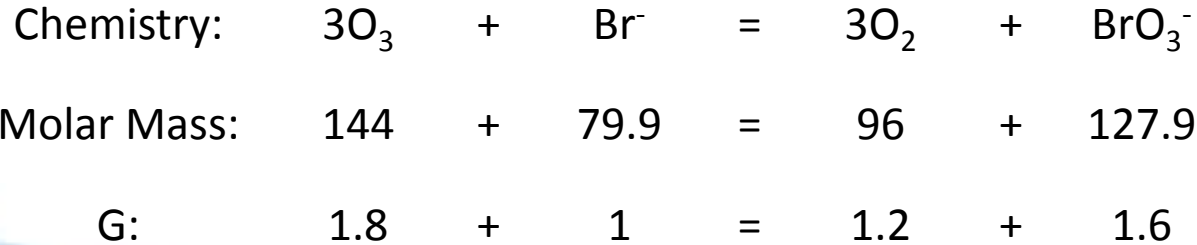


Bromate Formation from Ozonation of Bottled Water

Chemistry of Bromate Formation



Starting with 0.1 ppm of ozone and 0.020ppm bromide

Stoichiometrically, only 0.036 ppm of ozone is required to make 0.032ppm (32ppb) of bromate.

If we start off with 0.1 ppm, it is only possible on a mass basis, to make 32ppb bromate.

Ozone is always in excess. Starting with 0.1 ppm ozone, we have a 2.7 times excess. Starting with 0.05 ppm ozone, we have 1.35 times excess. Therefore, in most cases, dissolved ozone is not the limiting reactant as bromide concentration is going to be stoichiometrically less than the “practical” low limit of 0.05 ppm ozone.

Factors Affecting Bromate Formation

1. Ozone concentration.

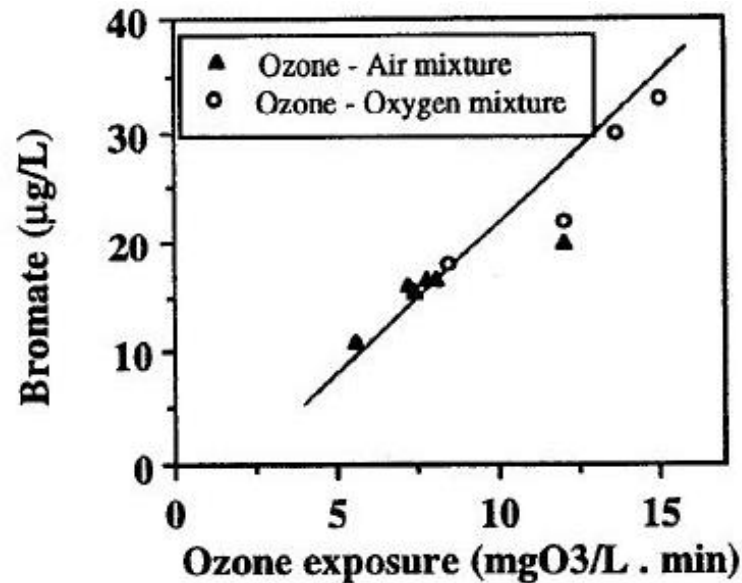
- The higher the starting ozone concentration, the higher the final bromate concentration.

2. C_t Value

- C_t is Concentration (ppm) x Time (min)
- Higher C_t values = Higher bromate
- C_t value is what happens in the ozone reaction vessel **plus** what happens in the bottle.
- C_t value needs to be minimised in reaction vessel by reducing the concentration in the reaction vessel, volume in the vessel and/or reducing the exit ozone concentration.

Factors Affecting Bromate Formation

This curve demonstrates that C_t value of 15 will give higher bromate than C_t 7.



8-b: Importance of the nature of the ozone-containing gas

Figure 8.

Bromate ion formation as a function of the C_t criteria (*Experimental conditions*: Temperature: $\approx 20^\circ\text{C}$; DOC: 2.5 mg/L; initial bromide ion $\approx 60 \mu\text{g/L}$; pH = 7.9).

Factors Affecting Bromate Formation

Example 1.

- If reaction vessel is run at 180 L/min and volume = 2.26 m³. Ozone = 0.1 ppm
- Contact time = 12.5 min.
- $C_t = 12.5 \times 0.1 = 1.25$
- (See example C_t additions for what happens in the bottle)
- C_t addition for bottle = 14.
- Therefore, total **CT = 15.25**

Example 2.

- If reaction vessel is run at 180 L/min and = 2.26 m³. Ozone = 0.05 ppm
- Contact time = 12.5 min.
- $C_t = 12.5 \times 0.05 = 0.63$
- C_t addition for bottle = 7.
- Therefore, total $C_t = 7.63$

Calculation of C_t and the decay of Ozone

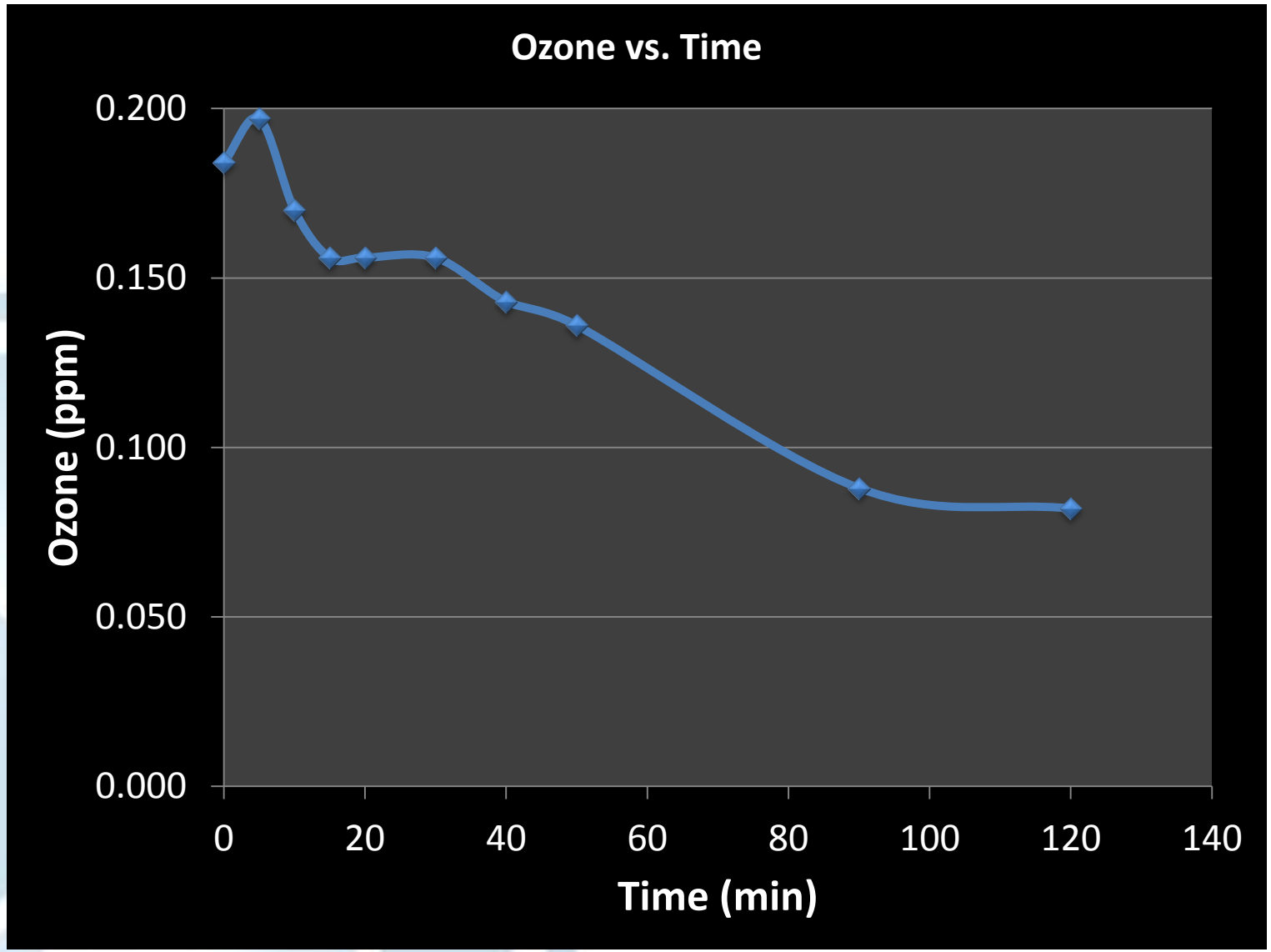
Exponential decay:

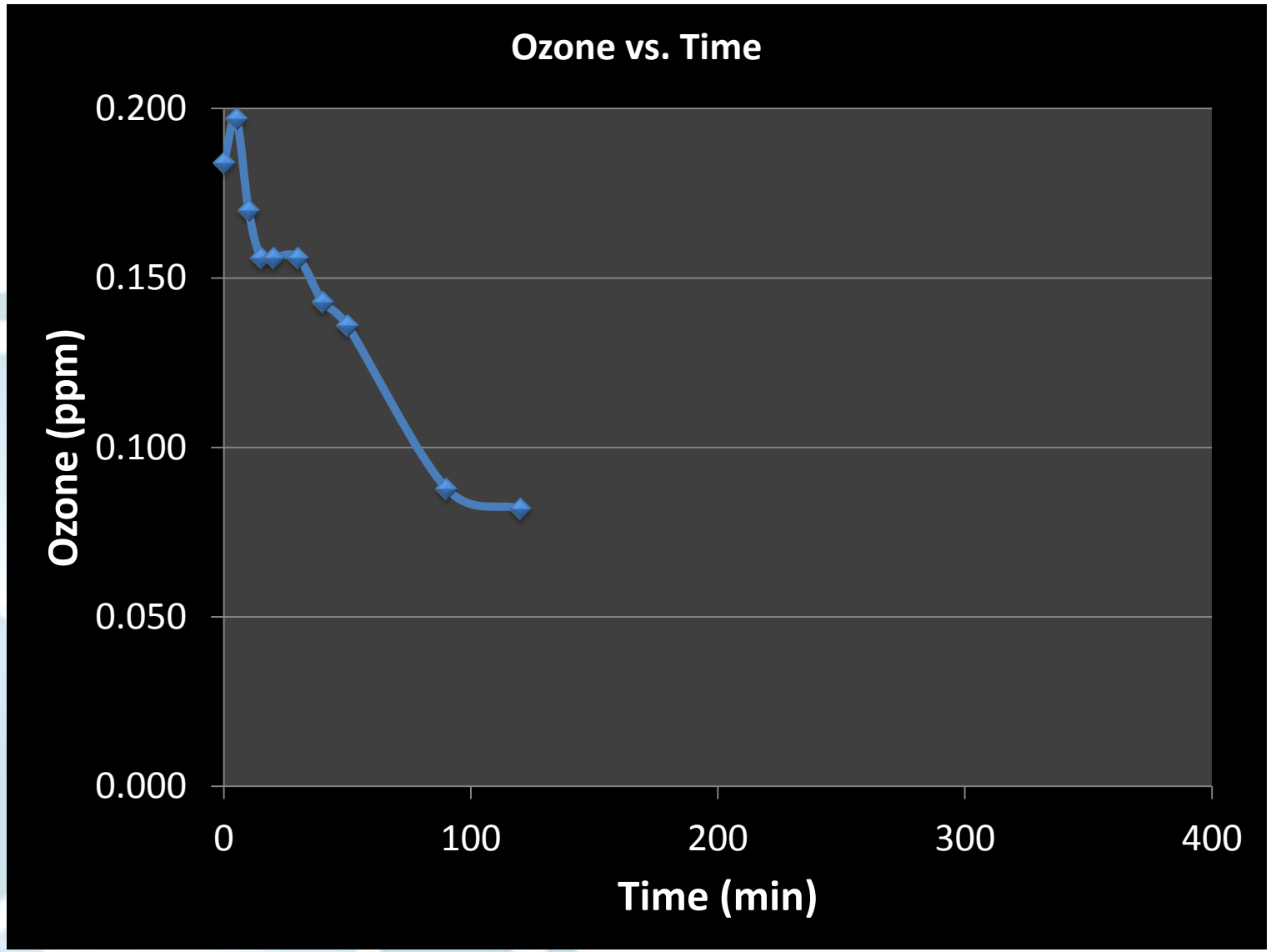
$$N(t) = N_0 e^{-kt}$$

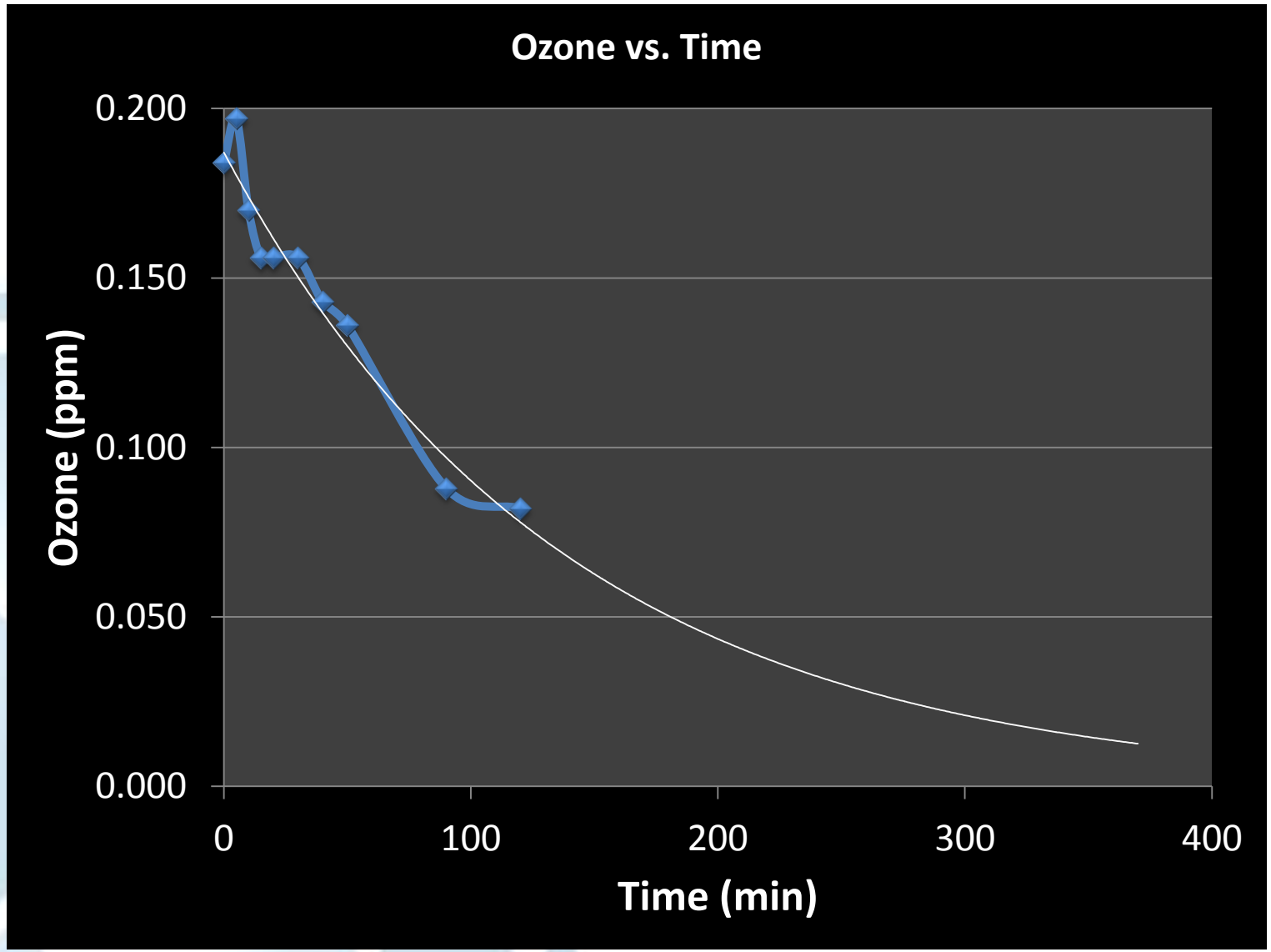
(this tells us based on a starting value N_0 , how much is left ($N(t)$) at time ' t ')

Ozone decay in bottle at Bottler A

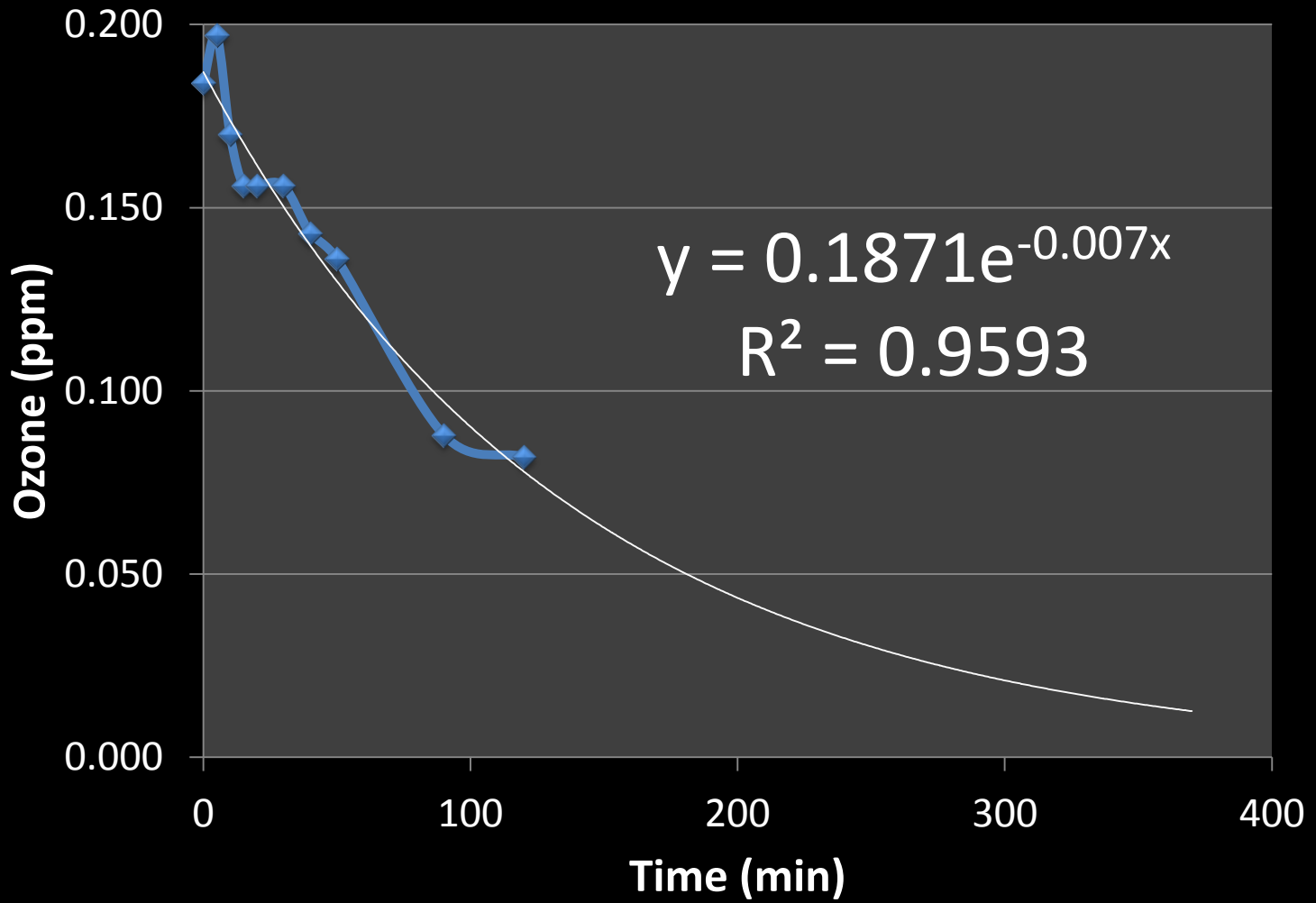
Time (min)	Ozone reading (ppm)
0	0.184
5	0.197
10	0.170
15	0.156
20	0.156
30	0.156
40	0.143
50	0.136
90	0.088
120	0.082







Ozone vs. Time



Decay of Ozone

Exponential decay:

$$N(t) = N_0 e^{-kt}$$

This tells us based on a starting value N_0 , how much is left ($N(t)$) at time ' t '

Decay of Ozone

Exponential decay for that sample:

$$N(t) = 0.1871e^{-0.007t}$$

t	$N(t)$
0	0.187
240	0.035
600	0.003
1440	0.000

Decay of Ozone

Exponential decay for that sample:

$$N(t) = 0.1871e^{-0.007t}$$

The number to take from this equation is the k value and then apply it to different starting concentrations

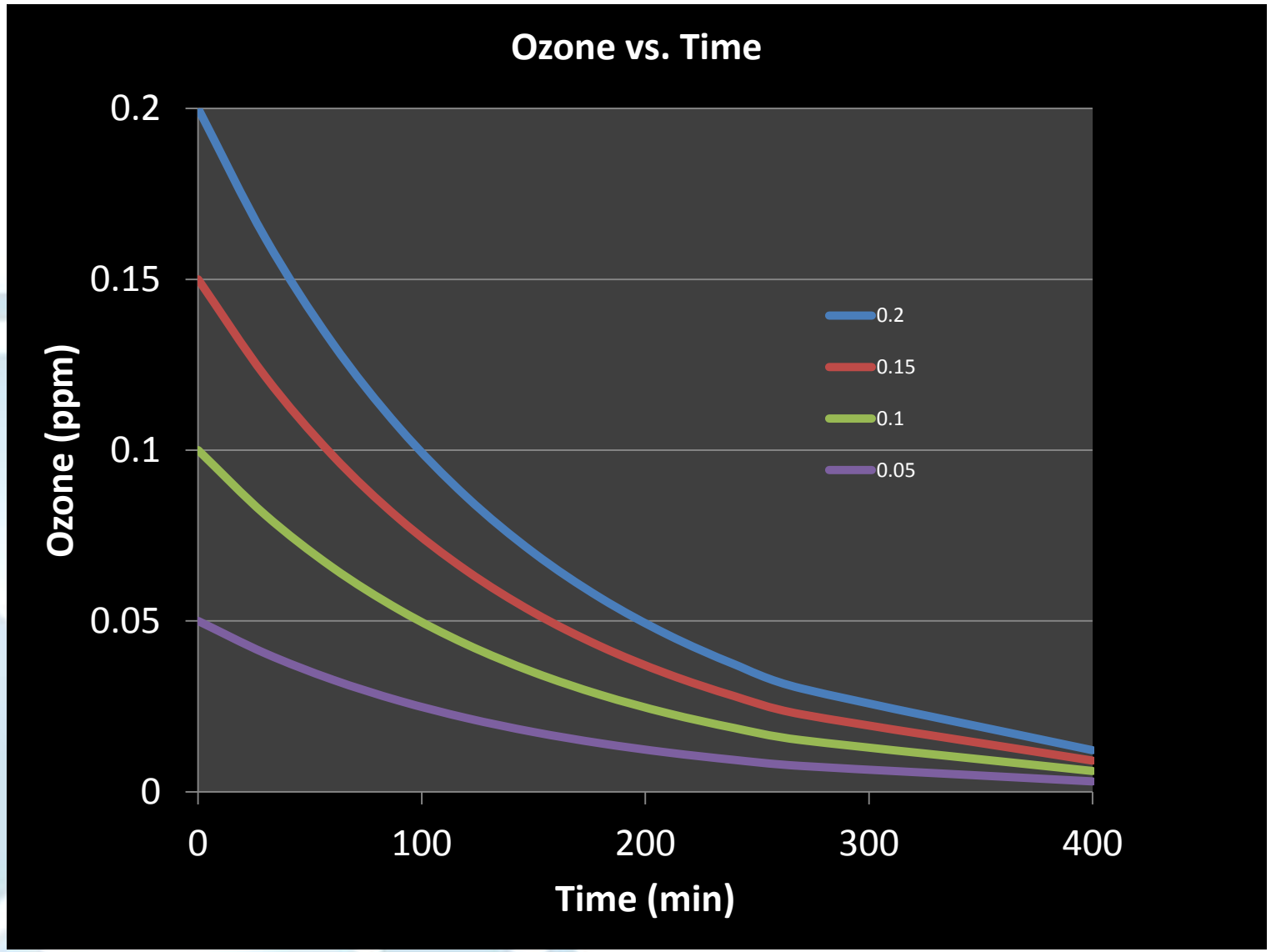
Crude Modelling Example

Modelling exponential decay for other scenarios:

$$N(t) = N_0 e^{-0.007t}$$

Where $N_0 =$

- $0.20 - N(t) = 0.20e^{-0.007t}$
- $0.15 - N(t) = 0.15e^{-0.007t}$
- $0.10 - N(t) = 0.10e^{-0.007t}$
- $0.05 - N(t) = 0.05e^{-0.007t}$



Area under the Curve

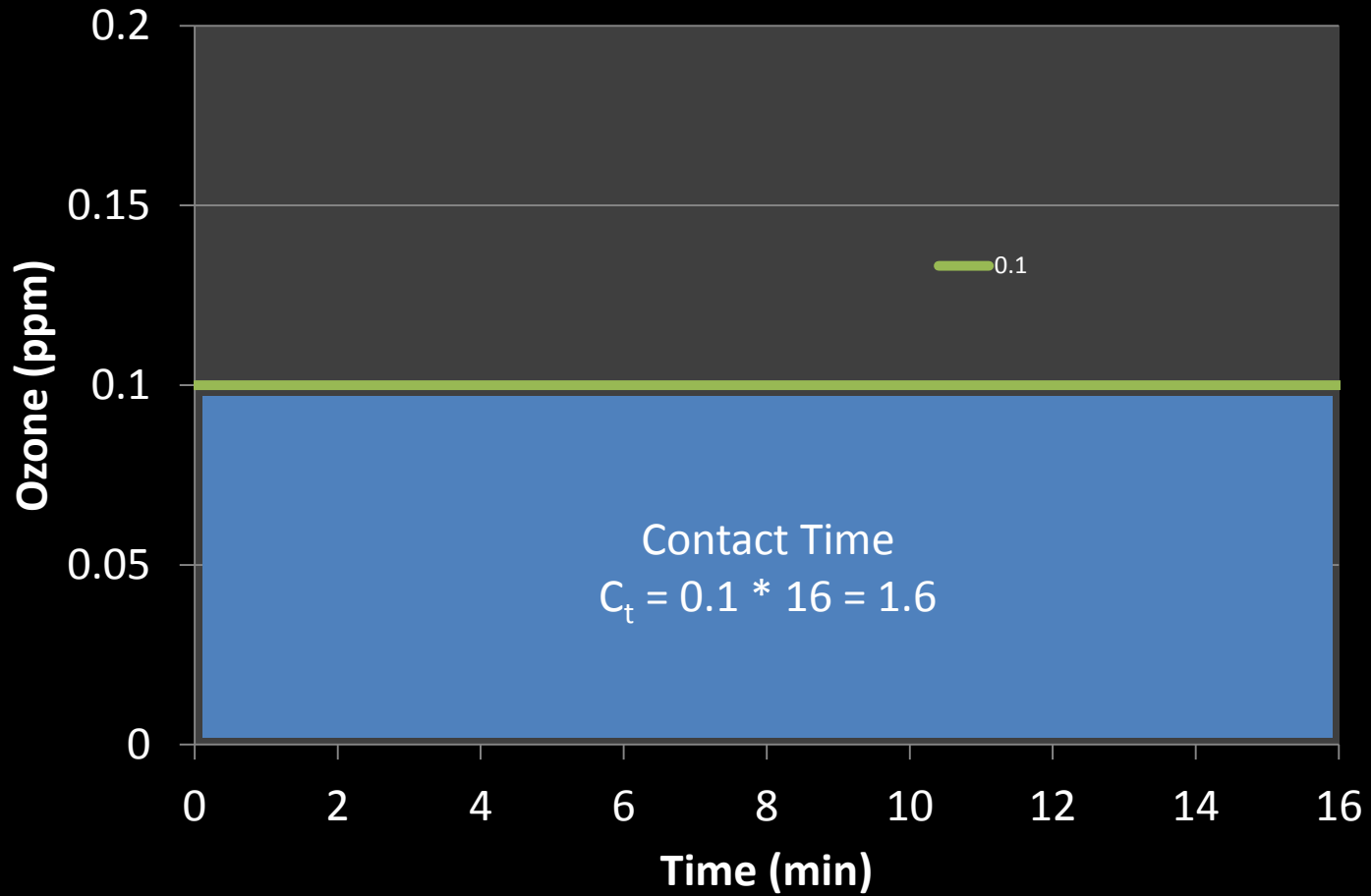
What is C_t ?

$$C_t = C \times t$$

Contact time = concentration (ppm) x time (min)

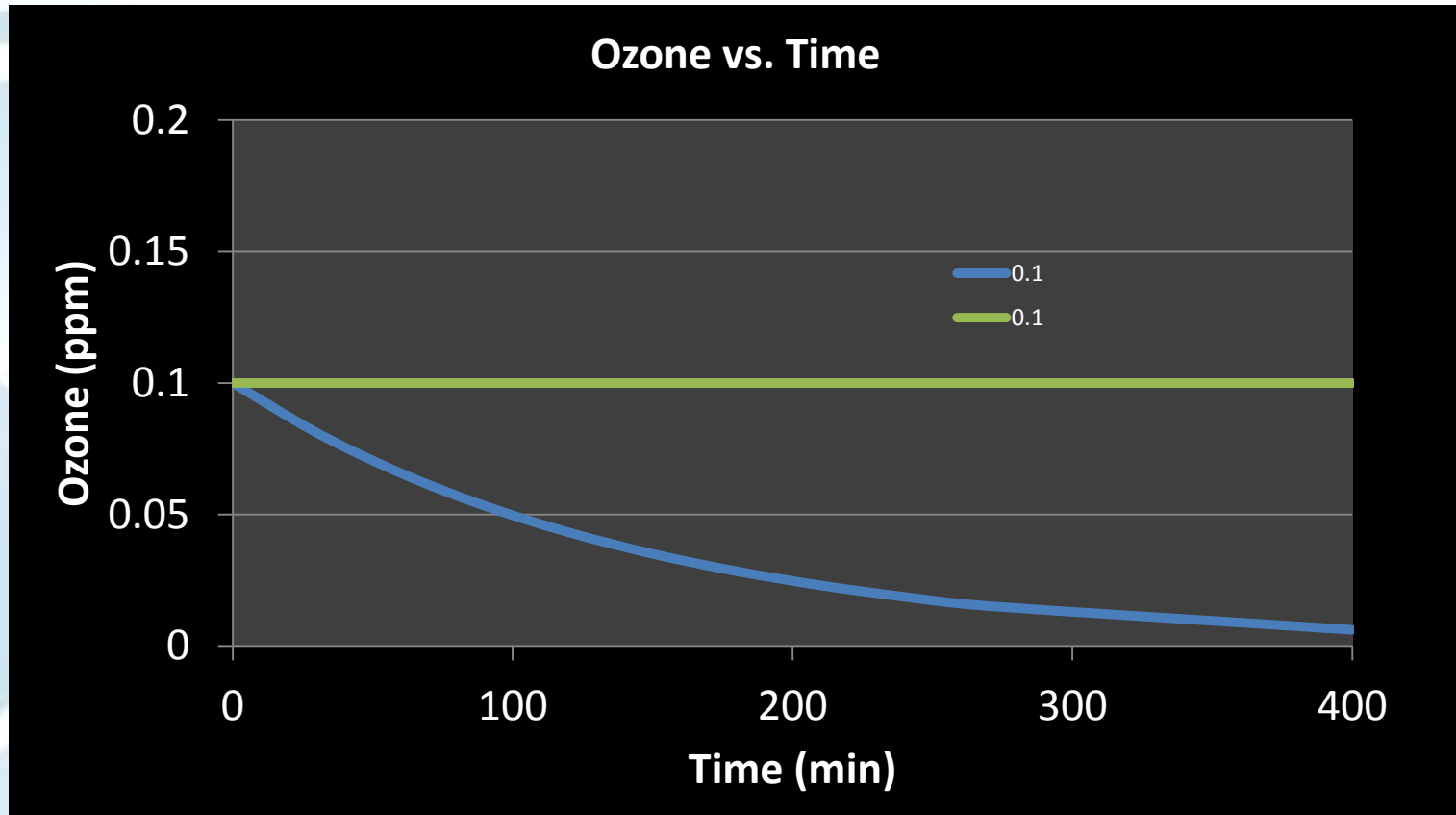
This is the area under the curve.

Ozone vs. Time

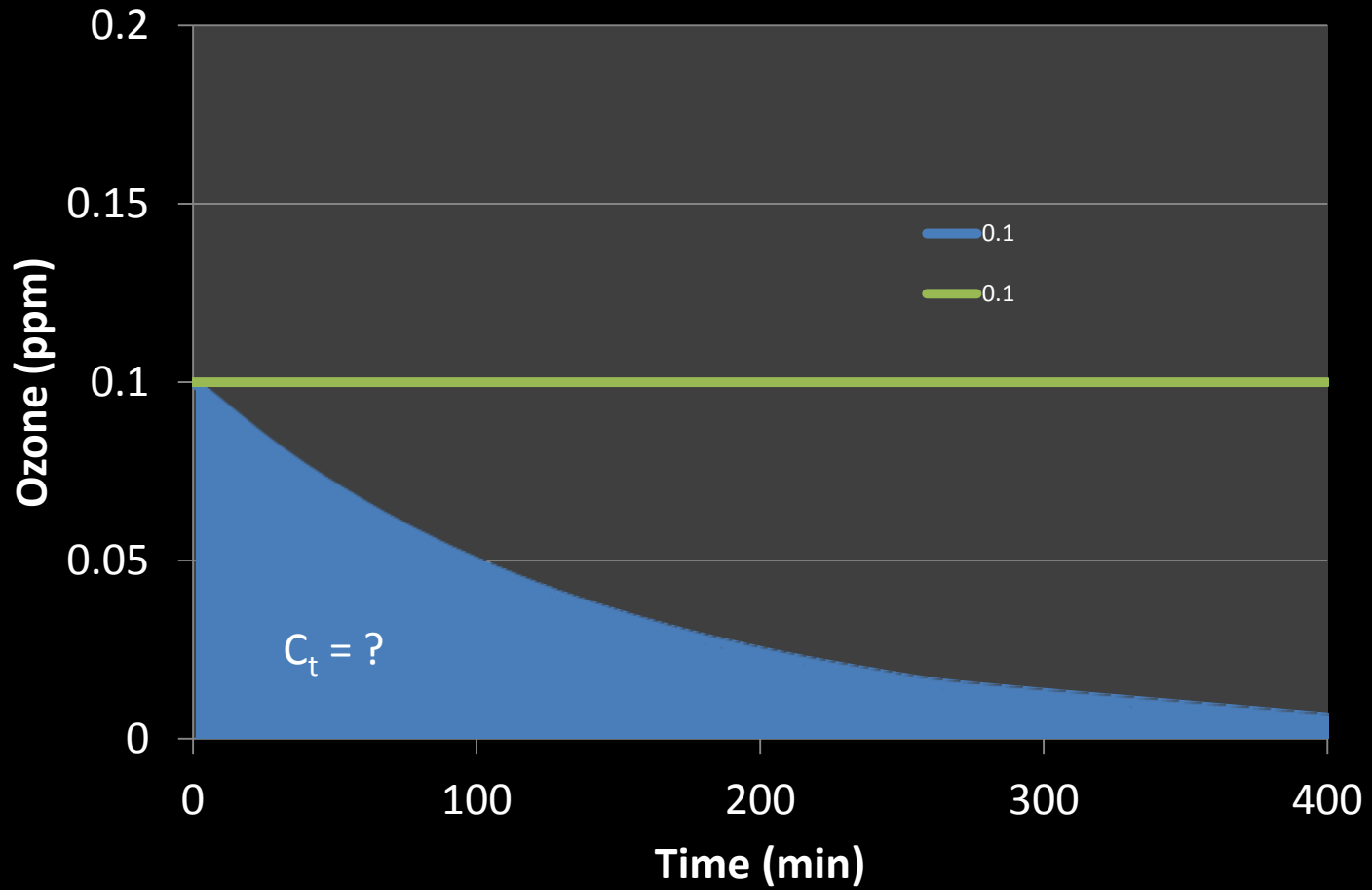


Area under the Curve

But the curve is changing with time



Ozone vs. Time



Integration – Area under the Curve

Exponential decay:

$$N(t) = N_0 e^{-kt}$$

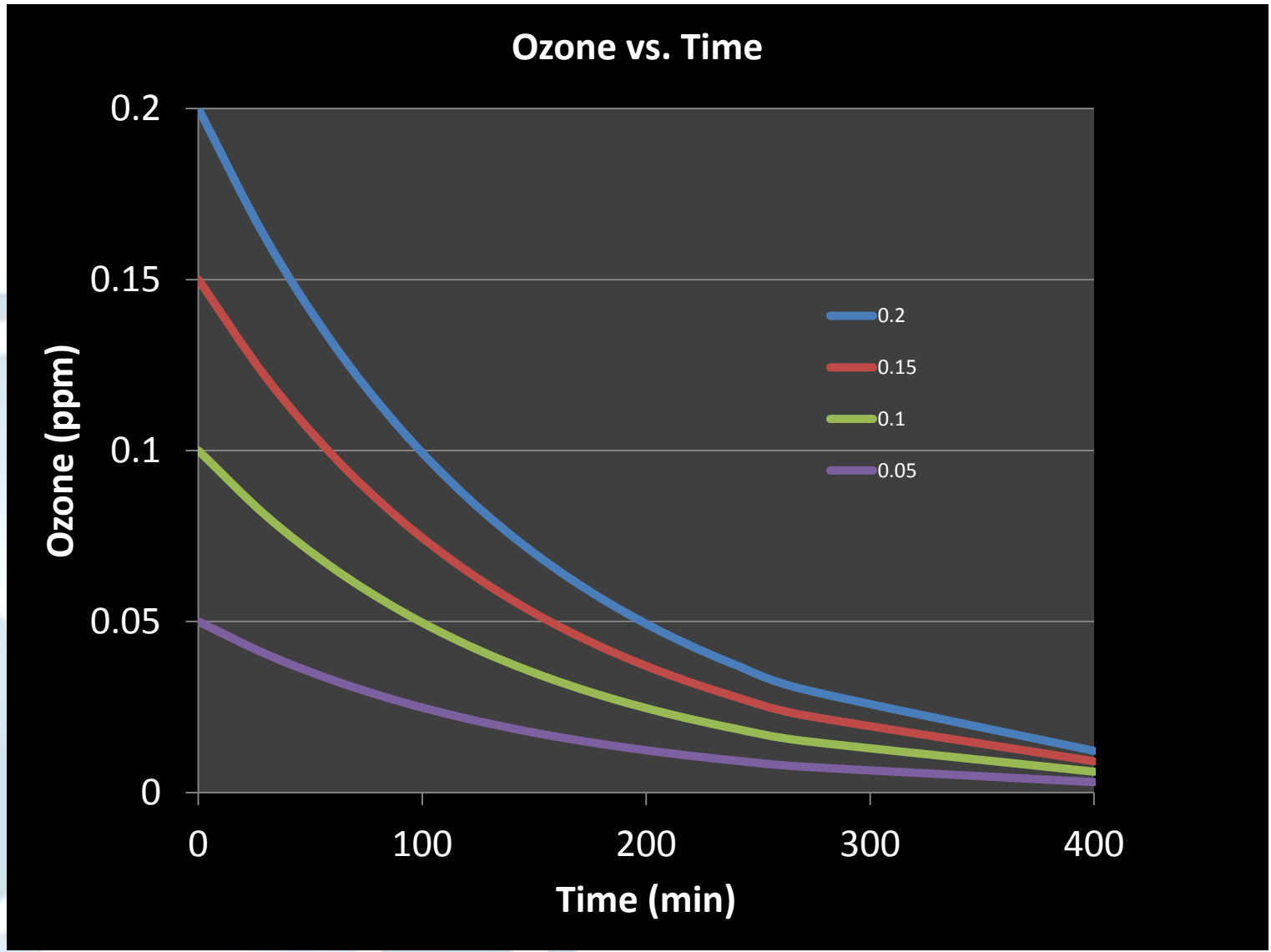
Integration to find area under the curve:

$$\int_0^t N(t) = \frac{N_0}{-k} [e^{-kt}]_0^t = C_t$$

Applying to Model

We just modelled the decay of ozone in the bottle for 4 different starting concentrations.





Applying to Model - Results

We have defined no ozone remaining as a result of 0 to three decimal places, ie: 0.000.

Ozone will be 0 after approximately 12 hrs (720 min).

$$\int_0^{720} N(t) = \frac{N_0}{-0.007} [e^{-0.007t}]_0^{720} = C_t$$

Applying to Model - Results

Conc. (ppm)	Total C_t (mg.min.L ⁻¹)
0.20	28.4
0.15	21.3
0.10	14.2
0.05	7.1

Discussion

- Exposure or C_t is a concept from the USEPA
- C_t is the governing factor for formation of Bromate
- Historically, reaction vessels are designed around obtaining a C_t of between 1.0 and 4.0
- Consideration must be given to the total exposure time, not just the time in the vessel.

Discussion

- Once the ozone leaves the treatment area, it is still present and reacting
- This deals with inadequacies in the bottle.
- Consideration must be given to this work done by the ozone in the bottle
- Consider a 'total' C_t

Note

- This is very generic modelling
- Based on one set of results
- Further tests to quantify 'k' decay rates in actual bottles

Factors Affecting Bromate Formation

3. Temperature

- Higher temp = higher bromate.
- Can't really alter the temperature of storage or bottling. Reaction vessel is inside so this will be kept cool.
- In the bottle, rate of decay of ozone is increased at higher temps. Therefore, if bottles are stored in warm area, ozone will decay faster and thus, CT is reduced to reduce bromate.

4. Bicarbonate

- Higher bicarbonate = slower decomposition of ozone = higher CT value = higher bromate.
- Can't really reduce bicarbonate without putting the water through a softener and this will change the water "characteristics" which may/may not be acceptable.

Factors Affecting Bromate Formation

5. Method of Ozone Generation

- From our reading, there is no significant difference between oxygen generated ozone and air generated ozone as far as bromate formation is concerned.

6. pH

- Lower pH produces lower bromate.
- It is not easy to reduce pH in the water without affecting the organoleptic properties of the water. CO_2 could be used for pH reduction.

7. Disinfection

- It is clear that at the lowest measurable ozone concentration, enough CT would be obtained for bacteria and virus control.

Where to From Here?

Based on the factors which influence bromate formation, some things can be practically done.

1. Decide how important the ozone concentration exiting the reaction vessel (entering the bottles) is. Reduce the ozone concentration to the lowest acceptable value (0.05 ppm?)
2. Do ozone decay tests (at different ozone residuals) to determine what the ozone residual is in the bottle after x hours and then plot the decay curves to determine the CT contribution from ozone in the bottle.
3. Store bottles in warm area to increase decomposition rate of ozone residual.



Paul Grover & Associates can provide design advice about bromate minimisation strategies and can be involved in the following activities:

1. Ozone decay testing and CT calculations.
2. Pilot plant testing
3. Provision of plant design options for existing and new ozone system
4. System design including P&ID, mech, elec, control and 3D modeling
5. Control system design for ozone destruction
6. Audits for existing systems

[Please contact us](#) for a fee proposal if this is of interest.

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