

## Mid-term Exam

Closed Book, Open Notes

Answer question #1 and any two of the remaining six questions:

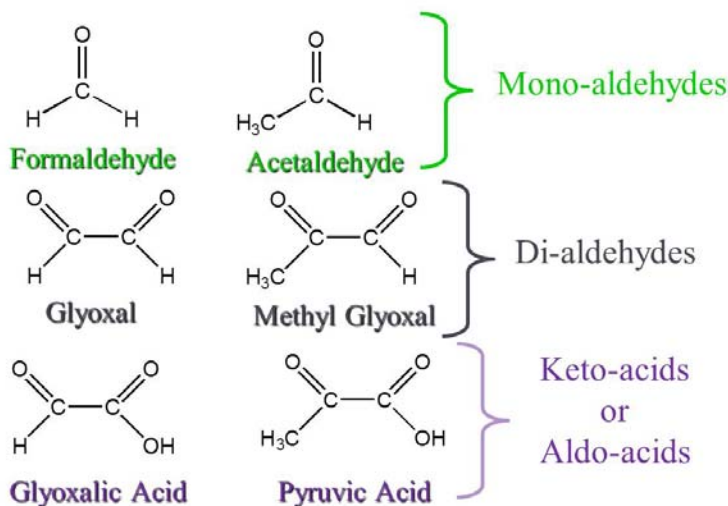
(#1 is worth 40%, #2-6 is worth 30% each)

### 1. (40%) General Question.

Low molecular weight aldehydes, ketones and keto-acids are known byproducts of ozonation in drinking water treatment. Most common are 1, 2 and 3-carbon members of these groups (see figure below), but larger compounds containing up to 12-carbons may be formed as a result of the reaction of ozone with natural organic matter in water.

If you were asked to develop an analytical method to measure the concentrations of each of these compounds, what would you propose as a likely successful approach? Be specific about the method, including the instrument you would propose to use and any necessary sample preparation. Please keep in mind that there is no single correct answer to this. I'm really looking for your reasoning as you consider the various possibilities.

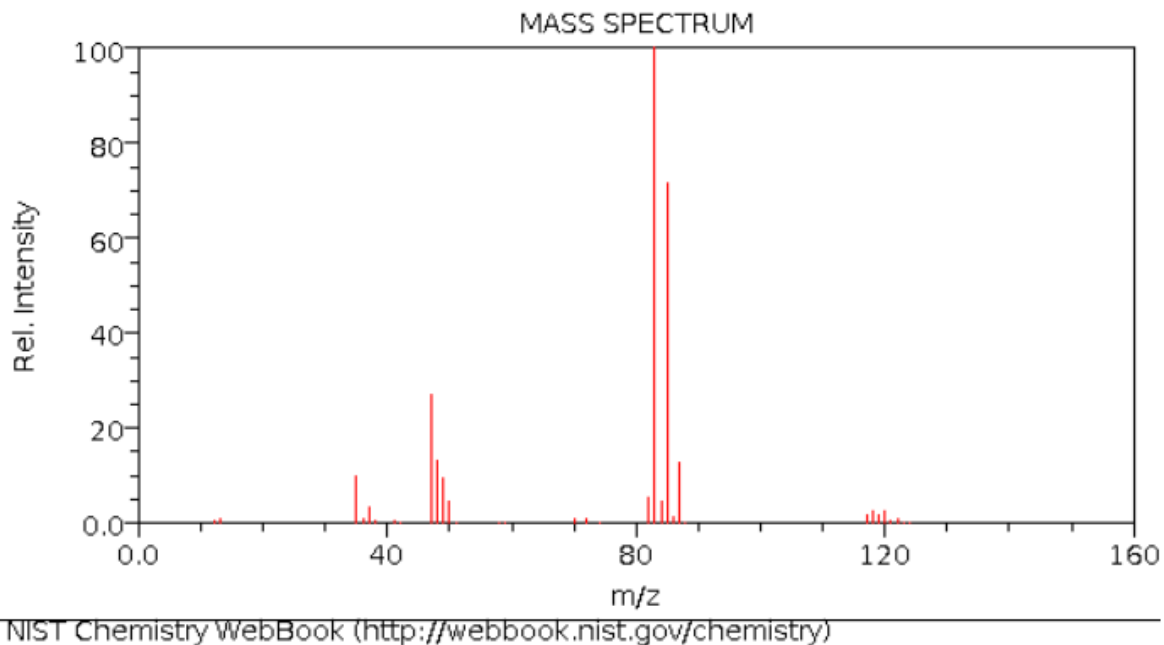
### Common Ozone Byproducts



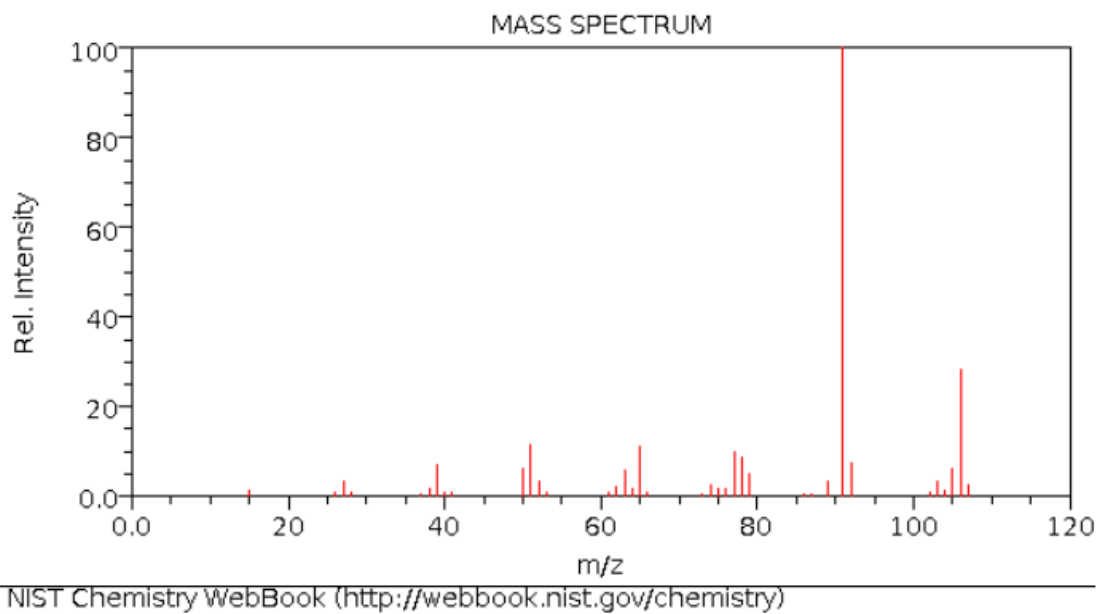
## 2. GC/MS (electron impact)

Interpret the mass spectrum depicted in just one of the four figures below. Indicate your rationale for the determination of empirical formulae for each of the major fragment ions, as well as for the molecular ion. Propose a structure for the parent molecule.

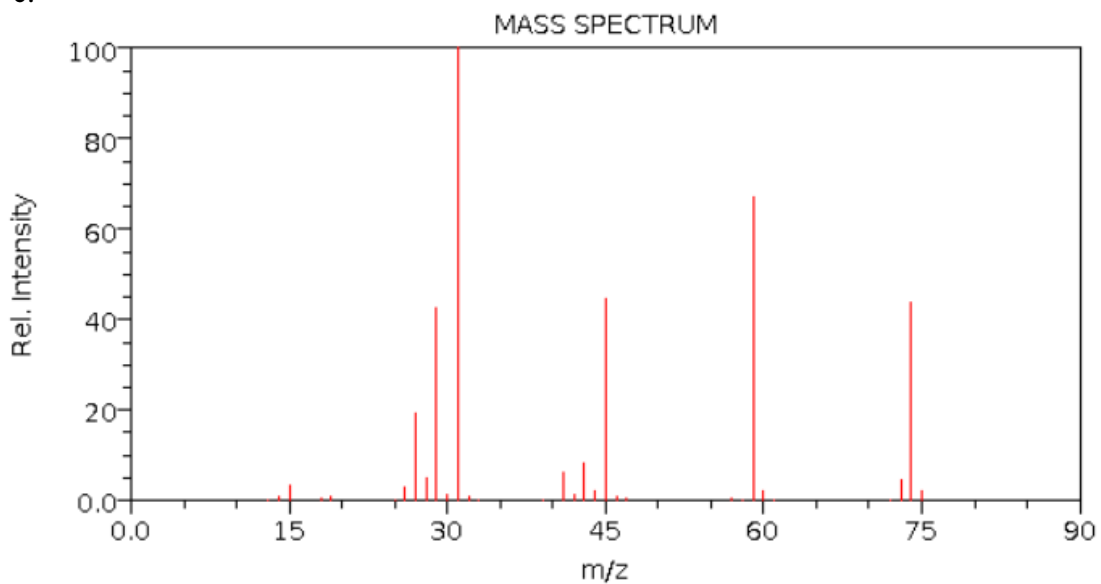
a.



b.

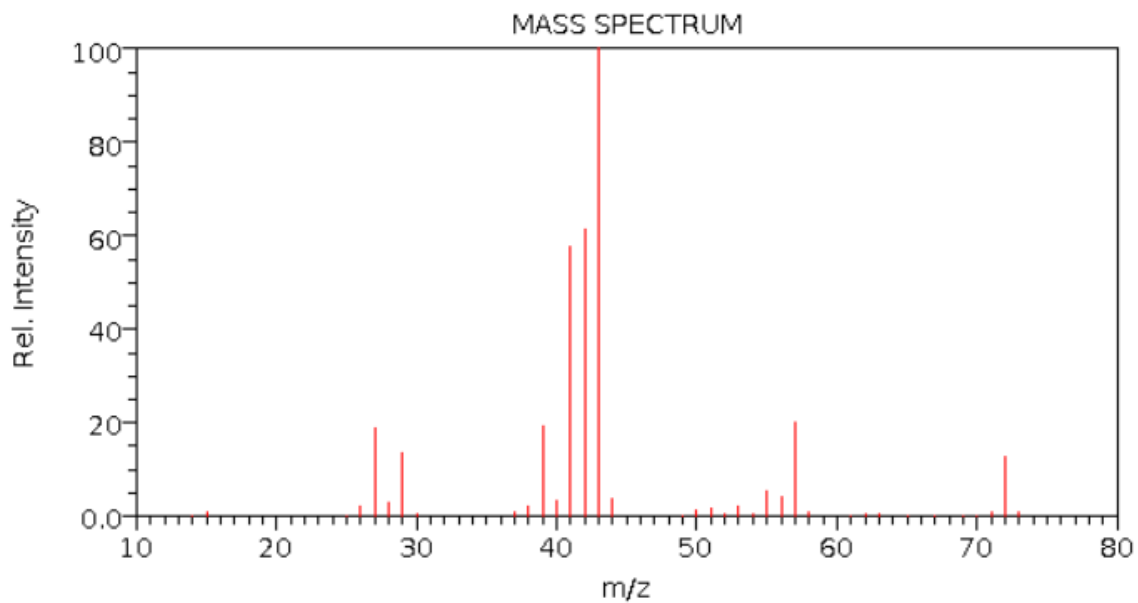


c.



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

d.



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

### 3. Sample Preparation

A 200-mL aqueous sample is being extracted in a sequential batch mode with ethyl acetate (EtAc). Pollutant "Y" has an EtAc/water dimensionless partition coefficient of 10.

- After one extraction with 20 mL of EtAc, how much of the original amount of pollutant "Y" remains in the water phase?
- What is the overall % of pollutant "Y" that would be extracted into the EtAc phase if 4 sequential extractions using 20 mL of the organic phase were made?
- What is the relative concentration of "Y" in the final combined EtAc extract as compared to its initial concentration in the aqueous sample?

$$f_e = \frac{1}{1 + \left(\frac{1}{K_D}\right)\left(\frac{V_w}{V_s}\right)}$$

$$f_{2e} = f_e + (1 - f_e)f_e$$

	Volumes (mL)		total solvent	Fraction remaining		Aggregate		Aggregate Conc	
	Water	solvent		Water	Solvent	Water	Solvent	Water	Solvent
1st extraction	200	20	20	0.5	0.5				5
2nd extraction	200	20	40	0.5	0.5	0.25	0.75		3.75
3rd extraction	200	20	60	0.5	0.5	0.125	0.875		2.916667
4th extraction	200	20	80	0.5	0.5	0.0625	0.9375		2.34375

### 4. Detection Limits

A series of replicate measurements were made for glyoxal in identical aliquots of a drinking water sample. The measurements are as follows:

0.023 µg/L	0.044 µg/L	0.025 µg/L
0.029 µg/L	0.025 µg/L	0.024 µg/L
0.026 µg/L	0.022 µg/L	

- Assuming that these measurements represent concentrations near the method detection limit (MDL), what would you calculate the MDL to be?
- What do you calculate the Limit of Quantitation (LOQ) to be?

Just taking the data and compiling as is, we get the following standard deviation, MDL and LOD:

	0.023
	0.029
	0.026
	0.044
	0.025
	0.022
	0.025
	0.024
std dev	<a href="#">0.007086</a>
MDL	0.021
LOD	0.064

However, it does seem that the 0.044  $\mu\text{g/L}$  result is an outlier. We could use some statistical test to see if it is really from a different distribution. I'd be inclined to assume it is. Under those circumstances, the MDL and LOD are much lower:

	0.023
	0.029
	0.026
	discarded
	0.025
	0.022
	0.025
	0.024
std dev	<a href="#">0.002268</a>
MDL	0.007
LOD	0.020

### 5. General T/F

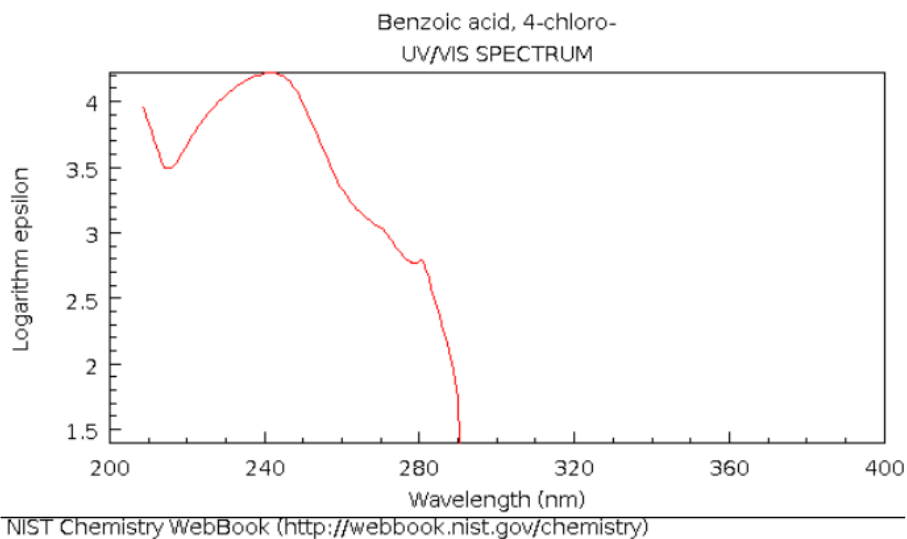
Answer each of the following as either true (T) or false (F).

- F   Atomic absorption spectrophotometry relies on formation of ions prior to detection
- T   Diode array spectrophotometers use diodes instead of photomultipliers

- c.   T   One important type of sample preparation in gas chromatography is derivatization, which can enhance detection
- d.   F   Stray light is never a problem with open geometry spectrophotometers
- e.   T   Volatile organic compounds may be lost prior to analysis for TOC due to the inorganic carbon purge step
- f.   T   LC/MS most often uses electrospray ionization or atmospheric pressure chemical ionization
- g.   F   Most gas chromatographic detectors use light emission for detection of compounds leaving the GC column.
- h.   F   Detection by ICP/MS can be enhanced by use of an L'vov platform
- i.   T   Chromatographic separations generally improve as particle size, or film thickness decreases
- j.   T or F   Sample preparation in LC/MS is intended to help avoid detector overload

## 6. Absorbance

Explain how you would measure the exact concentration of an aqueous solution of 4-chloro-benzoic acid (also known as para-chlorobenzoic acid) using only a spectrophotometer (see plot of molar absorptivity below). Be specific. Assume the sample you want to analyze is in the range of 1-10 mM.



## Reference Material

**Table 2.1.** Natural isotopic abundances of common elements.<sup>a</sup>

Element	A		A + 1		A + 2		Element type
	Mass	Per cent	Mass	Per cent	Mass	Per cent	
H	1	100	2	0.015			"A"
C	12	100	13	1.1 <sup>b</sup>			"A + 1"
N	14	100	15	0.37			"A + 1"
O	16	100	17	0.04	18	0.20	"A + 2"
F	19	100					"A"
Si	28	100	29	5.1	30	3.4	"A + 2"
P	31	100					"A"
S	32	100	33	0.80	34	4.4	"A + 2"
Cl	35	100			37	32.5	"A + 2"
Br	79	100			81	98.0	"A + 2"
I	127	100					"A"

<sup>a</sup>Wapstra and Gove (1971).

<sup>b</sup>1.1 ± 0.02, depending on source.

<i>Element</i>	<i>A Isotope</i>	<i>Mass (abundance)</i>	<i>A+1 Isotope</i>	<i>Mass (abundance)</i>	<i>A+2 Isotope</i>	<i>Mass (abundance)</i>
Carbon	<sup>12</sup> C	12.00000 (98.89)	<sup>13</sup> C	13.00335 (1.11)		
Hydrogen	<sup>1</sup> H	1.007825 (99.985)	<sup>2</sup> H	2.01410 (0.015)		
Nitrogen	<sup>14</sup> N	14.00307 (99.63)	<sup>15</sup> N	15.00011 (0.37)		
Oxygen	<sup>16</sup> O	15.99491 (99.759)	<sup>17</sup> O	16.99914 (0.037)	<sup>18</sup> O	17.99916 (0.204)
Fluorine	<sup>19</sup> F	18.99840 (100)				
Silicon	<sup>28</sup> Si	27.97693 (92.21)	<sup>29</sup> Si	28.97649 (4.70)	<sup>30</sup> Si	29.97376 (3.09)
Phosphorous	<sup>31</sup> P	30.97376 (100)				
Sulfur	<sup>32</sup> S	31.97207 (95.0)	<sup>33</sup> S	32.97146 (0.76)	<sup>34</sup> S	33.96786 (4.22)
Chlorine	<sup>35</sup> Cl	34.96885 (75.53)	<sup>37</sup> Cl	36.96590 (24.47)		
Bromine	<sup>79</sup> Br	78.9183 (50.54)	<sup>81</sup> Br	80.9163 (49.46)		
Iodine	<sup>127</sup> I	126.9044 (100)				