in the derivations of Eqs. (16) to (20), initially applying the principle of conservation of mass to  $I_3^-$  and replacing the rate of loss in the cathodic turbulent region,  $J_{I_3}$ , with  $[L_{I_3}]_0$ , given by Eq. (13), yields the relationship between the concentration of ozone sampled into the ECC and the external current as,

$$\frac{di}{dt} + \left(\frac{1}{\tau_h}\right)i = \left(\frac{1}{\alpha \cdot \tau_h}\right)[O_3] \quad (22)$$

where  $\tau_h$  is the response time of an ECC when the overall rate of the system is limited by the hetero-transfer rate of the electrons, and is defined as

$$\tau_h = \frac{V}{A \cdot k_h} \quad (23)$$

#### *General form of the New Equation*

Notably, the relationship between the concentration of  $I_3^-$  and the external current when the overall rate of the system or the current magnitude at the external circuit is limited by the diffusion rate of tri-iodide is similar to that when the overall rate is limited by the hetero-transfer rate of the electrons, as given by Eqs. (15) and (21), respectively. Similarly, the relationships between the ozone concentration and the external current in the two limiting cases are similar to each other, as given by Eqs. (20) and (22), respectively. For simplicity, the general response time of an ECC,  $\tau$ , is defined as,

$$\tau = \frac{V}{A \cdot k} = \begin{cases} \tau_d & \text{for diffusion-limited case} \\ \tau_h & \text{for hetero-transfer-limited case} \end{cases} \quad (24)$$

where  $k$  is a general mass transfer constant and is  $k_d$  or  $k_h$  in the diffusion-limited case or the hetero-transfer-limited case, respectively. More generally, a transition in which  $\tau$  is between  $\tau_d$  and  $\tau_h$  is expected. A general form of the relationship between the concentration of  $I_3^-$  in the cathodic turbulent solution and the external current is obtained in terms of  $\tau$ :

$$[I_3^-]_c = \frac{i}{A \cdot k \cdot 2F} = \frac{\tau}{V} \left(\frac{i}{2F}\right) \quad (25)$$

Similarly, a general form of the relationship between the concentration of ozone sampled into an ECC and the external current of the ECC is obtained:

$$\frac{di}{dt} + \left(\frac{1}{\tau}\right)i = \left(\frac{1}{\alpha \cdot \tau}\right)[O_3] \quad (26)$$

Eq. (26) suggests that the external current of an ECC will naturally undergo first-order decay. As well, the concentration of ozone sampled into the ECC is proportionally to both the external current and its time derivation rate. The concentration of tri-iodide is directly related to the external current, as indicated by Eq. (25). Therefore Eq. (26) implies that the tri-iodide will naturally undergo first-order decay in the cathode solution and that ozone is the source of the tri-iodide.

Eq. (26) describes the relationship between the concentration of ozone that is sampled into an ECC and the external current of the ECC. The concentration of ozone sampled into an ECC is thus obtained from Eq. (26) as,

$$[O_3] = \frac{\alpha \cdot \tau}{1} \frac{di}{dt} + \alpha \cdot i \quad (27)$$

With reference to Eq. (1), when the correction coefficient of the reaction stoichiometry  $\xi$ , the pump sampling efficiency  $\eta_p$  and the background current  $i_b$  are also considered, the ozone concentration in Eq. (27) becomes,

$$[O_3] = \frac{\alpha \cdot \xi \cdot \eta_p \cdot \tau}{1} \frac{d(i-i_b)}{dt} + \alpha \cdot \xi \cdot \eta_p \cdot (i-i_b) \quad (28)$$

Eq. (28) is the final, new equation that is suggested to be used to determine the concentration of ozone as measured by an ECC ozonesonde. Notably, if the first term on the right-hand side of Eq. (28), which is a derivative with respect to time, is omitted, then Eq. (28) is identical to Eq. (1). Therefore, the old equation, Eq. (1), is the steady-state form of the new equation, Eq. (28).

The new equation, Eq. (28), needs one more parameter, the response time  $\tau$ , than does the old equation, Eq. (1). The  $\tau$ , given by Eq. (24), is either the time-scale of the diffusion of tri-iodide within the diffusion layer or the time-scale of transport of the electrons through the electrode surface. Notably, the two response times can be experimentally determined by measuring the variation of the external current because the transport rates of both the tri-iodide and the electrons are simultaneously link to the magnitude of the external current.

### Experimental Set up

A commercial Model 6A ECC (SPC, USA) was used in this study. The cathode solution of the ECC was prepared from 1% KI with a buffer, as described in an ozonesonde manual (SPC, 1999). The cathode and anode solutions were made using deionized water and A.C.S. analyzed grade chemicals. A Sabio Gas Dilution Calibrator (Model 4010) was used as the ozone source for the experimental ECC. The calibrator showed good agreement ( $\pm 1\%$  at 100 ppbv) when compared to the ozone calibrator standard maintained by Taiwan Environmental Protective Administration. Before the experiment, the experimental ECC was conditioned with ozone free air for two hours to clean the sampling tube. Then, the calibrator consecutively provided ozone free air, 100 ppb of ozone, and ozone free air for the experimental ECC. Each concentration level was kept for 10 minutes, and changes of the different concentration levels were automatically controlled by the calibrator. To demonstrate the power of the new equation, ozone concentrations in the ECC were determined using both the new and the old equations, Eq. (1), respectively, and compared to the provided ozone concentrations. The response time  $\tau$ , needed in Eqs. (27) or (28), can be derived from the variation of the residual current of the ECC during its final exposure to ozone-free air. In this period of exposure, the ozone concentrations in Eq. (27) can be set to zero. As a result, Eq. (27) is reduced to

$$\frac{di}{dt} + \left(\frac{1}{\tau}\right)i = 0, i = i_0 \text{ when } t = 0 \quad (29)$$

where  $i_0$  is the initial magnitude of the external current at  $t = 0$ , which is the moment when the ECC was exposed to ozone-free air immediately after the exposure to 100 ppb ozone. The exact solution to Eq. (29) can be easily obtained as,

$$i = i_0 e^{-t/\tau} \quad (30)$$

or

$$\ln(i) = \ln(i_0) - \frac{t}{\tau} \quad (31)$$

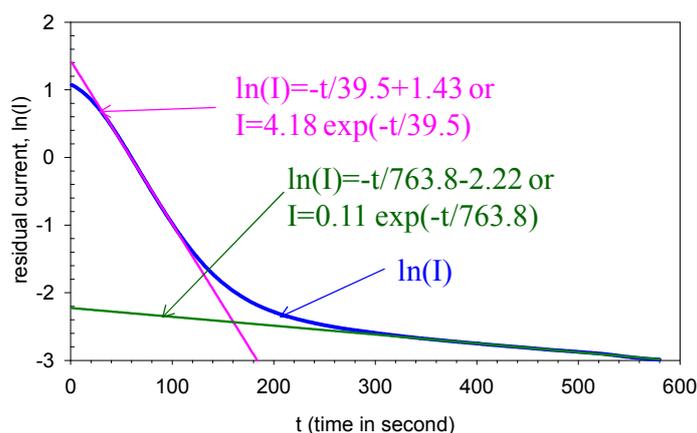
Therefore, fitting the data of the residual current in the period of exposure to ozone-free air using Eq. (31) can yield the response time needed in Eqs. (27) or (28).

## RESULTS AND DISCUSSION

### Response Time of External Electronic Current of an ECC

Fig. 4 plots the variation of the external current of an ECC ozonesonde on a logarithmic scale upon exposure to ozone-free air immediately after exposure to 100 ppb of ozone. Clearly, the residual current decayed relatively quickly and stably in the first 100 s, passing through a transitional period at 100–300 s, and entering a period of relatively slow and stable decay after 300 s. Fitting the data of the residual current using Eqs. (30) and (31) yields response times in the periods of relatively fast and slow decay of 39.5 and 763.8 s, respectively. The decay behavior of the residual current was consistent with the results of Vomel and Diaz (2010). The two time-scales of the decay of the residual current are supposed to  $\tau_d$  and  $\tau_h$ , respectively. Notably, ozone is the source of  $I_3^-$  in the cathode solution through the reactions that are described by Eqs. (2) and (4). During the period of exposure to 100 ppb of ozone, the cathode solution contains plenty of  $I_3^-$ . When the ECC is then exposed to ozone-free air, the production of  $I_3^-$  in the cathode solution halts. However,  $I_3^-$  is still abundant in the cathode solution because it had been produced in large amounts during the period of exposure to 100 ppb of ozone. The residual  $I_3^-$  continuously diffuses from the cathodic turbulent region to the vicinity of the cathode, where it undergoes a reduction reaction. This process explains the presence of the residual current during the period of exposure to ozone-free air. Moreover, the residual current (Fig. 4) decreases with time because the concentration of  $I_3^-$  in the cathode solution decreases with time owing to the continuous reduction reaction. In the initial 100 s of exposure to ozone-free air, the concentration of  $I_3^-$  in the cathodic solution is relatively high. Therefore, the overall rate of the system is diffusion-limited with the proposed  $\tau_d = 39.5$  s. After 300 s of exposure of ozone-free air, the concentration of  $I_3^-$  continues to fall. The electromotive potential becomes small, which is determined by  $[I_3^-]_0$ . Consequently, the overall rate of the system becomes the hetero-limited, with the proposed  $\tau_h = 763.8$  s.

The proposed  $\tau_d$  can also be theoretically estimated using Eq. (18) and the definition of  $k_d = D/\delta$  in Eq. (7).



**Fig. 4.** Variations of residual current of an ECC on a logarithmic scale (blue line) as it is exposed to ozone-free air right after exposure to 100 ppb ozone at  $t = 0$ . The purple and green lines are the regression lines to derive the first response time and to the second response time, respectively.

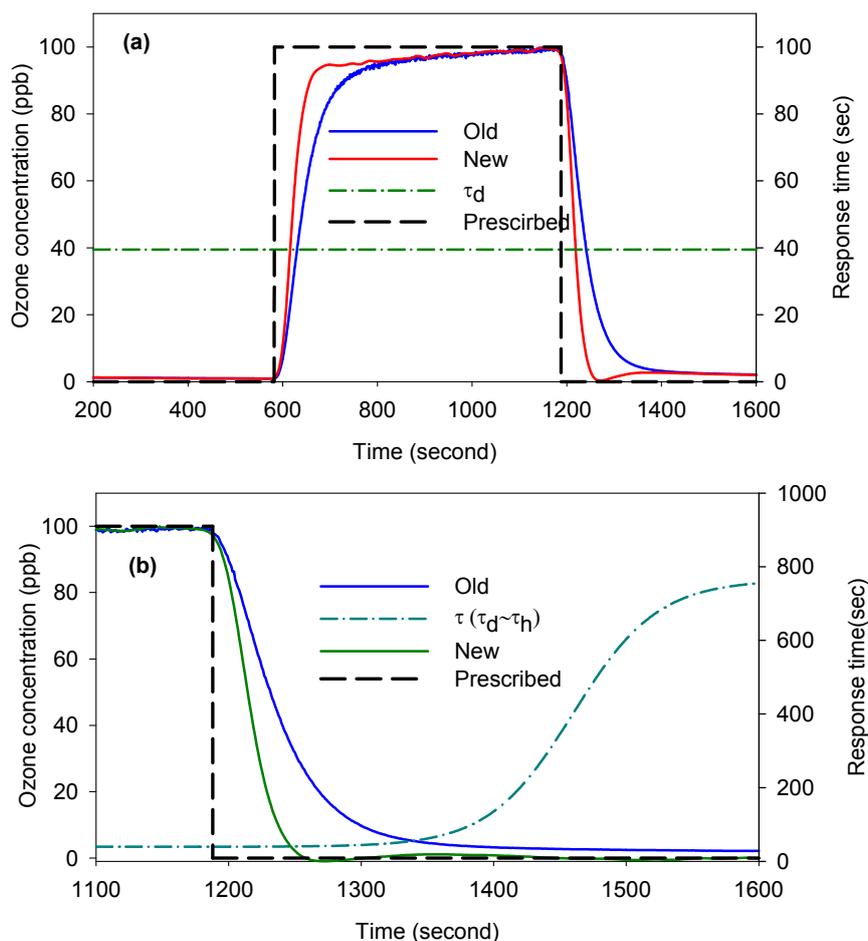
According to Cantrel *et al.* (1997), the  $D$  of  $I_3^-$  is about  $0.000014 \text{ cm}^2/\text{s}$ . From another investigation,  $\delta$  is in the range  $0.001\text{--}0.01 \text{ cm}$  (Bard and Faulkner, 2001). As a result,  $k_d$  of  $I_3^-$  is in the range  $0.0014\text{--}0.014 \text{ cm/s}$ . The  $V$  and  $A$  for an ECC are  $2.5 \text{ cm}^3$  and  $20 \text{ cm}^2$ , respectively (Komhyr *et al.*, 1995). Based on these data, the estimated  $k_d$  is at  $9\text{--}90 \text{ s}$ . The time scale of the fast response, the proposed  $\tau = 39.5 \text{ s}$  (Fig. 4), is in the range of the estimated  $\tau_d$ , further supporting the speculation herein that the response time of the residual current in the period of fast decay in Fig. 4 is governed by  $\tau_d$ , which is the time-scale of diffusion of  $I_3^-$  in the diffusion layer around the cathode. The proposed  $\tau_h$  is unable to check with a theoretical estimation because  $k_h$  is not available in the knowledge of the authors.

#### Validation of the New Data Processing Equation

The variations of the ozone concentrations of the ECC that are determined using both the new equation, Eq. (28), and the old equation, Eq. (1), are compared to the prescribed ozone variations in Figs. 5(a) and 5(b). For simplicity, in the determination of the ozone concentrations using the two equations, the correction coefficient of the reaction stoichiometry and the pump sampling efficiency are set to unity and the background current is set to zero. In Fig. 5(a), the required response time in the new equation was set to the proposed  $\tau_d = 39.5 \text{ s}$ , which is the first response time that was obtained from Fig. 4. In Fig. 5(b), the required response time in the new equation was set to the proposed  $\tau_d = 39.5 \text{ s}$  from the beginning of the experiment to  $1350 \text{ s}$ , and to a time-dependent response time between the proposed  $\tau_d = 39.5 \text{ s}$  and  $\tau_h = 763.8 \text{ s}$  after  $1350 \text{ s}$ . Clearly, the ozone concentrations that are determined using the new equation respond to the changes in the prescribed ozone concentrations more quickly than those determined using the old equation (Figs. 5(a) and 5(b)). The concentrations that are determined using the new equation respond approximately 50% faster to the prescribed concentrations than do those obtained using the old equation as estimated from Figs. 5(a) and 5(b). However, the ozone concentrations that were determined using the new equation do still deviate somewhat from the

prescribed concentrations. We believe that these deviations partially arise from the fact that the real concentrations of ozone generated by the commercial ozone calibrator and provided to the test ECC during the experiment were not actually as prescribed. In Fig. 5(a), the differences between the ozone concentrations that were determined using the new equation with the proposed  $\tau_d$  and those determined using the old equation become very small as the experimental time exceeds  $1400 \text{ s}$ , suggesting that the new equation with the proposed  $\tau_d$  fails effectively to correct for the determined ozone concentrations after  $1400 \text{ s}$ . After  $1400 \text{ s}$  the ECC had been exposed to ozone-free air for long enough that reduction reaction of the residual tri-iodide in the cathode solution was limited by the hetero-transfer of electrons. To improve the accuracy of the determined ozone concentration using the new equation in such circumstances, the new equation should be used with the proposed  $\tau_h$  rather than  $\tau_d$ .

The use of a time-dependent response time with the new equation further improves the determined ozone concentrations, as indicated in Fig. 5(b). The determined ozone concentrations in Fig. 5(b) are closer to the prescribed, zero concentration of ozone than are those in Fig. 5(a). However, this improvement is based on an *ad hoc* use of the response time with the new equation. The automatic determination of a suitable, time-dependent response time for use with the proposed new equation will require further experimental and theoretical study. Fortunately, during normal concentrations of ozone measurement, the overall rate of the system is likely to be limited by the diffusion rate of tri-iodide in the cathode solution. Therefore, the new equation with a  $\tau_d$  can be utilized in most situations to determine ozone concentrations measured by an ECC ozonesonde. Fig. 5(a) also reveals that the use of the new equation with the proposed  $\tau_d$  for determining ozone concentrations measured by an ECC ozonesonde is always better than the old equation. Additionally, the new equation, described by Eq. (28), may require the use of a smoothing filter to remove the noise in the external current because the term  $di/dt$  in the new equation is sensitive to small variations in the external current.



**Fig. 5.** Comparison among prescribed ozone concentrations and those measured by an ECC determined using the new and the old equations, (a) the new equation with a constant response time,  $\tau_d = 39.5$  s, (b) the new equation with a time-dependent response time between  $\tau_d = 39.5$  s and  $\tau_h = 763.8$  s.

## SUMMARY

Based on the assumption that the overall rate of the system for an ECC is caused by slow diffusion of tri-iodide in a diffusion layer and the slow heterogeneous transfer rate of electrons through the surfaces of the electrode, a new, first-order differential equation is derived for determining the ozone concentration of an ECC ozonesonde. The generally accepted equation for determining the ozone concentration of an ECC ozonesonde is the steady-state form of the new equation. Ozone concentrations determined using the new equation reflect actual changes in the concentration of ozone that is sampled into an ECC approximately 50% faster than those determined using the old equation in this study. More tests must be conducted in both the laboratory and the field to explore further the advantages and limits of the proposed equation.

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