Updated: 12 October 2014

Print version

CEE 772:
Instrumental Methods in Environmental Analysis

Lecture #8

Specialized Analyzers: Total Organic Carbon & Total Nitrogen

(Skoog, Chapts. 16C, 24D; pp.399-401, 632-636)

(Harris, Chapt. 16-6 & 17-4)
(pp.430, 457-461)

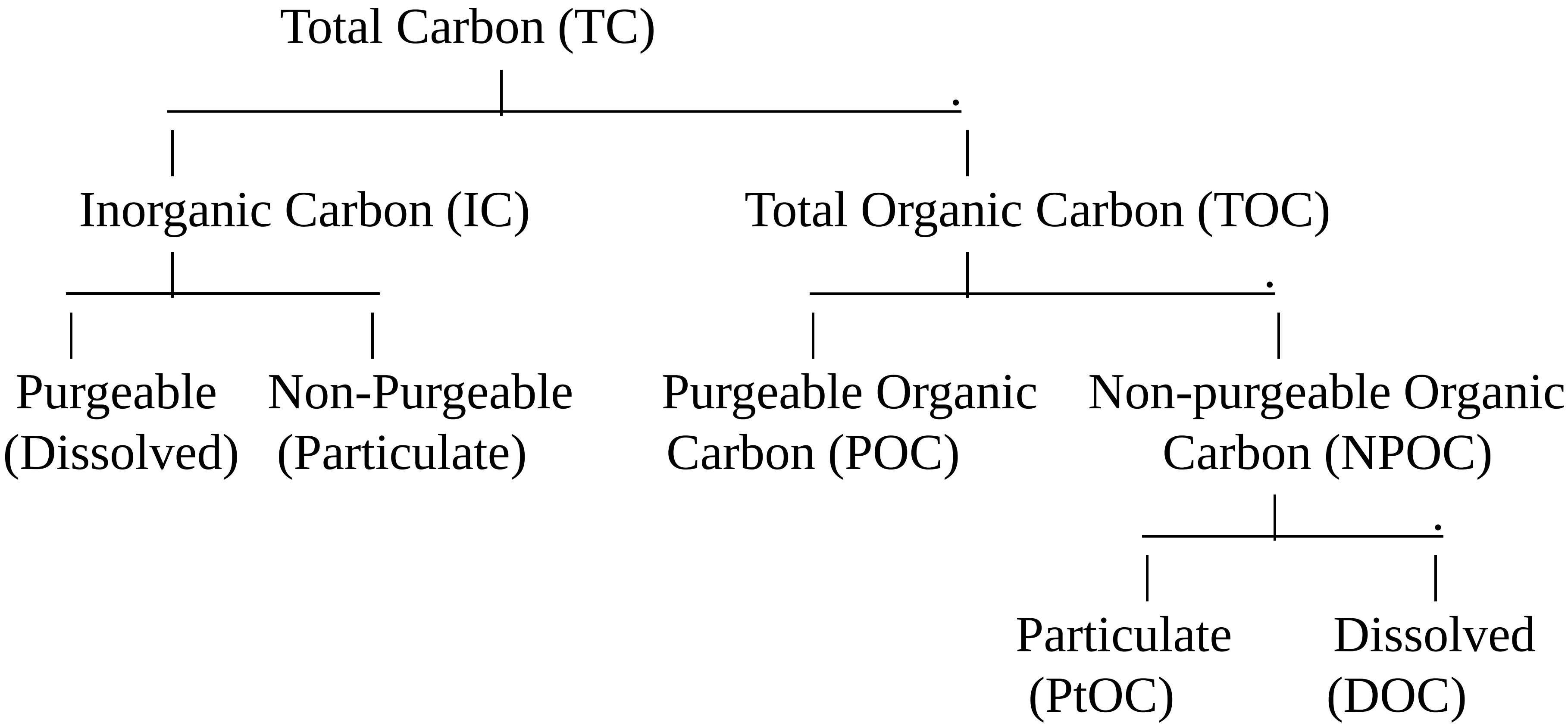
Literature on TOC

1. “Selection of a TOC Analyzer”, Crane, G.A.; American Laboratory, July 1988, page 52.
2. Standard Methods for the Examination of Water and Wastewater, 20th Edition – 5310A
3. “Oxidation and Detection Techniques in TOC Analysis”, Small, R.A. et al; American Laboratory, February 1986, page 144.
4. “The Total Organic Carbon Analyzer and It’s Application to Water Research”, Emery, R.M. et all; Journal WPCF, September 1971.
5. “Comparison of High-Temperature and Persulfate Oxidation Methods for Determination of Dissolved Organic Carbon in Freshwaters”, Kaplan, L.A.; American Society of Limnology and Oceanography, January 1992.
6. “Freshwater DOC Measurements by High-Temperature Combustion: Comparison of Differential (DTC-DIC) and DIC Purging Methods”, Fukushima, T. et al; Water Research, 30(11) 2717, November 1996.
7. Water Research 34(14)3575 2000
8. Water Research 35(13)3057 2001

What is TOC?

- **T**otal **O**rganic **C**arbon
- Organic contaminants (NOM's, insecticides/herbicides, agricultural chemicals) – reach surface water via rainfall runoff
- Industrial organics due to spills
- Domestic/Industrial wastewater effluent

Fractionation & Nomenclature



Total Carbon (TC)

Inorganic Carbon (IC)

Total Organic Carbon (TOC)

Purgeable (Dissolved)

Non-Purgeable (Particulate)

Purgeable Organic Carbon (POC)

Non-purgeable Organic Carbon (NPOC)

Particulate (PtOC)

Dissolved (DOC)

TOC vs. TC & IC

- TOC = Total Carbon (TC) – Inorganic Carbon (IC)
- TOC = all carbon atoms covalently bonded in organic molecules
- TC is a measure of all the carbon in the sample
- IC = carbonate, bicarbonate, and dissolved carbon dioxide
  - IC is often analyzed in liquid samples by acidifying with an inorganic acid to pH 2 or lower, then sparging for a few minutes with a stream of gas
- POCs (or VOC) = the fraction of TOC removed from an aqueous solution from gas stripping under specified cond.
- NPOC = the fraction of TOC not removed by gas stripping
- DOC = the fraction of TOC that passes through a 0.45 µm-pore diameter filter
- PtOC (or “suspended org. carbon) = the fraction of TOC retained by a 0.45 µm-pore diameter filter

Distinguishing TOC from TIC

- Direct NVTOC measurement
  - remove IC by acidification and purge

- Most common approach
  - Can result in loss of OC due to precipitation at low pH

- By difference: two channel
  - Measure TC (high temp) and IC (low temp)
  - Subtract

- Used by old Beckman analyzers
  - Separate channels
  - Two separate measurements

- By difference: gas & liquid
  - Measure TC and PC (both high temp)
  - Subtract

- Some analyzers have a Purgeable carbon (PC) cycle
  - Again requires 2 separate measurements

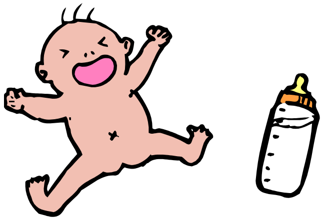
TOCs and Drinking Water

- Organic compounds may react with disinfectants to produce potentially toxic and carcinogenic compounds, or “disinfection by-products”
- Drinking water TOCs range from less than 100 µg/L to more than 25,000 µg/L
- Wastewater – TOC > 100 mg/L

Origins

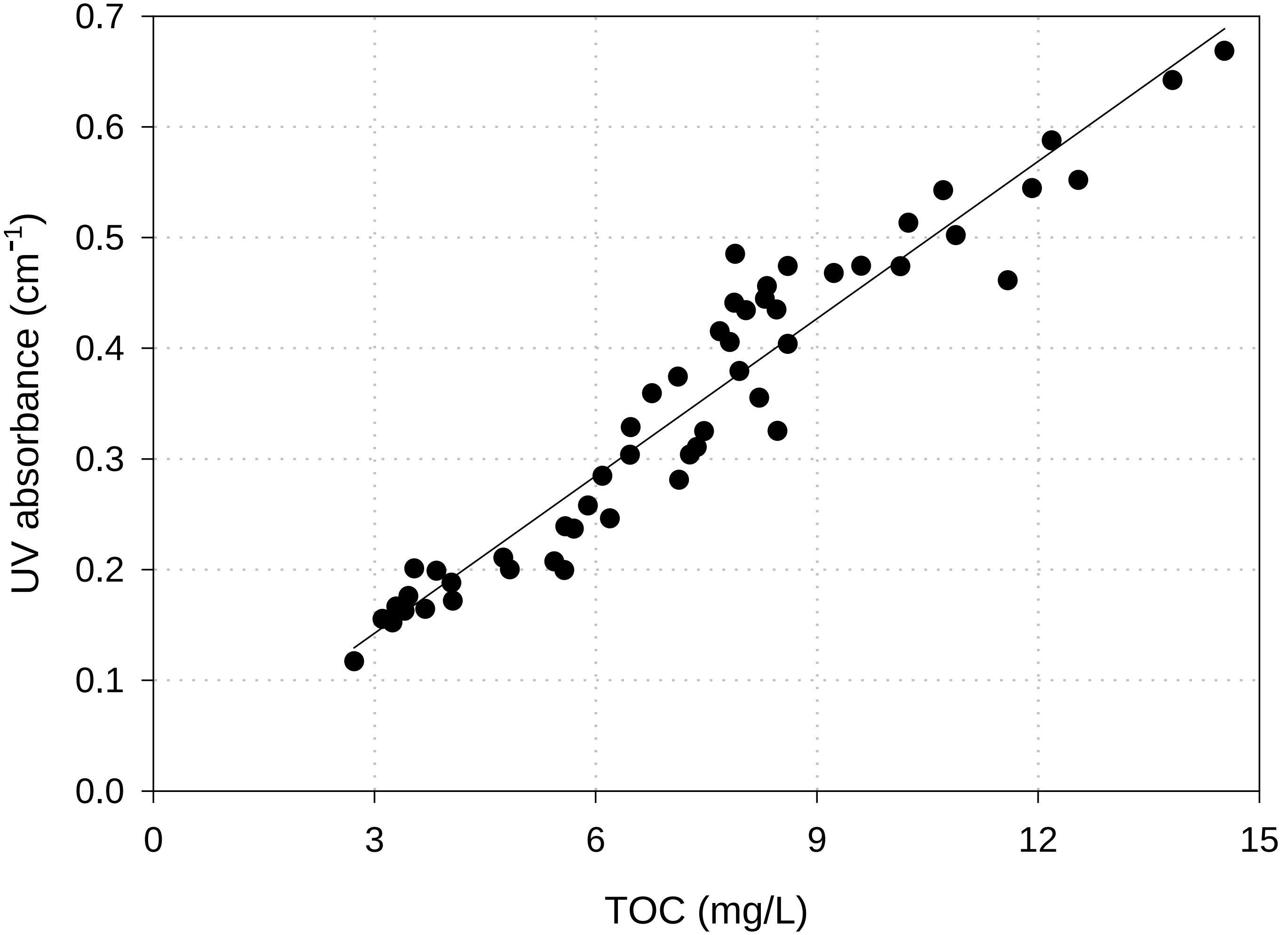
- Humic substances (humic and fulvic acids)
  - Organic detritus modified by microbial degradation
  - lignin origin vs microbial
  - resistant to further biodegradation
  - “old” organics

- Non-humics & Structurally-defined groups
  - may be relatively “new”
  - includes many biochemicals and their immediate degradation products
  - generally more biodegradable
  - concentrations are highly variable with season

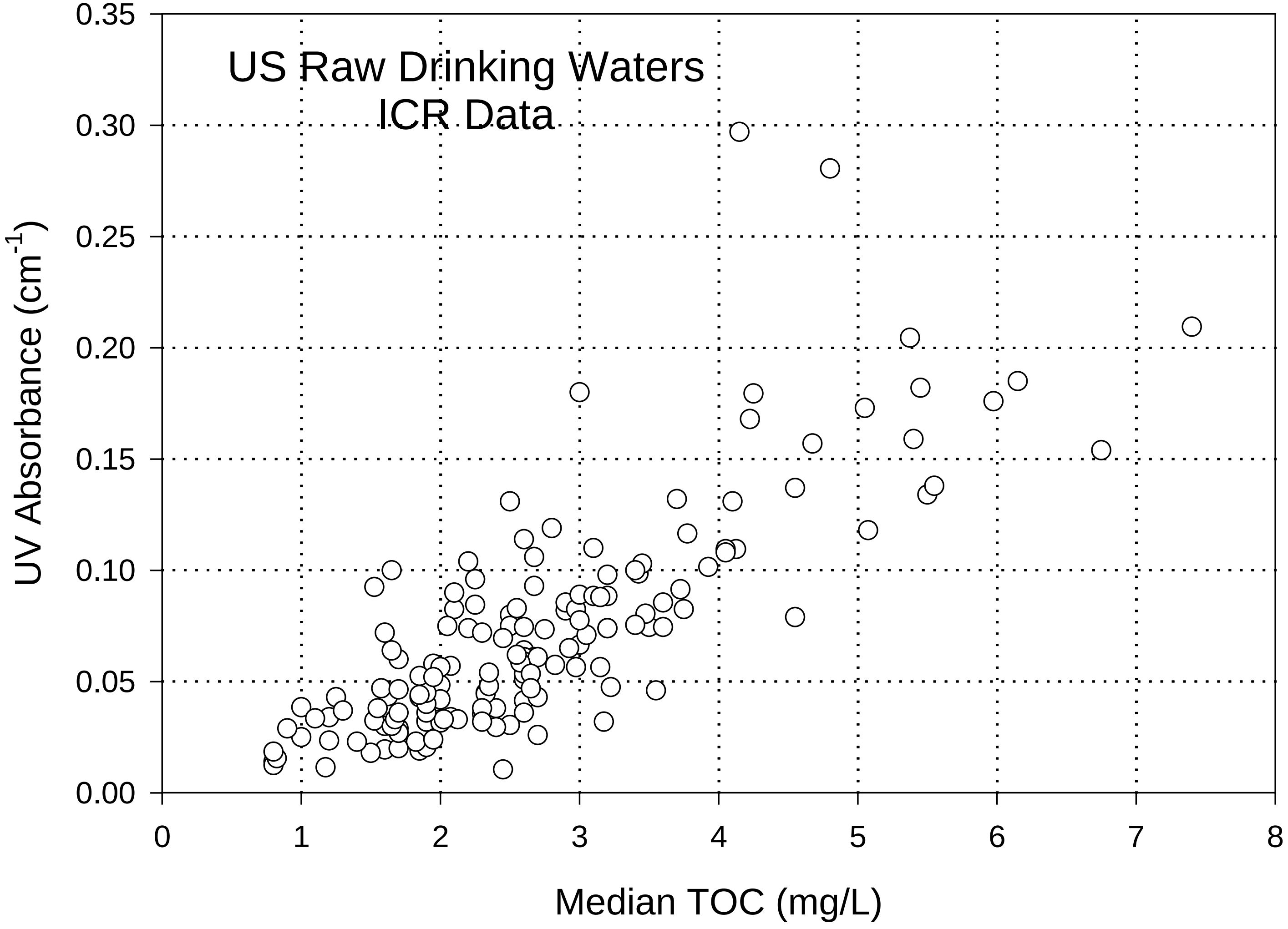


UV absorbance vs TOC: raw waters

Correlation Between TOC and UV absorbance for 53 samples of Grasse River Water (from Edzwald et al., 1985)



TOC in Large US WTPs

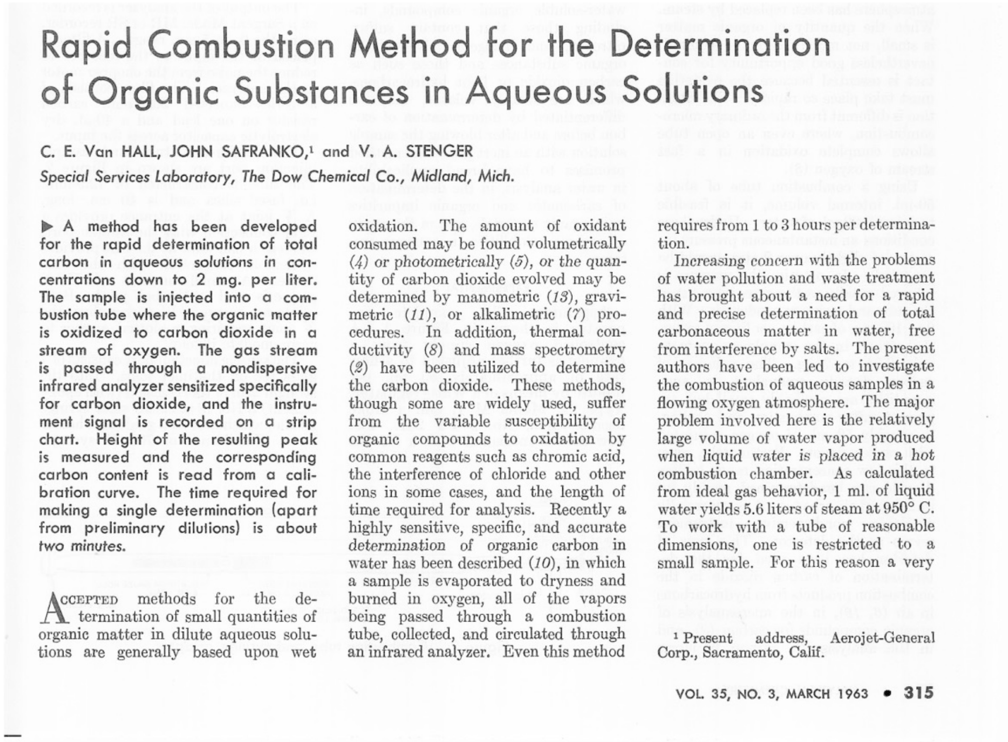


Methods of TOC Analysis

- High-Temperature Combustion Method
- Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method
- Wet-Oxidation Method (equipment for this method is no longer manufactured)

TOC Analyzer

- March 1963
- Required a Beckman L/B infrared analyzer
- Need to wait for development of a turnkey instrument (Beckman 915)



Rapid Combustion Method for the Determination of Organic Substances in Aqueous Solutions

C. E. Van HALL, JOHN SAFRANKO,[1] and V. A. STENGER

Special Services Laboratory, The Dow Chemical Co., Midland, Mich.

▶ A method has been developed for the rapid determination of total carbon in aqueous solutions in concentrations down to 2 mg. per liter. The sample is injected into a combustion tube where the organic matter is oxidized to carbon dioxide in a stream of oxygen. The gas stream is passed through a nondispersive infrared analyzer sensitized specifically for carbon dioxide, and the instrument signal is recorded on a strip chart. Height of the resulting peak is measured and the corresponding carbon content is read from a calibration curve. The time required for making a single determination (apart from preliminary dilutions) is about *two minutes.*

ACCEPTED methods for the determination of small quantities of organic matter in dilute aqueous solutions are generally based upon wet oxidation. The amount of oxidant consumed may be found volumetrically (*4*) or photometrically (*5*), or the quantity of carbon dioxide evolved may be determined by manometric (*13*), gravimetric (*11*), or alkalimetric (*7*) procedures. In addition, thermal conductivity (*8*) and mass spectrometry (*2*) have been utilized to determine the carbon dioxide. These methods, though some are widely used, suffer from the variable susceptibility of organic compounds to oxidation by common reagents such as chromic acid, the interference of chloride and other ions in some cases, and the length of time required for analysis. Recently a highly sensitive, specific, and accurate determination of organic carbon in water has been described (*10*), in which a sample is evaporated to dryness and burned in oxygen, all of the vapors being passed through a combustion tube, collected, and circulated through an infrared analyzer. Even this method requires from 1 to 3 hours per determination.

Increasing concern with the problems of water pollution and waste treatment has brought about a need for a rapid and precise determination of total carbonaceous matter in water, free from interference by salts. The present authors have been led to investigate the combustion of aqueous samples in a flowing oxygen atmosphere. The major problem involved here is the relatively large volume of water vapor produced when liquid water is placed in a hot combustion chamber. As calculated from ideal gas behavior, 1 ml. of liquid water yields 5.6 liters of steam at 950° C. To work with a tube of reasonable dimensions, one is restricted to a small sample. For this reason a very

---

[1] Present address, Aerojet-General Corp., Sacramento, Calif.

VOL. 35, NO. 3, MARCH 1963 • 315

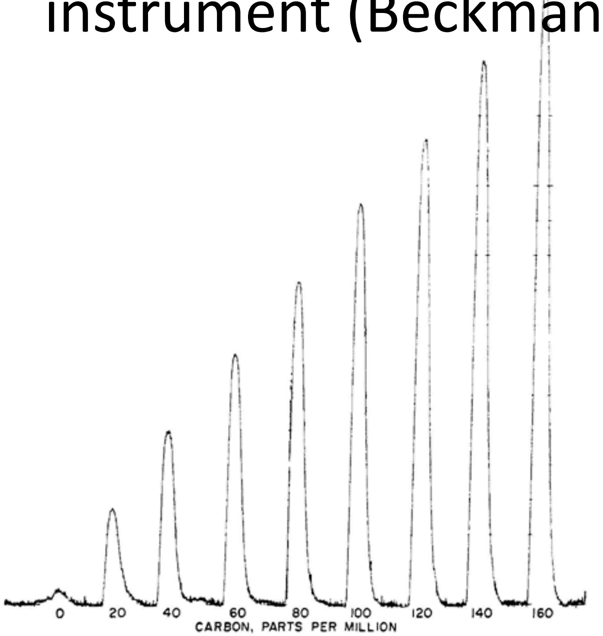


Figure 5. Calibration data

Standards. Acetic acid in water
Flow rate. 56 ml. per minute
Furnace temp. 950° C.

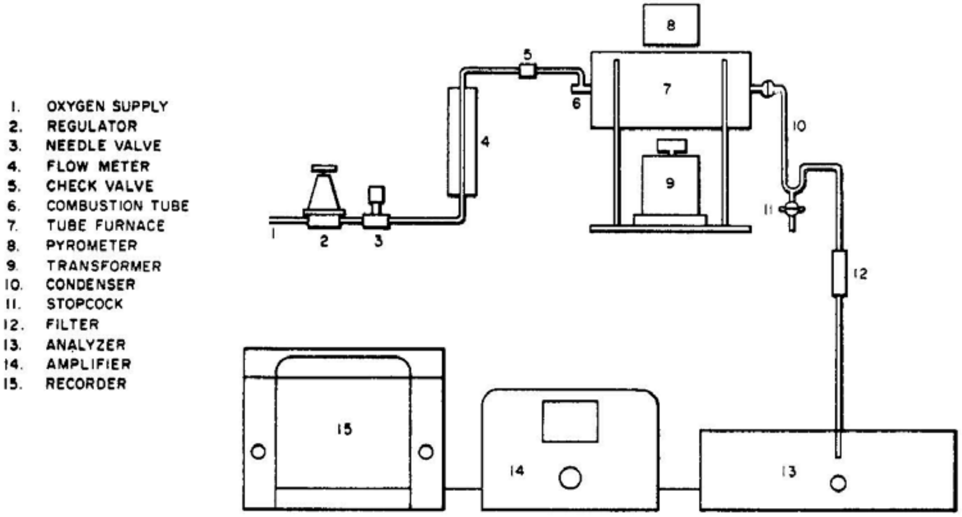


Figure 1. Schematic diagram of combustion apparatus

Great Recovery

- TOC

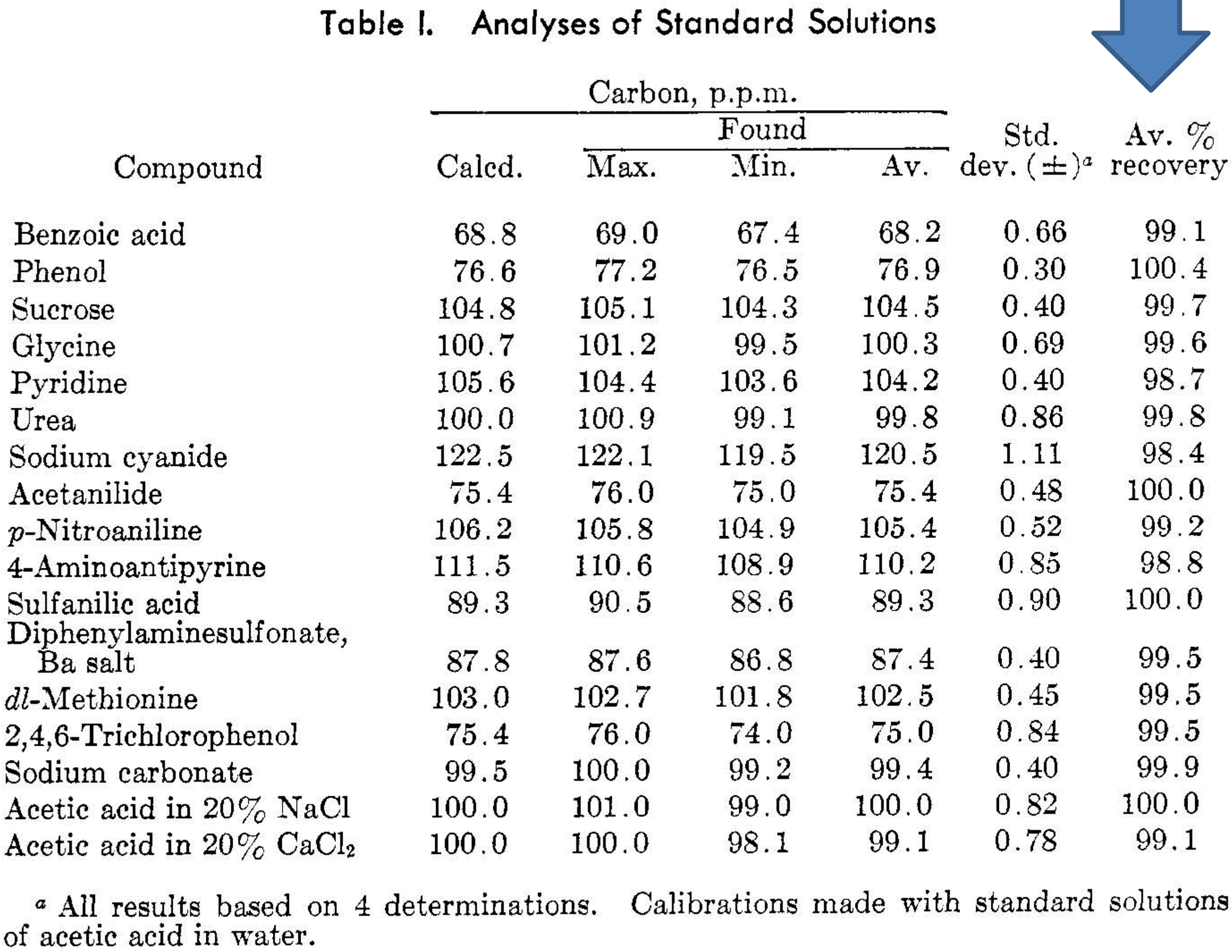


Table I. Analyses of Standard Solutions

Compound	Carbon, p.p.m. Calcd.	Found Max.	Found Min.	Found Av.	Std. dev. (±)[a]	Av. % recovery
Benzoic acid	68.8	69.0	67.4	68.2	0.66	99.1
Phenol	76.6	77.2	76.5	76.9	0.30	100.4
Sucrose	104.8	105.1	104.3	104.5	0.40	99.7
Glycine	100.7	101.2	99.5	100.3	0.69	99.6
Pyridine	105.6	104.4	103.6	104.2	0.40	98.7
Urea	100.0	100.9	99.1	99.8	0.86	99.8
Sodium cyanide	122.5	122.1	119.5	120.5	1.11	98.4
Acetanilide	75.4	76.0	75.0	75.4	0.48	100.0
p-Nitroaniline	106.2	105.8	104.9	105.4	0.52	99.2
4-Aminoantipyrine	111.5	110.6	108.9	110.2	0.85	98.8
Sulfanilic acid	89.3	90.5	88.6	89.3	0.90	100.0
Diphenylaminesulfonate, Ba salt	87.8	87.6	86.8	87.4	0.40	99.5
dl-Methionine	103.0	102.7	101.8	102.5	0.45	99.5
2,4,6-Trichlorophenol	75.4	76.0	74.0	75.0	0.84	99.5
Sodium carbonate	99.5	100.0	99.2	99.4	0.40	99.9
Acetic acid in 20% NaCl	100.0	101.0	99.0	100.0	0.82	100.0
Acetic acid in 20% $CaCl_2$	100.0	100.0	98.1	99.1	0.78	99.1

[a] All results based on 4 determinations. Calibrations made with standard solutions of acetic acid in water.

UMass TOC Instrumentation

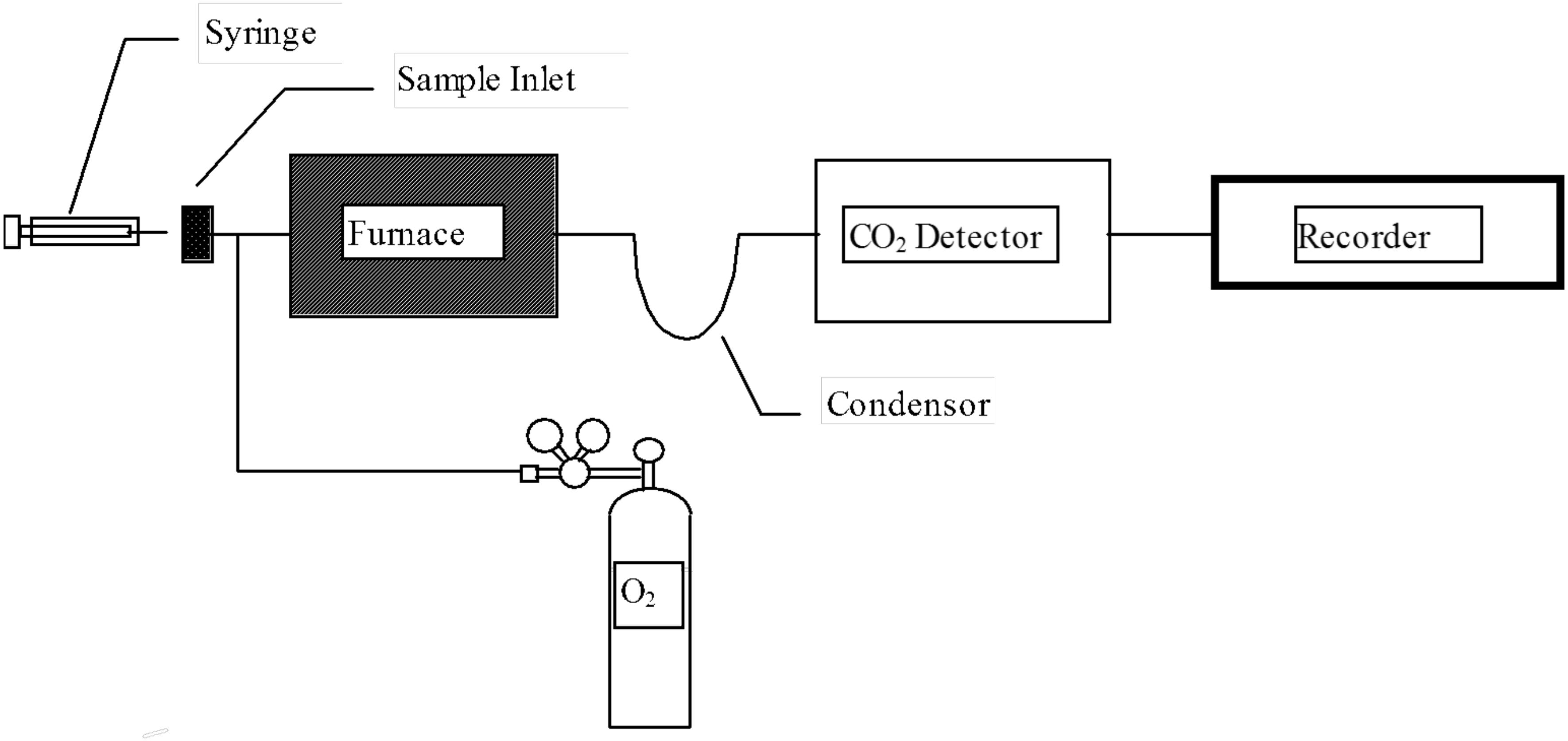
- High Temperature Pyrolysis
  - Beckman Corp., Model 915 (the first!)
  - Shimadzu Model 4000 (308 Elab II)
  - Shimadzu Model 5000 (201 & 308 Elab II)
- UV-Persulfate
  - Dohrmann Model DC-80 (Marston 24)
- Wet Chemical Oxidation
  - OI Corp., Model 700 with persulfate digestion (Environmental Institute)

High-Temperature Combustion Method

- Advantages:
  - Oxidizes particulates and solids
  - Rapid
  - Relatively interference-free
- Disadvantages
  - Low sensitivity (min. detectable conc. = 1 mg C/L or less depending on instrument)
  - Highest maintenance (particularly in high temp. components)
  - Prone to lose CO_2 in stream condensation phase
  - Problem recovering certain aromatics
  - Low salt tolerance
  - Difficult to obtain reliable system blanks
  - Can accumulate nonvolatile residues in the analyzer

Pyrolysis TOC Unit

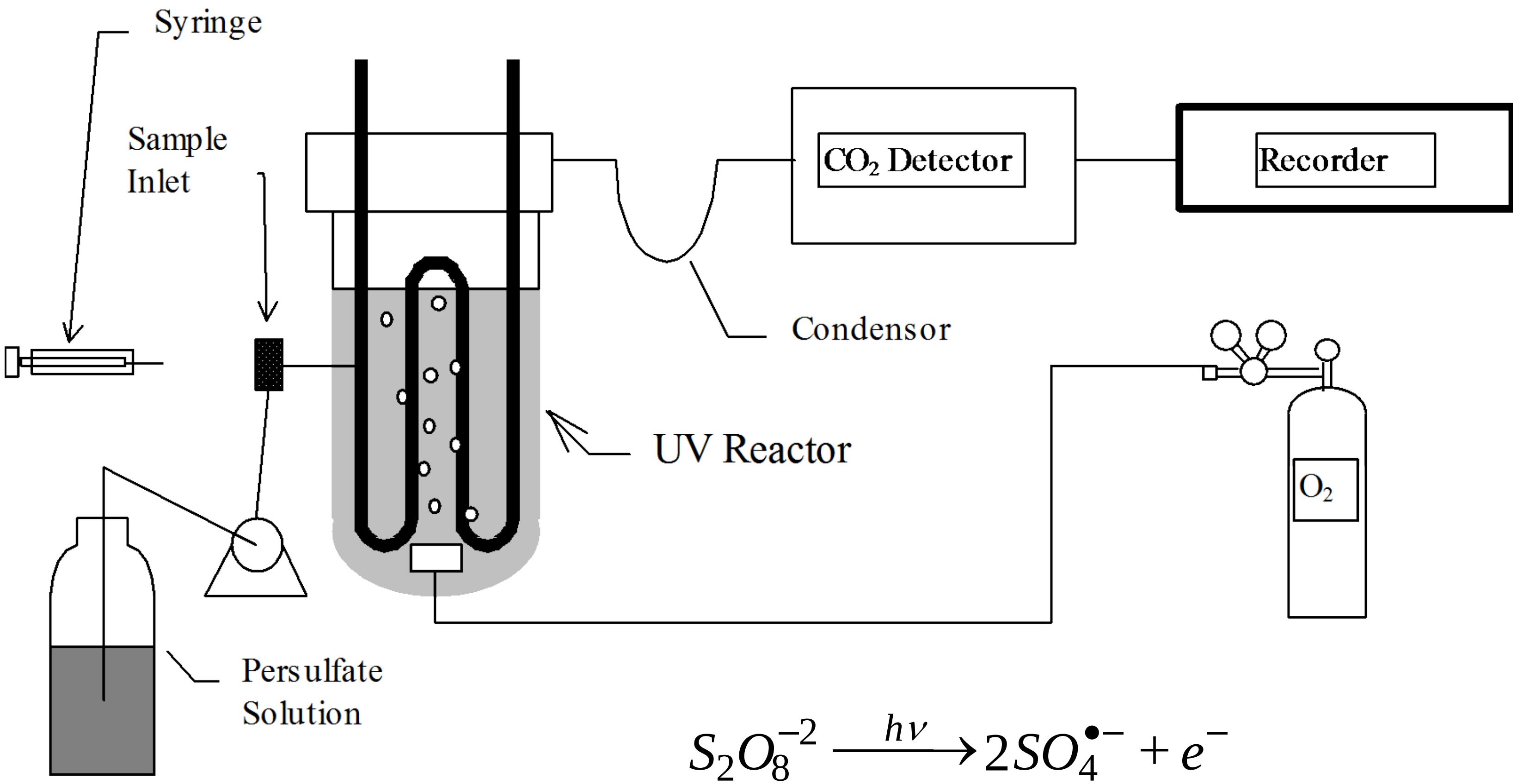
High temperature, in oxygen, with a cobalt catalyst



Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method

- Advantages:
  - High sensitivity (< 1 mg C/L samples)
  - Good recovery in most applications
  - Good precision
  - Low maintenance
  - Nonvolatile residuals are drained from the analyzer
- Disadvantages:
  - Potential interference with halide samples at CO_2 detection phase in oxygen-rich atmosphere

UV-Persulfate TOC Unit



$$S_2O_8^{-2} \xrightarrow{h\nu} 2SO_4^{\bullet-} + e^-$$

$$H_2O \xrightarrow{h\nu} H^{\bullet} + {}^{\bullet}OH$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{-2} + H^+ + {}^{\bullet}OH$$

Non-Dispersive Infrared Analysis (NDIR)

- All EPA approved methods for organic carbon analysis require NDIR method
- Measures infrared light absorbed by carbon dioxide as it passes through an absorption cell
- CO_2 Property $\rightarrow$ Absorbance = 4.26 µm (IR range)
- TSI Monitor – [CO_2] determined when the instrument is calibrated using pure nitrogen (0 ppm CO_2) and a known concentration of CO_2 such as 1000 or 5000 ppm

NDIR (con't)

- "Nondispersive" – no monochromator and infrared sources are broadband emitters
- Detector cells are pressure-sensitive: affected only by wavelengths absorbed by CO_2
- Interference caused by gases that have overlapping infrared absorption bands – like water vapor
  - Therefore, water vapor removed by condensation before getting to the detector

Beer's Law

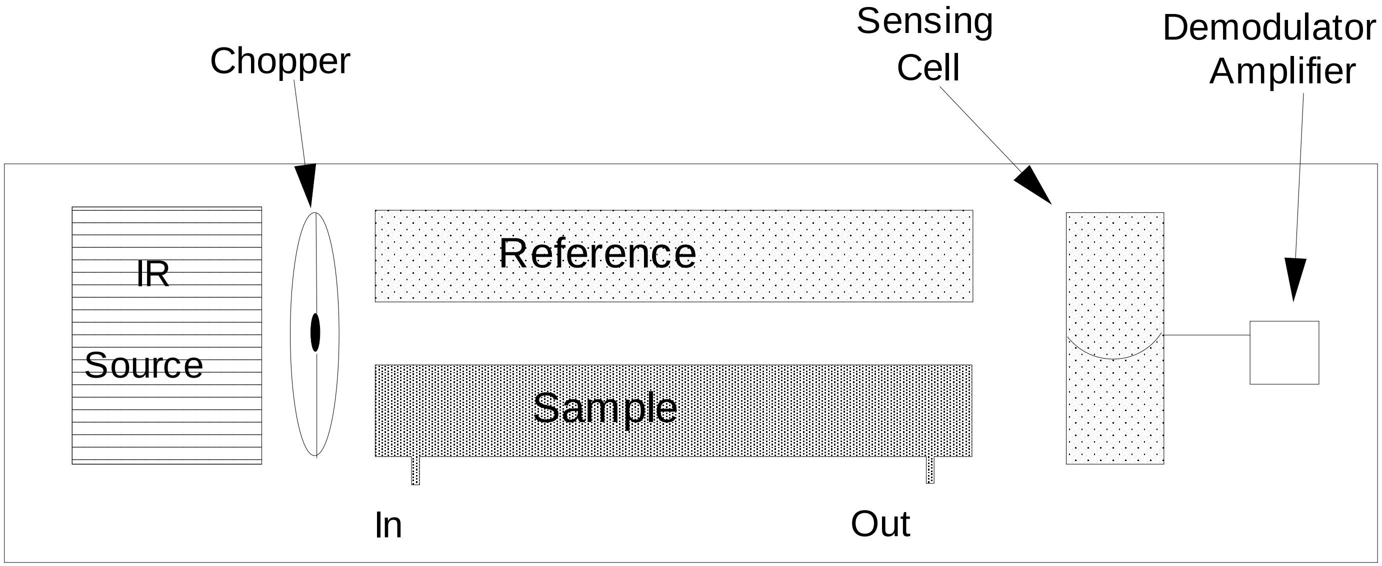
- $A = a*b*c$
  - A = Absorbance
  - a = absorptivity coefficient
  - b = path length
  - c = analyte (CO_2) concentration

OR

- $I = I_o e^{kP}$
  - I = intensity of light striking the IR detector
  - I_o = measured signal with 0 ppm CO_2
  - k = a system dependant constant
  - P = [CO_2]

CO_2 Analyzer

Arnold Beckman

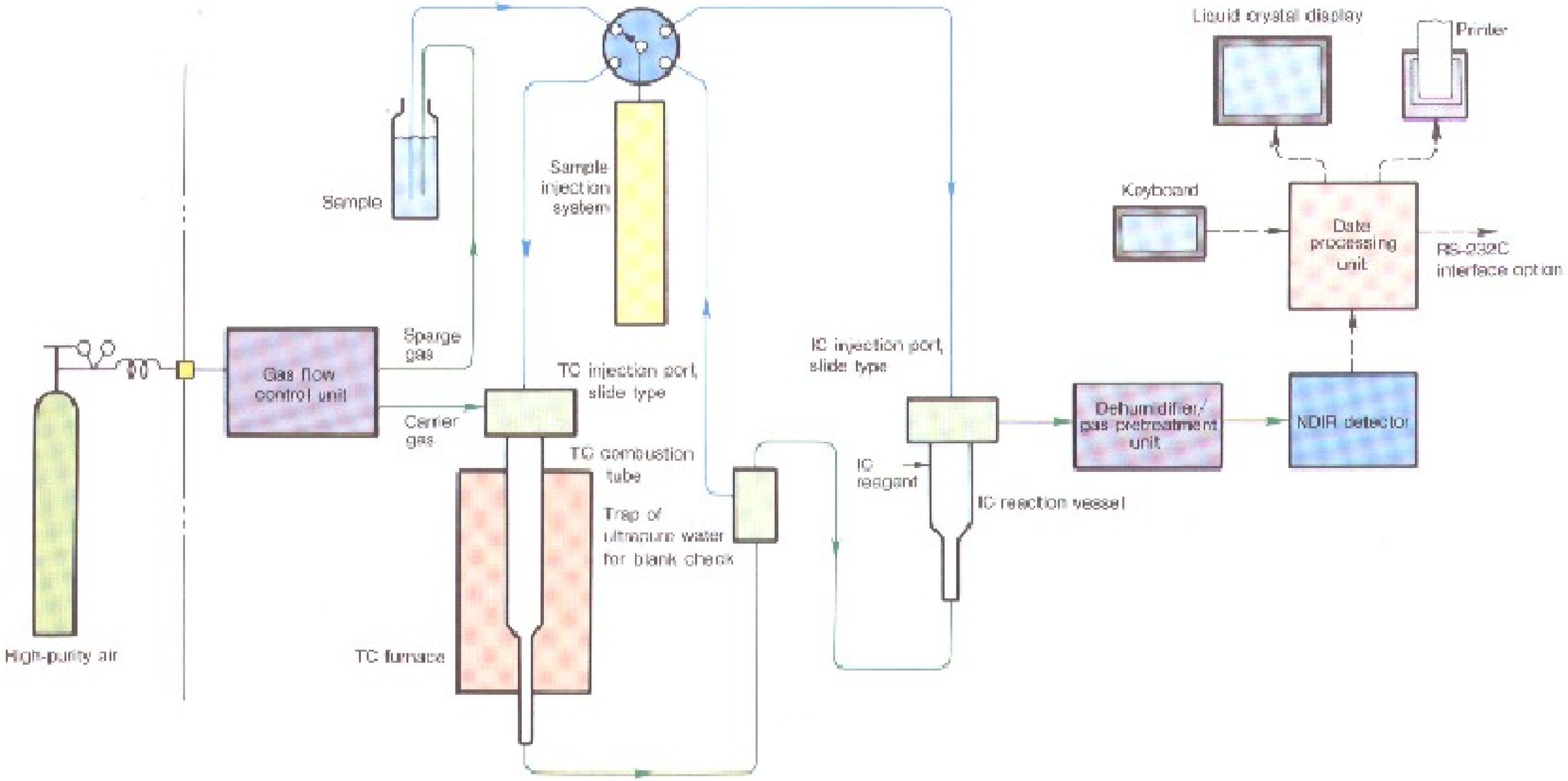


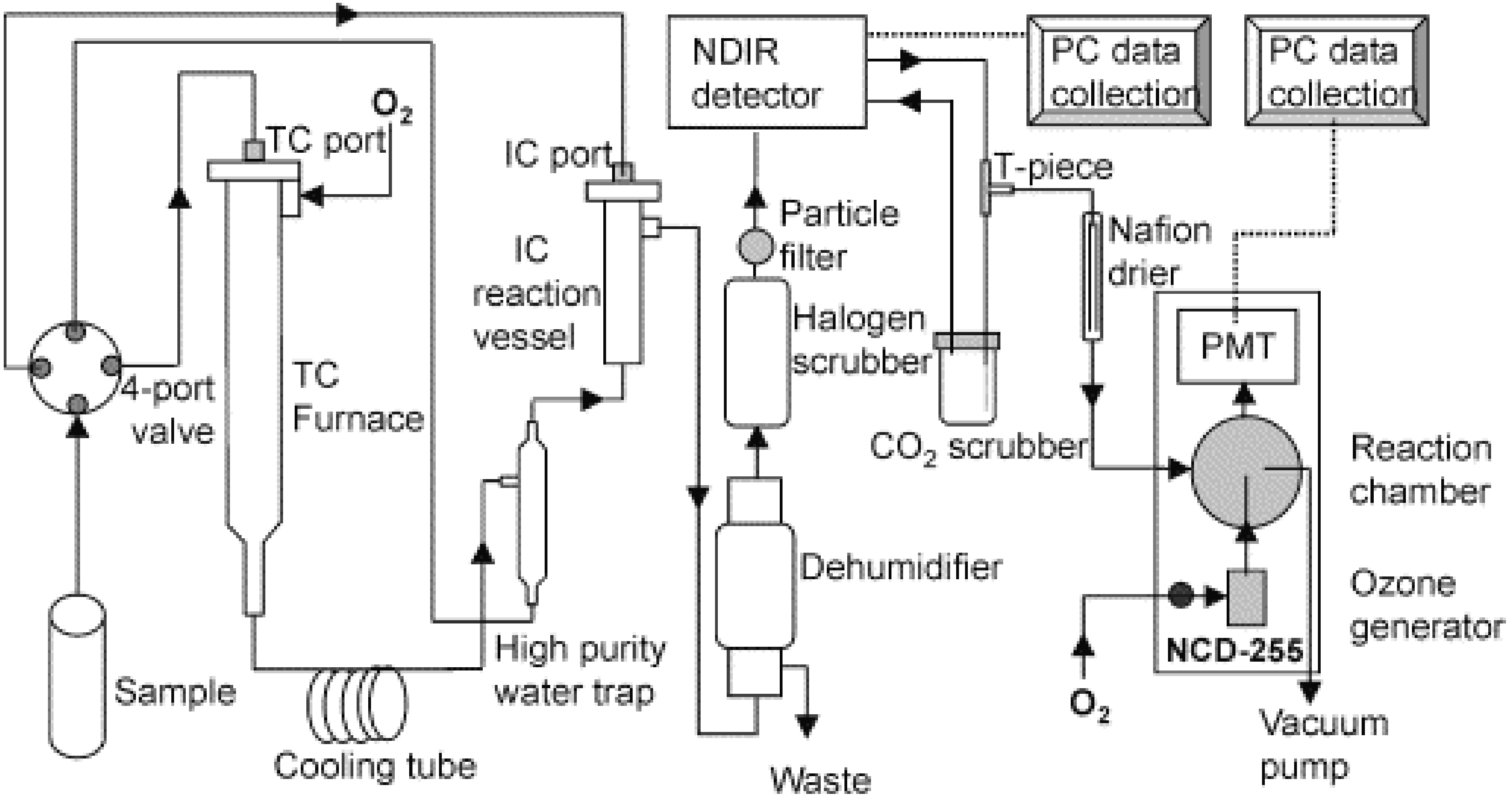
- Non-dispersive Infrared Analyzer (seen above)
- Electrolytic Conductivity Detection (interference from other ionic species)
- Coulometric Titration
- Reduction to CH_4, then FID (flame ionization detection) – longer testing times

Instrument Specs.
Shimadzu 5000

- Analyte = TC, IC, TOC (TC-IC), NPOC
- Method – Combustion (680^{o} C)/NDIR gas analysis
- Measuring Range = 4 ppb to 4000 ppb
- Avg. Analysis Time = 2 – 3 min. for both TC and IC
- Shimadzu ASI-5000 – Automatic Sample Injector
  - 78 vial or 16 vial turntables available
  - Rinsing between samples minimizes sample “carry-over”

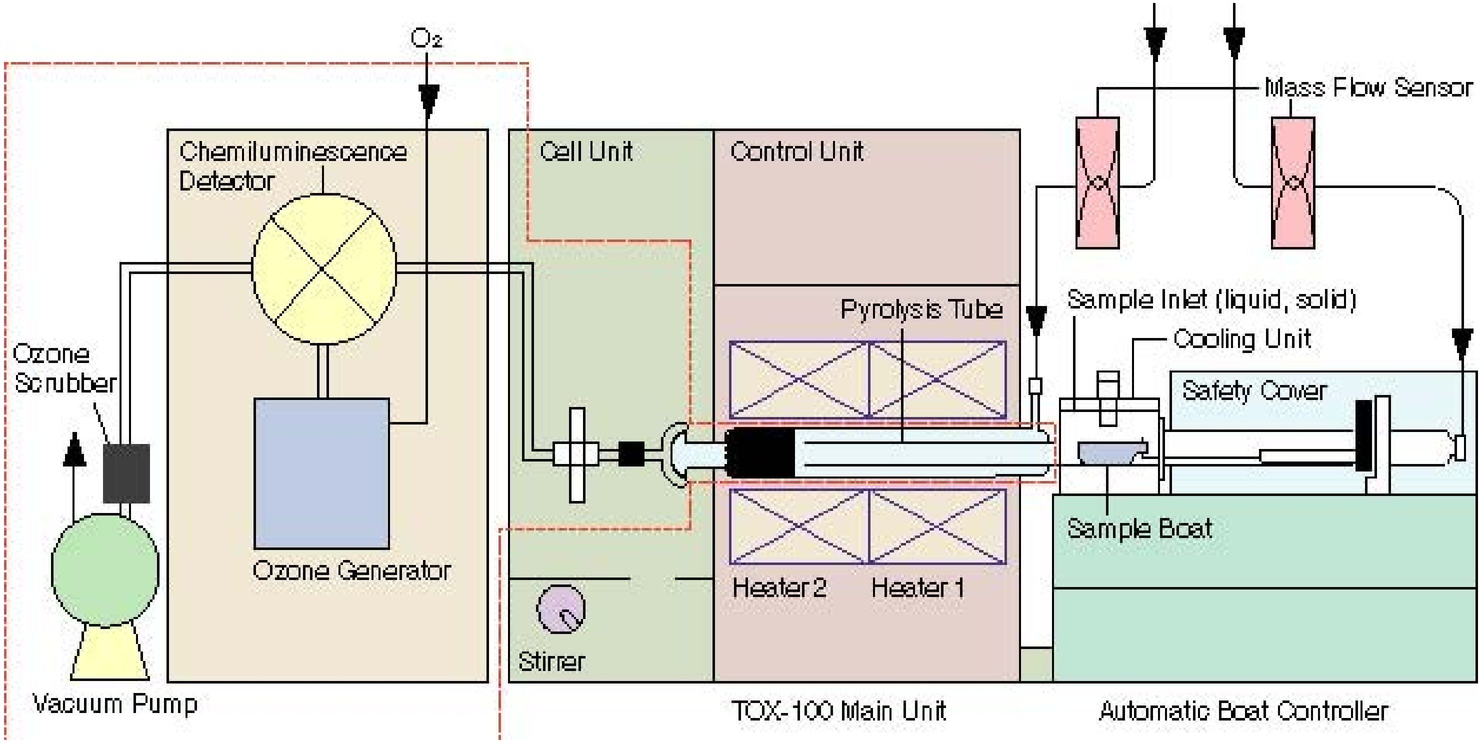
Shimadzu 5000 TOC Analyzer (schematic)





- Schematic diagram showing the coupled Shimadzu TOC 5000A HTCO–Sievers NCD 255 nitrogen chemiluminescence detector, and associated hardware.

- Mitsubishi Unit



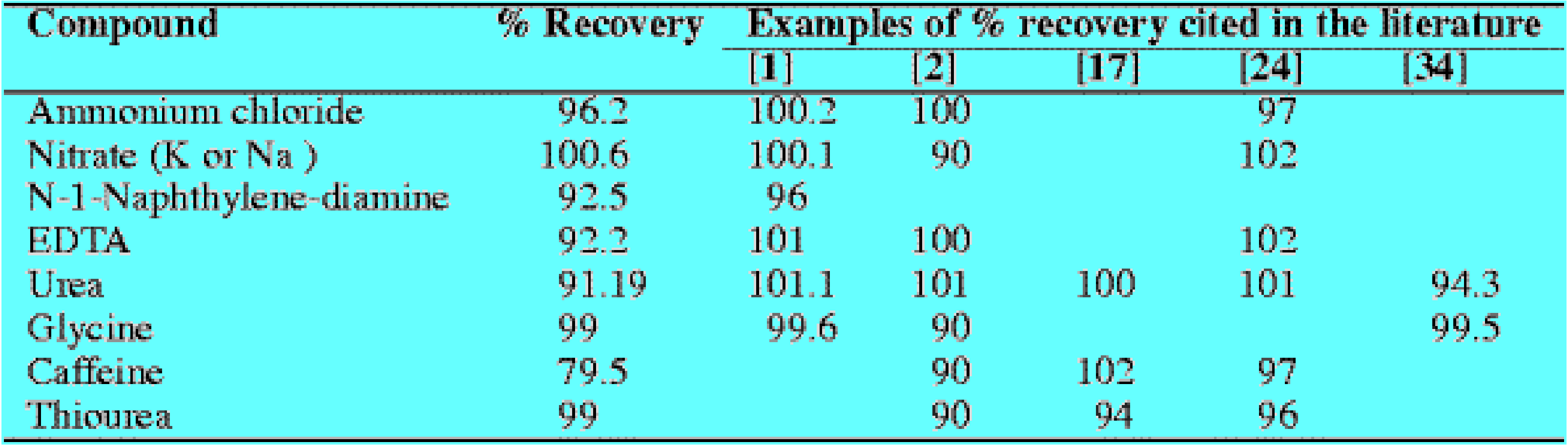
- Chemiluminescent detection

$$2\ NO+2\ O3\rightarrow 2\ NO2*+2\ O2$$

$$NO_2^*\rightarrow NO_2+h\nu$$

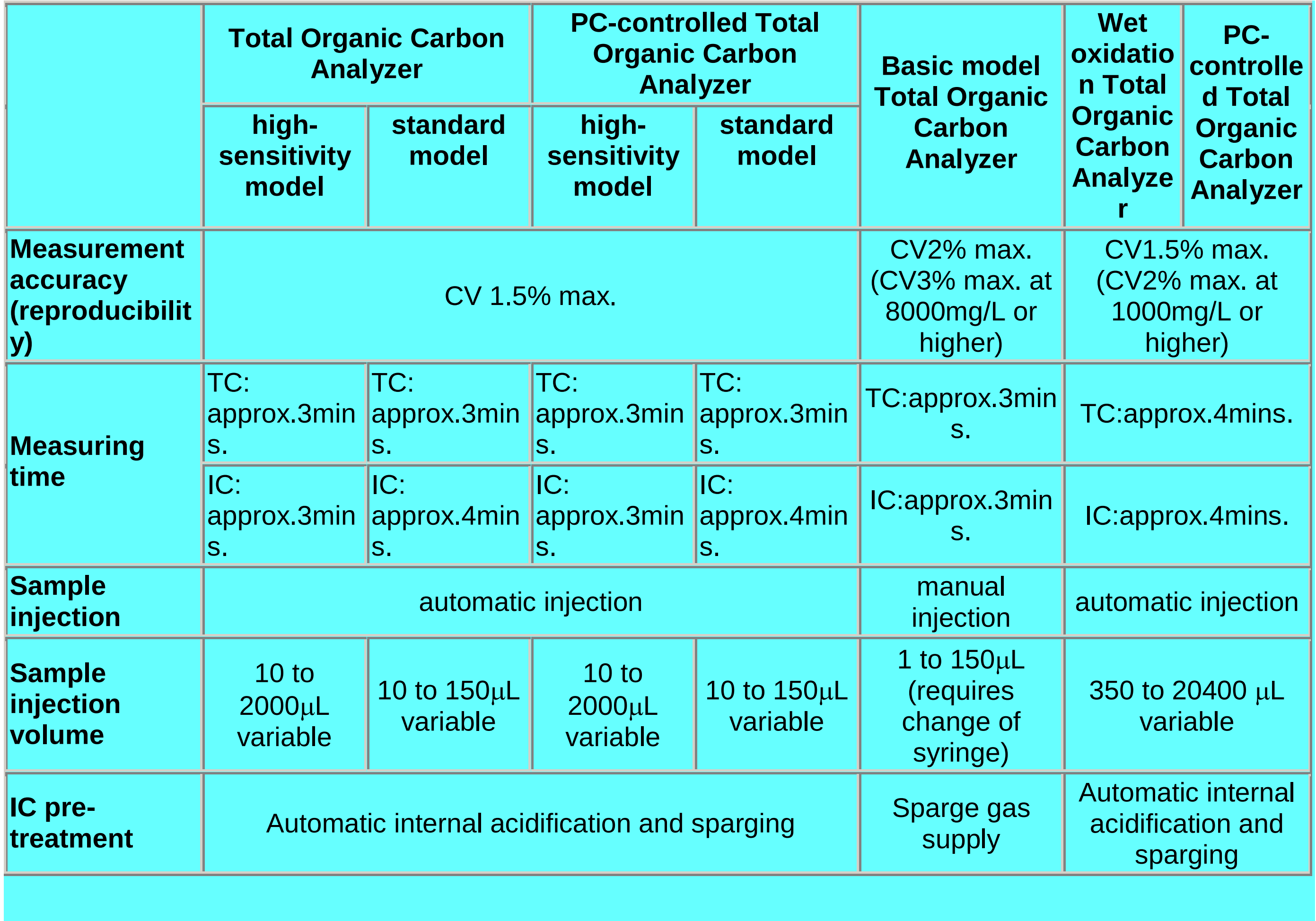
  - Rapid decay of the NO_2* produces light in the 590-2,900 nanometer range. This light is detected and amplified by a photomultiplier tube.

- Table 3. Recovery of N from commonly cited N compounds dissolved in ultrapure water using the coupled HTCO TOC–NCD method in our laboratory (recovery in relation to potassium phthalate/glycine standard), and literature results

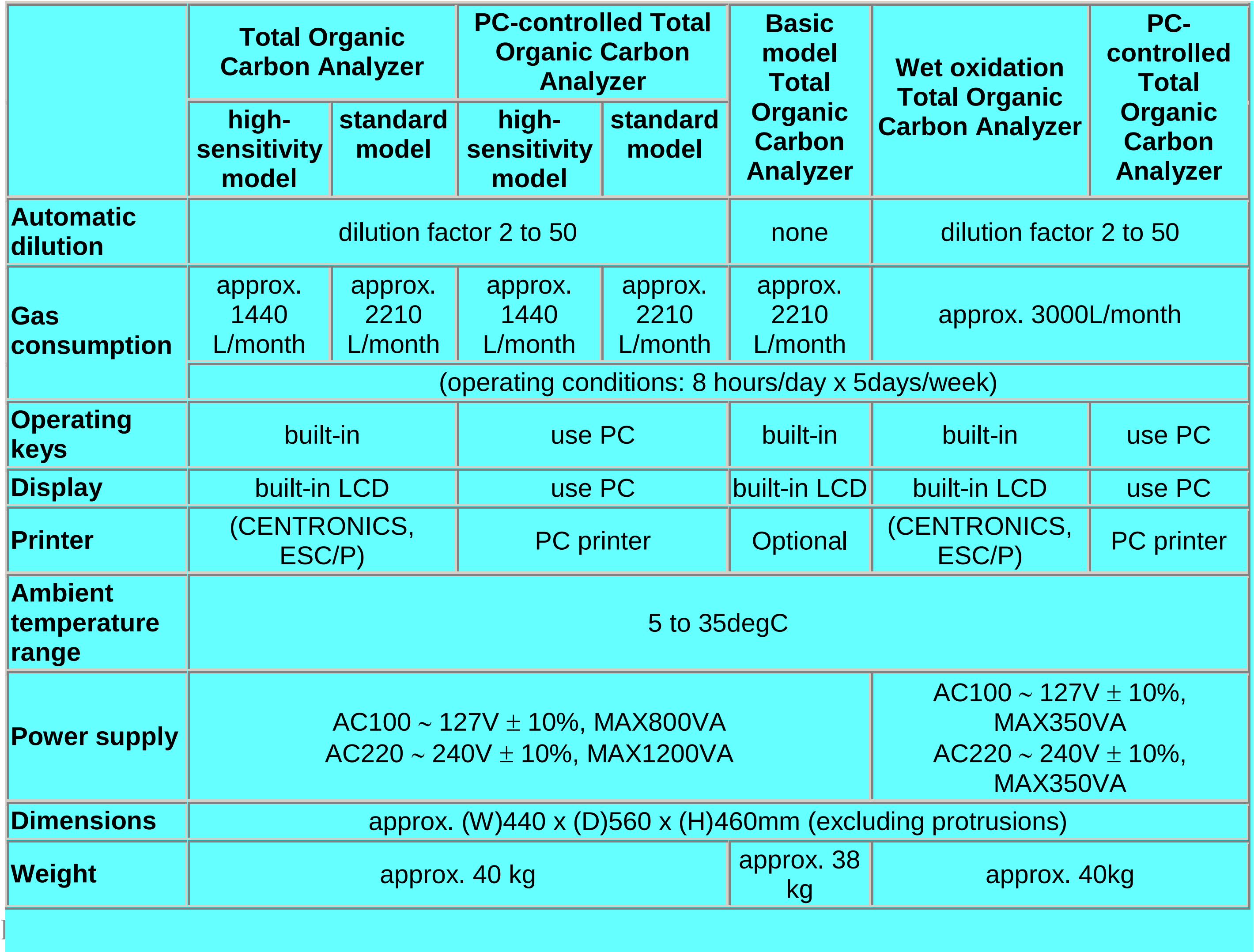


Compound	% Recovery	Examples of % recovery cited in the literature				
		[1]	[2]	[17]	[24]	[34]
Ammonium chloride	96.2	100.2	100		97	
Nitrate (K or Na)	100.6	100.1	90		102	
N-1-Naphthylene-diamine	92.5	96				
EDTA	92.2	101	100		102	
Urea	91.19	101.1	101	100	101	94.3
Glycine	99	99.6	90			99.5
Caffeine	79.5		90	102	97	
Thiourea	99		90	94	96	

	Total Organic Carbon Analyzer		PC-controlled Total Organic Carbon Analyzer		Basic model Total Organic Carbon Analyzer	Wet oxidation Total Organic Carbon Analyzer	PC-controlled Total Organic Carbon Analyzer
	high-sensitivity model	standard model	high-sensitivity model	standard model			
Model	TOC-VCSH	TOC-VCSN	TOC-VCPH	TOC-VCPN	TOC-VE	TOC-VWS	TOC-VWP
Measurement method	680 degC combustion catalytic oxidation/NDIR method					wet oxidation/NDIR	
Operation method	standalone		PC-controlled		standalone	standalone	PC-controlled
Measured items	TC,IC,TOC,NPOC (optional POC,TN)				TC,IC,TOC, NPOC (optional TN)	TC,IC,TOC,NPOC	
Applicable samples	aqueous sample (optional solid/gas samples)				aqueous sample	aqueous sample	
Measurement range (mg/L)	TC:0 to 25000 IC:0 to 30000	TC:0 to 25000 IC:0 to 3000	TC:0 to 25000 IC:0 to 30000	TC:0 to 25000 IC:0 to 3000	TC:0 to 20000 IC:0 to 20000	TC:0 to 3000 IC:0 to 2500	
Detection limit	4μg/L	50μg/L	4μg/L	50μg/L	----	0.5μg/L	



	Total Organic Carbon Analyzer		PC-controlled Total Organic Carbon Analyzer		Basic model Total Organic Carbon Analyzer	Wet oxidation Total Organic Carbon Analyzer	PC-controlled Total Organic Carbon Analyzer
	high-sensitivity model	**standard model**	**high-sensitivity model**	**standard model**			
Measurement accuracy (reproducibility)	CV 1.5% max.				CV2% max. (CV3% max. at 8000mg/L or higher)	CV1.5% max. (CV2% max. at 1000mg/L or higher)	
Measuring time	TC: approx.3mins.	TC: approx.3mins.	TC: approx.3mins.	TC: approx.3mins.	TC:approx.3mins.	TC:approx.4mins.	
	IC: approx.3mins.	IC: approx.4mins.	IC: approx.3mins.	IC: approx.4mins.	IC:approx.3mins.	IC:approx.4mins.	
Sample injection	automatic injection				manual injection	automatic injection	
Sample injection volume	10 to 2000µL variable	10 to 150µL variable	10 to 2000µL variable	10 to 150µL variable	1 to 150µL (requires change of syringe)	350 to 20400 µL variable	
IC pre-treatment	Automatic internal acidification and sparging				Sparge gas supply	Automatic internal acidification and sparging	

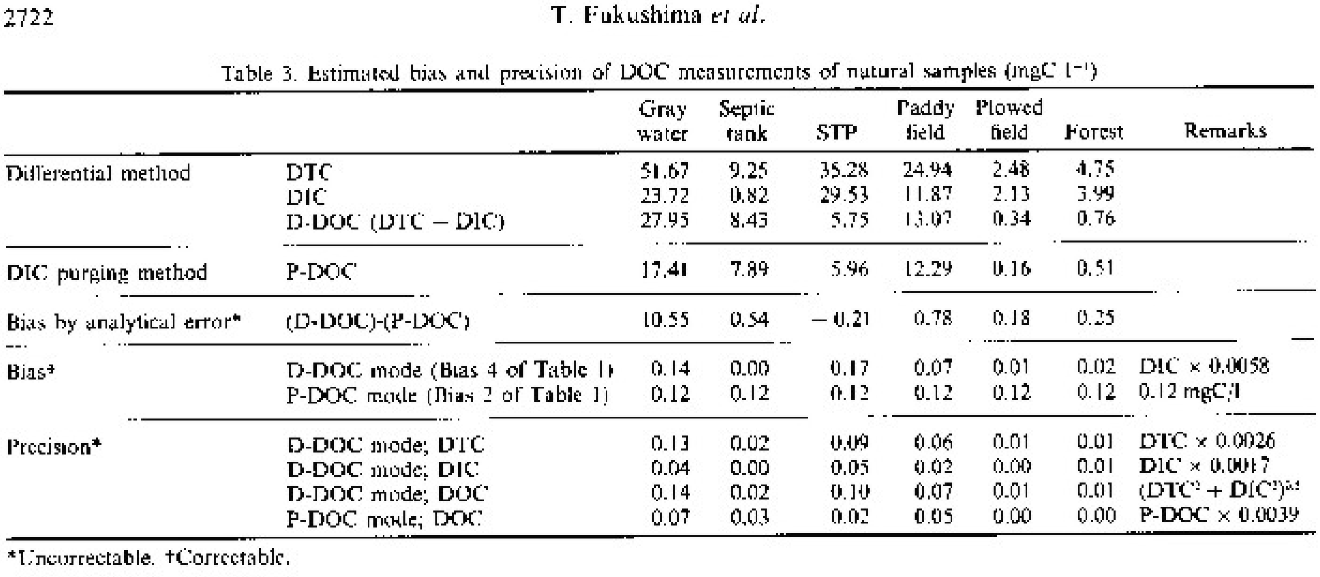


	Total Organic Carbon Analyzer		PC-controlled Total Organic Carbon Analyzer		Basic model Total Organic Carbon Analyzer	Wet oxidation Total Organic Carbon Analyzer	PC-controlled Total Organic Carbon Analyzer
	high-sensitivity model	**standard model**	**high-sensitivity model**	**standard model**			
Automatic dilution	dilution factor 2 to 50				none	dilution factor 2 to 50	
Gas consumption	approx. 1440 L/month	approx. 2210 L/month	approx. 1440 L/month	approx. 2210 L/month	approx. 2210 L/month	approx. 3000L/month	
	(operating conditions: 8 hours/day x 5days/week)						
Operating keys	built-in		use PC		built-in	built-in	use PC
Display	built-in LCD		use PC		built-in LCD	built-in LCD	use PC
Printer	(CENTRONICS, ESC/P)		PC printer		Optional	(CENTRONICS, ESC/P)	PC printer
Ambient temperature range	5 to 35degC						
Power supply	AC100 ~ 127V ± 10%, MAX800VA AC220 ~ 240V ± 10%, MAX1200VA					AC100 ~ 127V ± 10%, MAX350VA AC220 ~ 240V ± 10%, MAX350VA	
Dimensions	approx. (W)440 x (D)560 x (H)460mm (excluding protrusions)						
Weight	approx. 40 kg				approx. 38 kg	approx. 40kg	

Comparison of TOC levels

- Sample 1 – Bridgeport Hydraulic Company (BHC) potable water
  - Private water supply company in Connecticut
- Sample 2 – water taken from water fountain in Marcus Building on the UMass campus
- Sample 3 – water taken from Campus Pond to simulate raw water sample

TOC Analytical Accuracy and QA



2722 T. Fukushima *et al.*

Table 3. Estimated bias and precision of DOC measurements of natural samples (mgC l^{-1})

		Gray water	Septic tank	STP	Paddy field	Plowed field	Forest	Remarks
Differential method	DTC	51.67	9.25	35.28	24.94	2.48	4.75	
	DIC	23.72	0.82	29.53	11.87	2.13	3.99	
	D-DOC (DTC − DIC)	27.95	8.43	5.75	13.07	0.34	0.76	
DIC purging method	P-DOC	17.41	7.89	5.96	12.29	0.16	0.51	
Bias by analytical error*	(D-DOC)-(P-DOC)	10.55	0.54	− 0.21	0.78	0.18	0.25	
Bias†	D-DOC mode (Bias 4 of Table 1)	0.14	0.00	0.17	0.07	0.01	0.02	DIC × 0.0058
	P-DOC mode (Bias 2 of Table 1)	0.12	0.12	0.12	0.12	0.12	0.12	0.12 mgC/l
Precision*	D-DOC mode; DTC	0.13	0.02	0.09	0.06	0.01	0.01	DTC × 0.0026
	D-DOC mode; DIC	0.04	0.00	0.05	0.02	0.00	0.01	DIC × 0.0017
	D-DOC mode; DOC	0.14	0.02	0.10	0.07	0.01	0.01	$(DTC^2 + DIC^2)^{0.5}$
	P-DOC mode; DOC	0.07	0.03	0.02	0.05	0.00	0.00	P-DOC × 0.0039

*Uncorrectable. †Correctable.

- Fukushima et al – November 1996
- Used Shimadzu 5000
- Believed the differential method was more user friendly than the purging method, but both gave good results

TOC Analytical Accuracy and QA

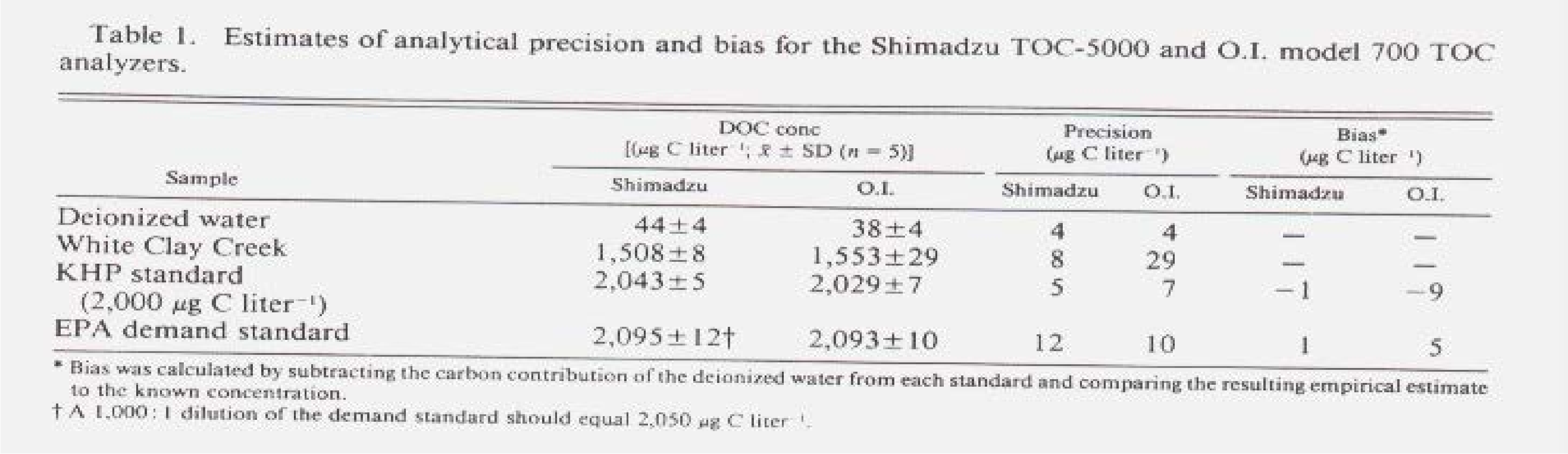


Table 1. Estimates of analytical precision and bias for the Shimadzu TOC-5000 and O.I. model 700 TOC analyzers.

Sample	DOC conc [(μg C liter^{-1}; $\bar{x}$ ± SD (n = 5)]		Precision (μg C liter^{-1})		Bias* (μg C liter^{-1})	
	Shimadzu	O.I.	Shimadzu	O.I.	Shimadzu	O.I.
Deionized water	44±4	38±4	4	4	—	—
White Clay Creek	1,508±8	1,553±29	8	29	—	—
KHP standard (2,000 μg C liter^{-1})	2,043±5	2,029±7	5	7	−1	−9
EPA demand standard	2,095±12†	2,093±10	12	10	1	5

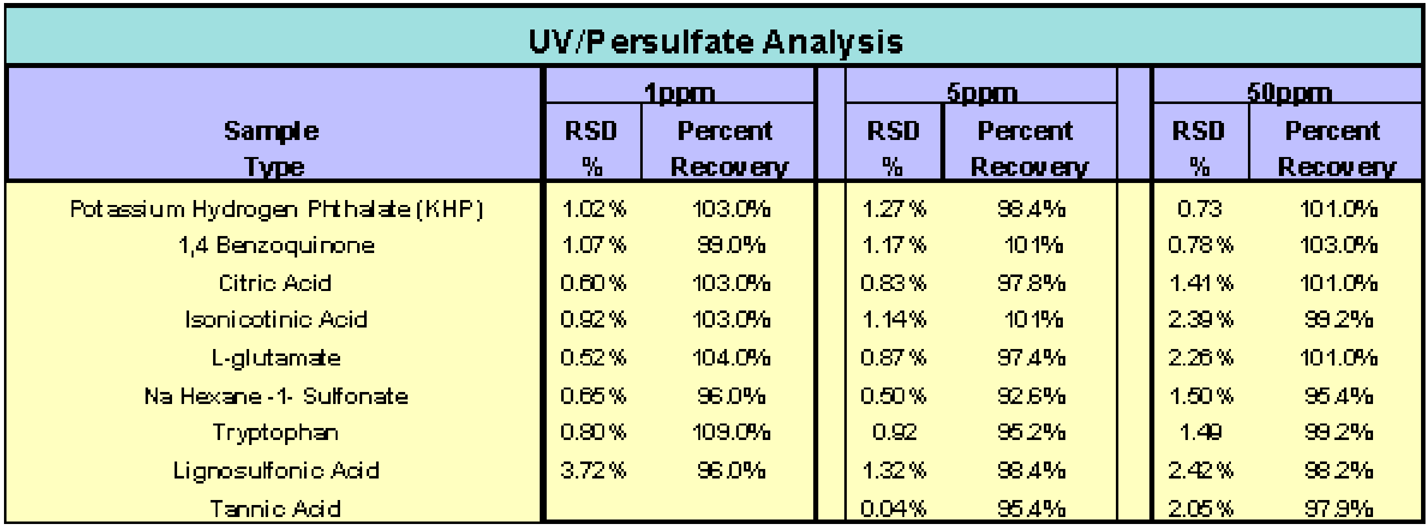
* Bias was calculated by subtracting the carbon contribution of the deionized water from each standard and comparing the resulting empirical estimate to the known concentration.

† A 1,000 : 1 dilution of the demand standard should equal 2,050 μg C liter^{-1}.

- Kaplan – January 1992
- Compared Shimadzu 5000 to O.I.Model 700 (persulfate oxidation method)
- Determined that Pt-catalyzed persulfate oxidation at 100^o C with an O.I. 700 underestimates DOC concentrations in freshwaters by ~5% when compared to the Shimadzu 5000, but considers that a “small source of error”.

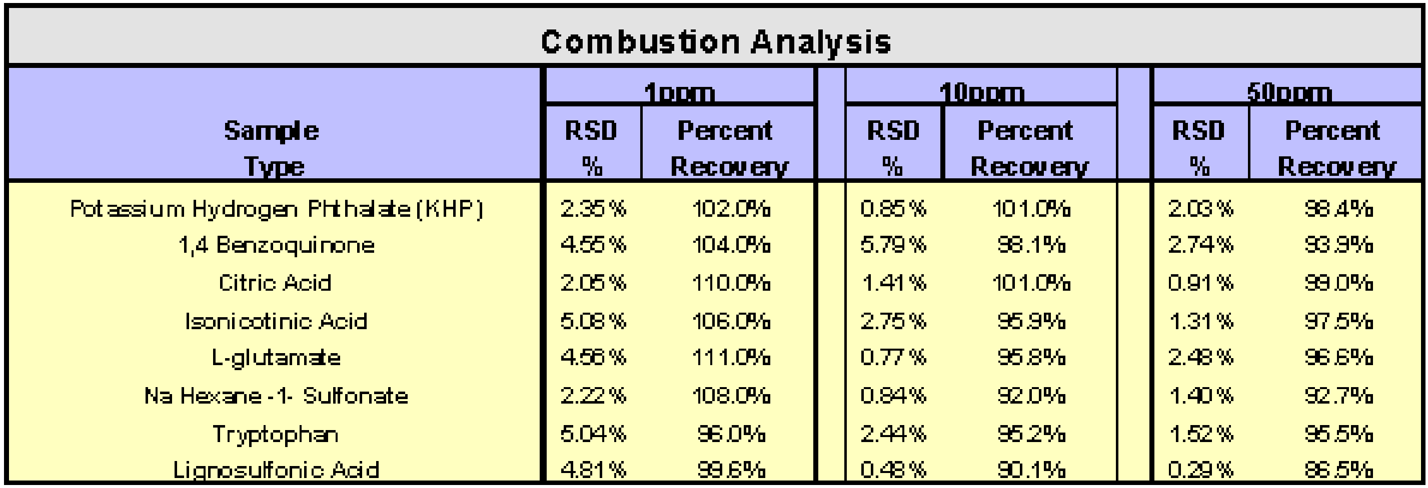
Comparison of methods

- From: [Tekmar application document]
- **TOC Analysis of Difficult Compounds**



UV/Persulfate Analysis

Sample Type	1ppm RSD %	1ppm Percent Recovery	5ppm RSD %	5ppm Percent Recovery	50ppm RSD %	50ppm Percent Recovery
Potassium Hydrogen Phthalate (KHP)	1.02 %	103.0%	1.27 %	98.4%	0.73	101.0%
1,4 Benzoquinone	1.07 %	99.0%	1.17 %	101%	0.78 %	103.0%
Citric Acid	0.60 %	103.0%	0.83 %	97.8%	1.41 %	101.0%
Isonicotinic Acid	0.92 %	103.0%	1.14%	101%	2.39 %	99.2%
L-glutamate	0.52 %	104.0%	0.87 %	97.4%	2.26 %	101.0%
Na Hexane -1- Sulfonate	0.65 %	96.0%	0.50 %	92.6%	1.50 %	95.4%
Tryptophan	0.80 %	109.0%	0.92	95.2%	1.49	99.2%
Lignosulfonic Acid	3.72 %	96.0%	1.32 %	98.4%	2.42 %	98.2%
Tannic Acid			0.04%	95.4%	2.05 %	97.9%



Combustion Analysis

Sample Type	1ppm RSD %	1ppm Percent Recovery	10ppm RSD %	10ppm Percent Recovery	50ppm RSD %	50ppm Percent Recovery
Potassium Hydrogen Phthalate (KHP)	2.35 %	102.0%	0.85 %	101.0%	2.03 %	98.4%
1,4 Benzoquinone	4.55 %	104.0%	5.79 %	98.1%	2.74%	93.9%
Citric Acid	2.05 %	110.0%	1.41 %	101.0%	0.91 %	99.0%
Isonicotinic Acid	5.08 %	106.0%	2.75 %	95.9%	1.31 %	97.5%
L-glutamate	4.56 %	111.0%	0.77 %	95.8%	2.48 %	96.6%
Na Hexane -1- Sulfonate	2.22 %	108.0%	0.84%	92.0%	1.40 %	92.7%
Tryptophan	5.04%	96.0%	2.44%	95.2%	1.52 %	95.5%
Lignosulfonic Acid	4.81 %	99.6%	0.48 %	90.1%	0.29 %	86.5%

- To next lecture