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CEE 772: Instrumental Methods in Environmental Analysis

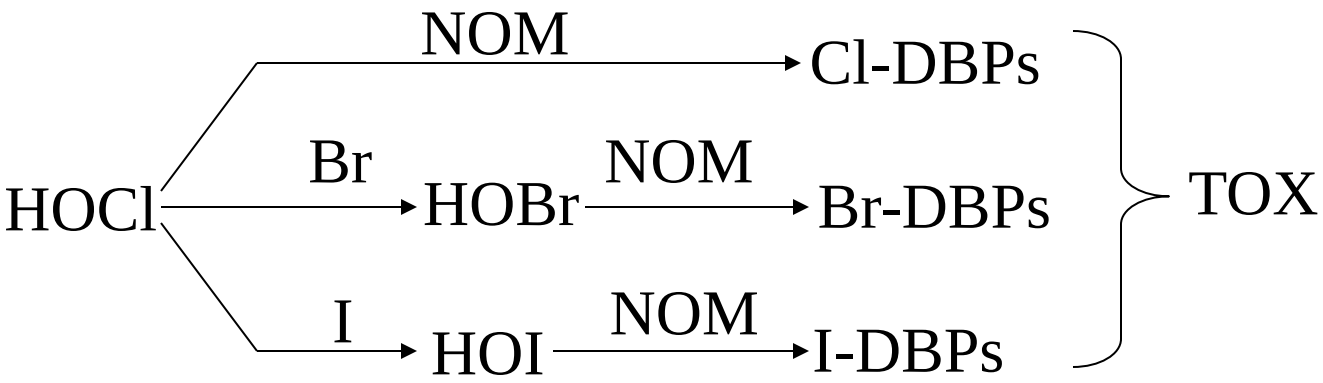
TOTAL ORGANIC HALOGEN (TOX)

(SKOOG, CHAPTS. 24D; PP.632-636)

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

Rassil Sayess & Dave Reckhow

TOX Formation



TOX=TOCl + TOBr + TOI

Other disinfectants: NH_2Cl, O_3, ClO_2

From: Guanghui Hua; 2004 WQTC

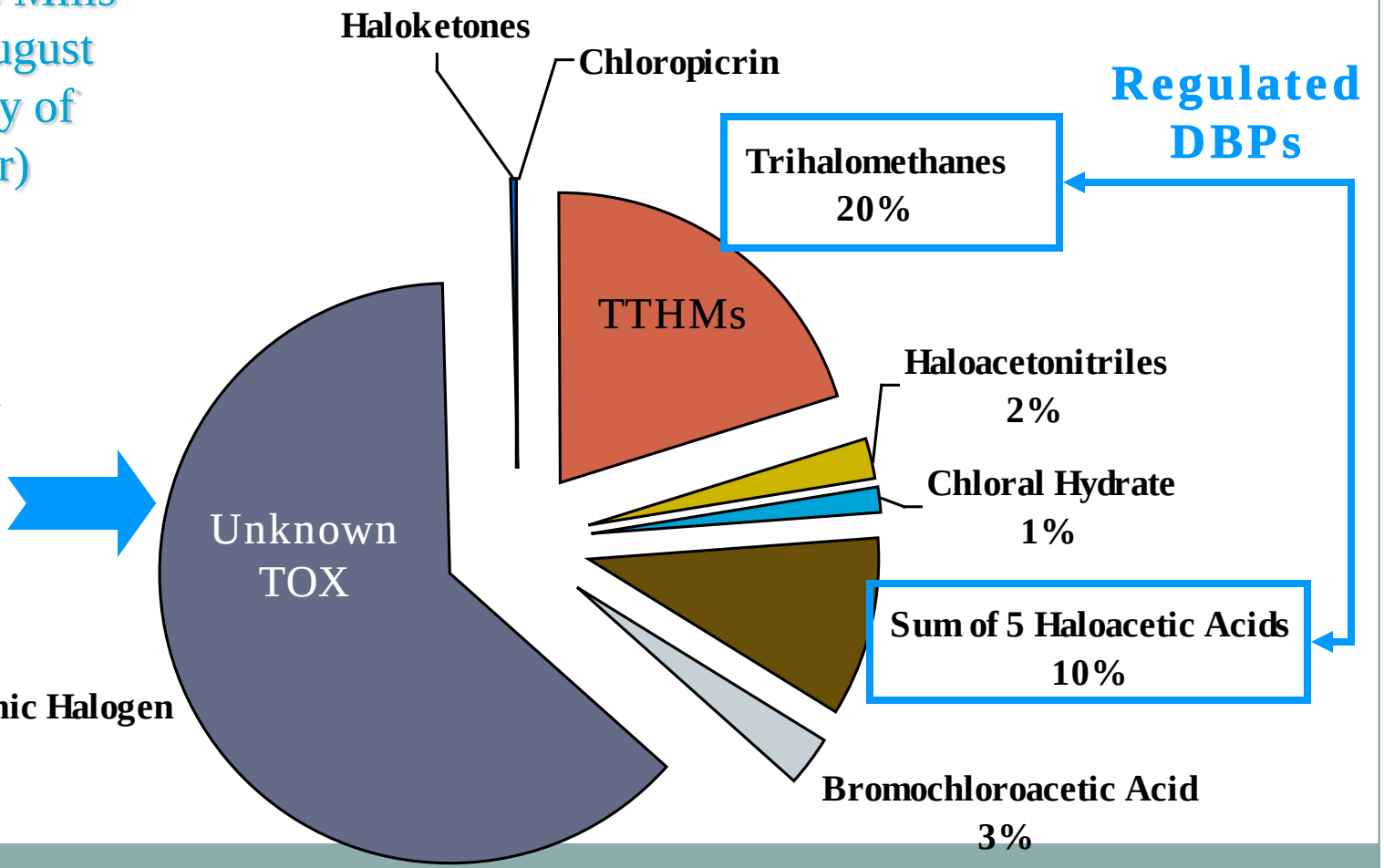
What do we know so far?

- 700 reported DBPs with limited number of quantitative and epidemiological data
- Approximately 50% of the TOX formed by drinking water chlorination is not accounted for➔ concern about the identity and concentrations of DBPs
- Heavier halogens result in higher toxicity in chlorinated and chloraminated drinking water

- Not feasible to account for each and every compound that might be formed in disinfected water
- Measures of TOX: A surrogate measure for organically-bound halogenated DBPs in a disinfected water sample.
- Comparing the TOX vales with the halides attributed to the identified DBPs: allow for the estimation of the unidentified TOX
- TOX analyzers: used to quantify amounts of organically-bound chlorine, bromine and iodine in raw and disinfected water samples

TOX: Known & Unknown

Data from the Mills Plant (CA) August 1997 (courtesy of Stuart Krasner)



But, the bad stuff is probably somewhere here

Which Compounds? The DBP Iceberg

THMs, THAAs

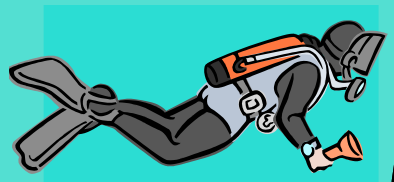
DHAAs

Stuart Krasner
AWWA

ICR Compounds

50 MWDSC DBPs

~700 Known DBPs



Susan Richardson
USEPA

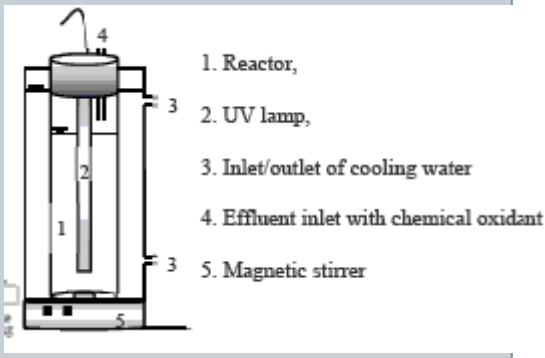
Halogenated Compounds

Non-halogenated Compounds

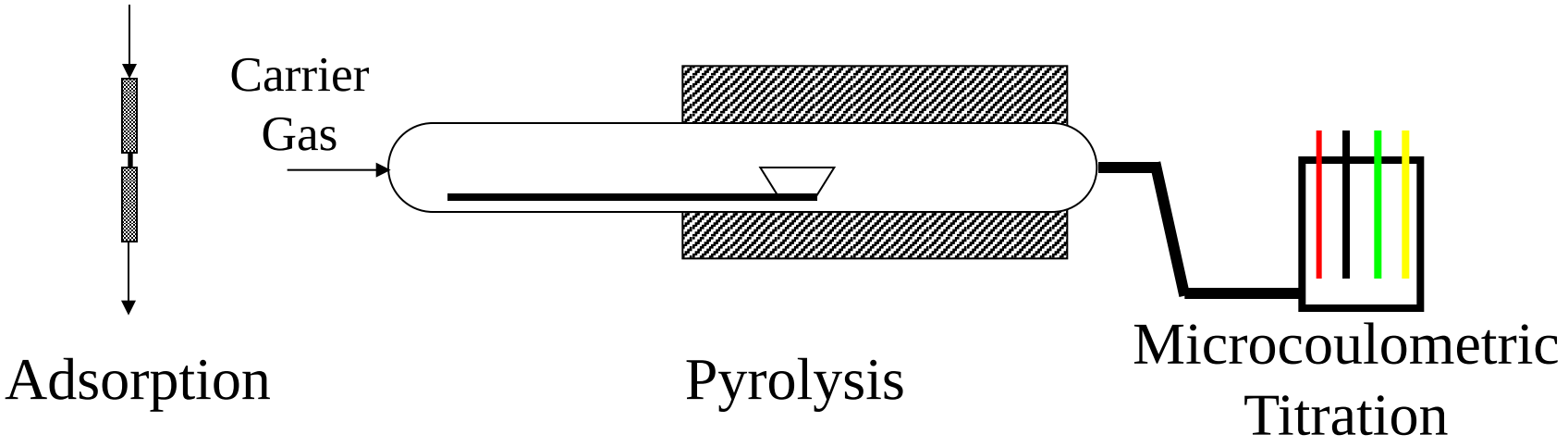
Rassil Sayess & Dave Reckhow

Methods to "measure" TOX

- Adsorption, pyrolysis, microcoulometric titration
  - Standard method
- UV/H_2O_2 oxidation/IC
- Neutron activation/γ ray spectroscopy
  - Can differentiate between the halogens
  - Very high cost
- Adsorption, nitrate wash, pyrolysis with Dohrmann or Euroglas then IC or ICP-MS
  - Can differentiate between the halogens



Conventional Method



Coulometry determine the amount of matter transformed during an electrolysis reaction by measuring the amount of electricity (in coulombs) consumed or produced.

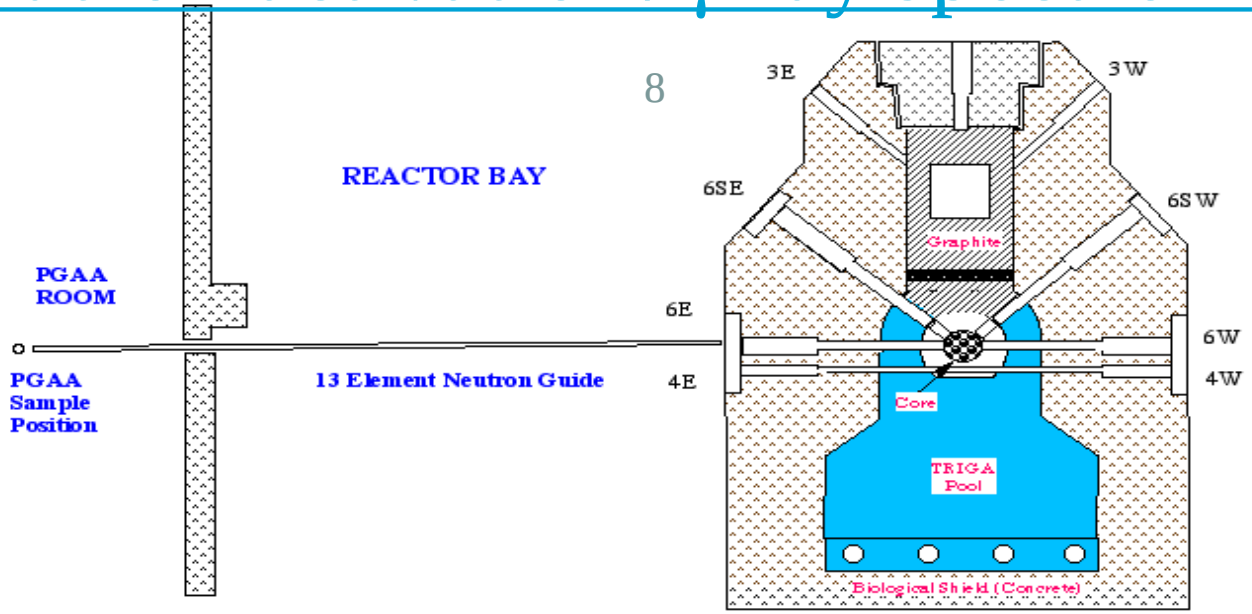
Drawbacks:

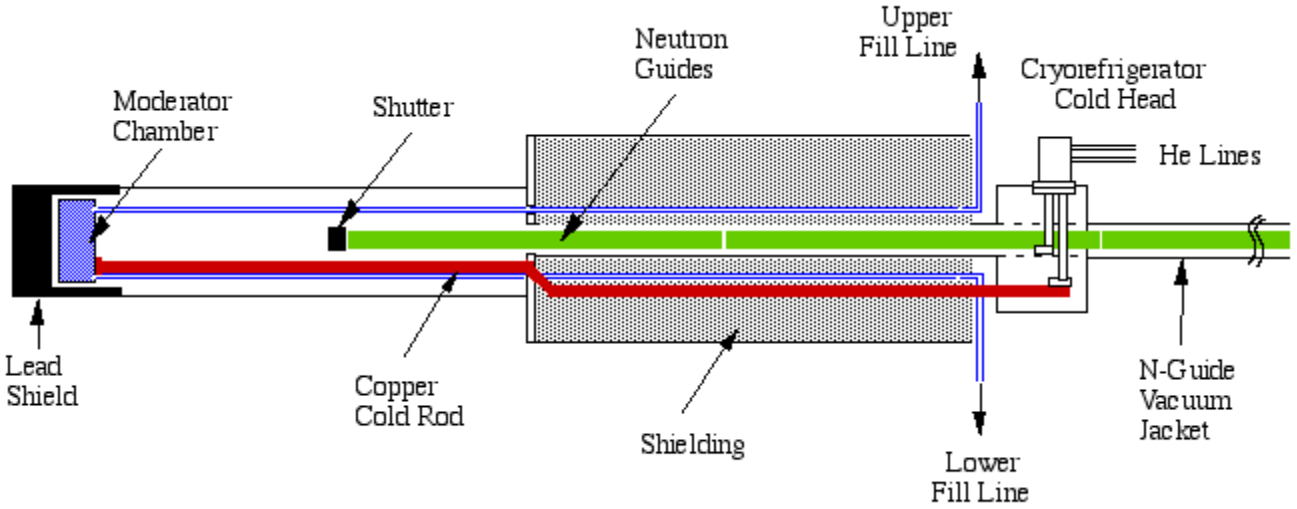
- Can not differentiate between Cl, Br and I.
- Calculated as the molar mass of organic halides, expressed as Cl.

From: Guanghui Hua; 2004 WQTC

Cornell Cold Neutron Source and PGAA Facility Layout

Neutron activation/γ ray spectrometry

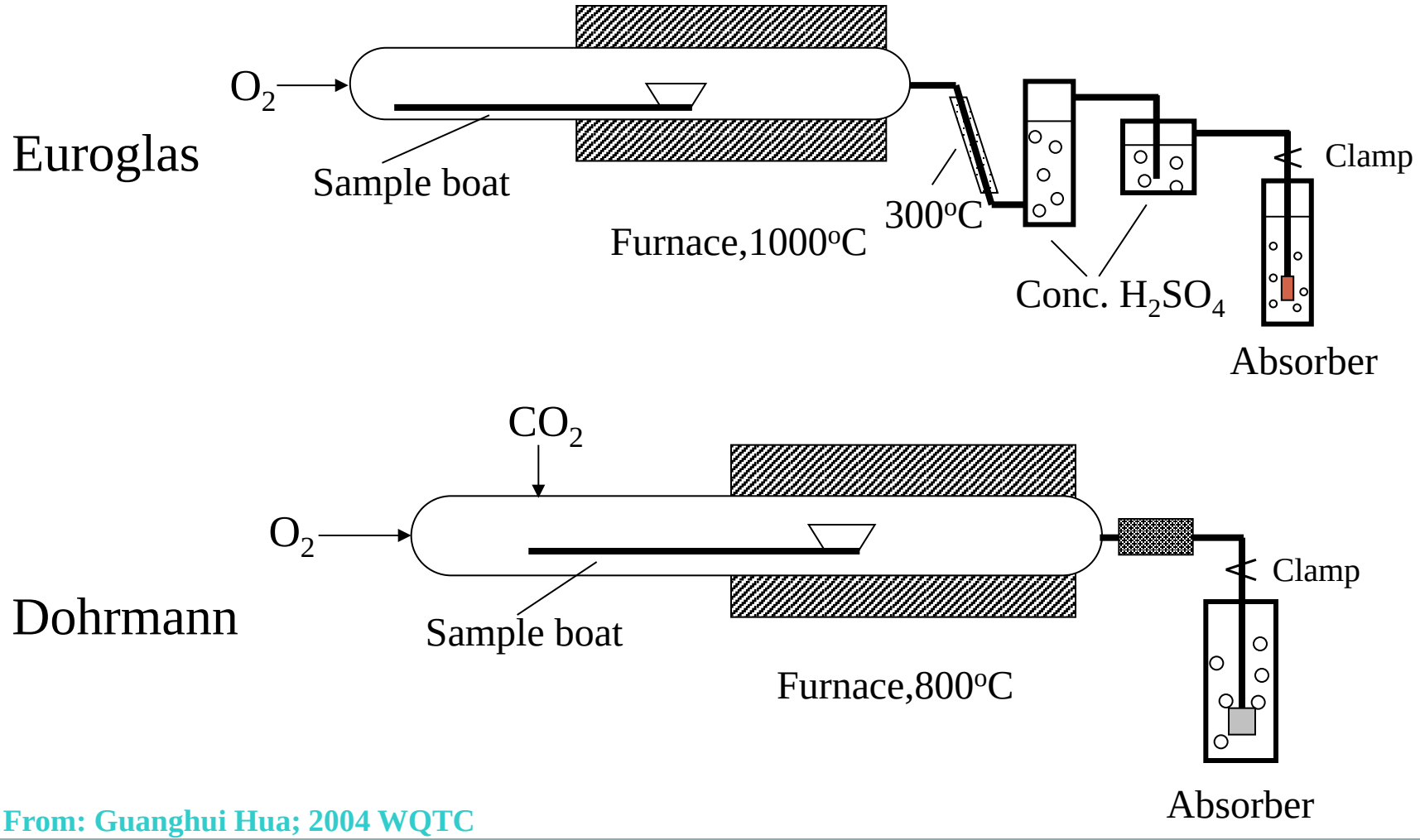




Hua and Reckhow, 2006a. Determination of TOCl, TOBr, and TOI in drinking water by pyrolysis and off-line ion chromatography. Anal. Bioanal. Chem.

- Comparing Dohrmann and Euroglas TOX instruments when coupled with IC
- Looking into effect of nitrate wash on recovery
- Comparing Dohrmann and Euroglas TOX instruments in coulometry mode

Schematic Diagrams of the Absorption Systems

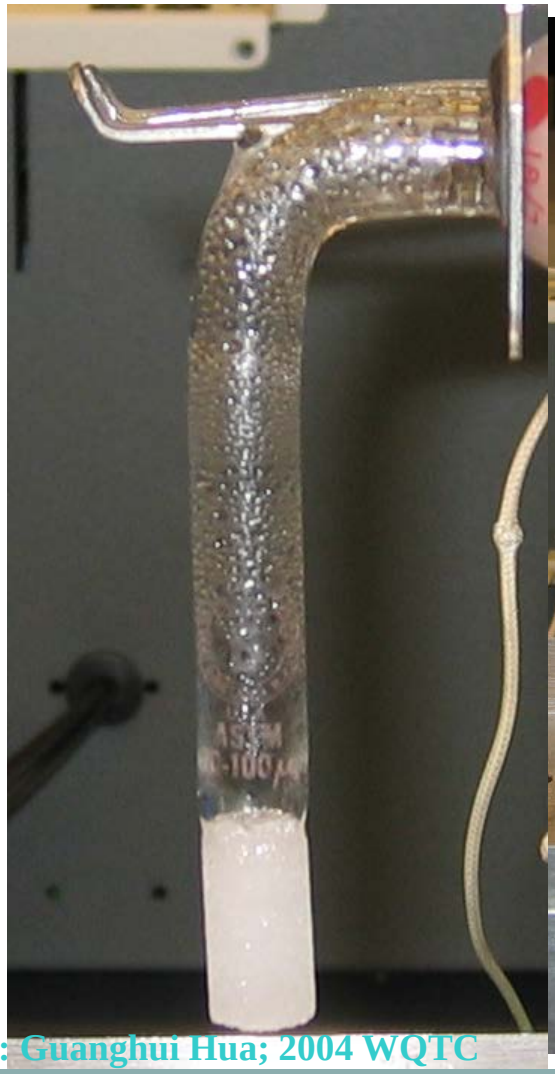


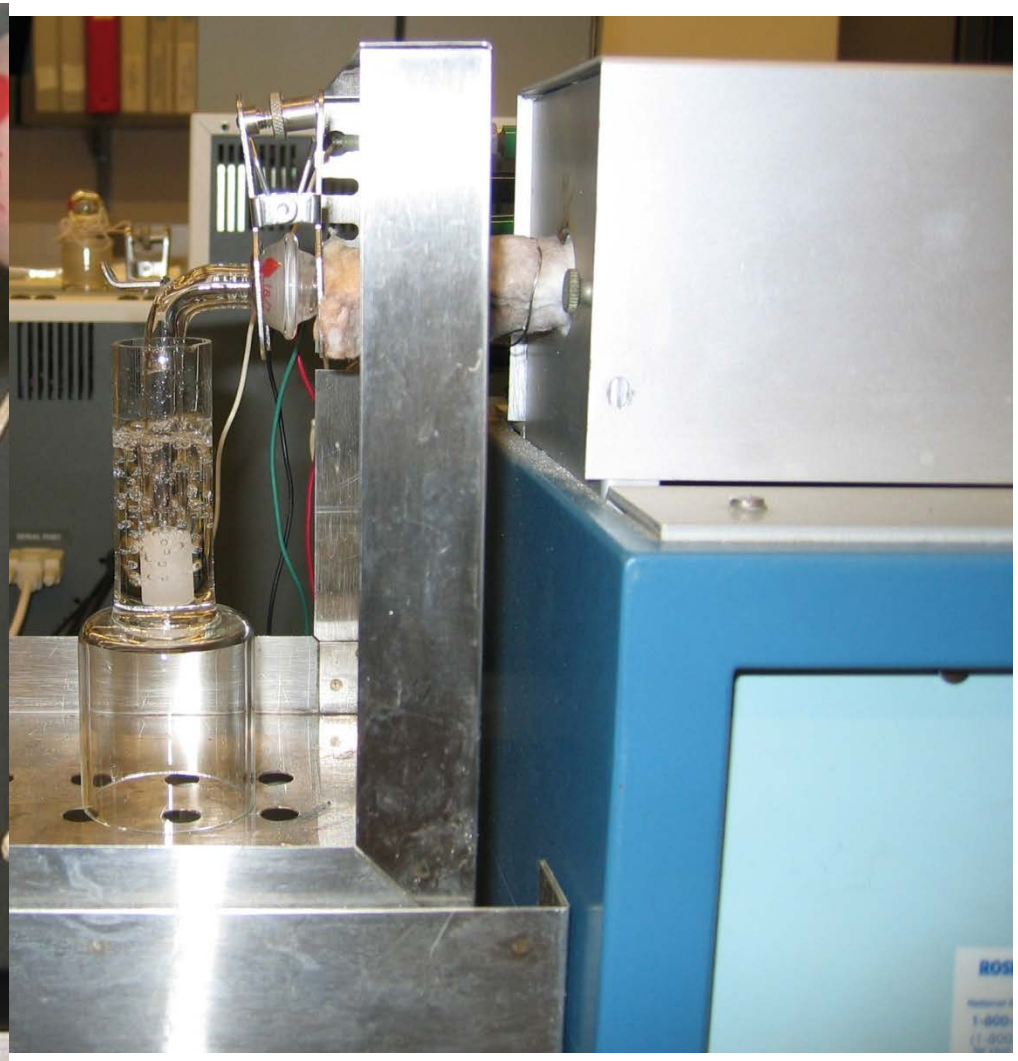
From: Guanghui Hua; 2004 WQTC

Schematic Diagrams of the Absorption Systems

	Dohrmann	Euroglas
Gas	O2 (carrier) CO2 (auxiliary)	O2 (carrier)
Drying prior to combustion	250 decC, 2 min CO2 gas only	1.5 min
Furnace temperature (deg C)	800 O2 only	1000
Exit temperature (degC)	-	300
Acid to remove the water vapour in the off-gas	-	H2SO4
Reaction gas containing hydrogen halides collected	15 mL then 5 mL rinse=20 mL	15 mL then 5 mL rinse=20 mL

Dohrmann Absorption System





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Step 1: adsorption, nitrate wash, combustion, off-gas collection

Step 2:

- Use of IC machine for chloride
  - Gives peaks at specific retention times

Selected GACs for the Tests

Characteristics	Carbon Identification		
	CPI-002 (standard)	***CPI-001***	***F-600***
Supplier	CPI	CPI	Calgon
Source	Coconut	Coconut	Coal
Particle Size	100-200 mesh (149-249 um opening)	100-200 mesh (149-249 um opening)	Granular
Background	0.4 μgCl/40mg	≤1.0 μgCl/40mg	Unknown

From: Guanghui Hua; 2004 WQTC

Nitrate wash after adsorption

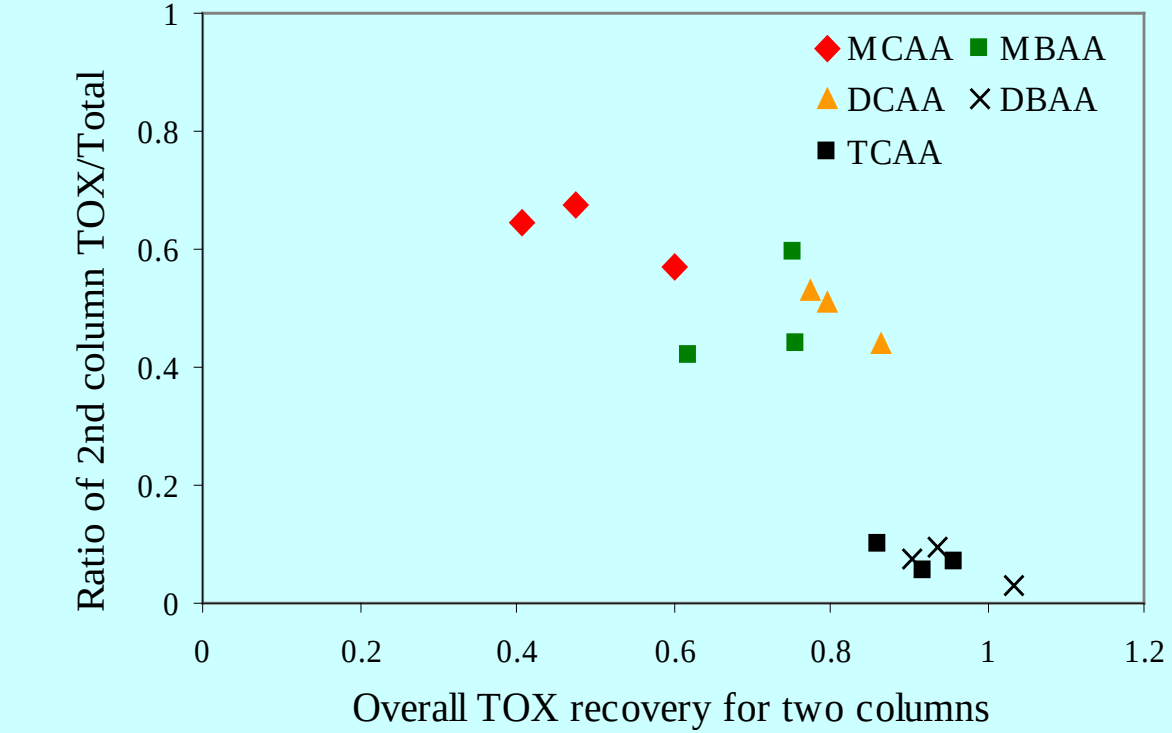
- Purpose: to remove interferences related to inorganic halides so that we don't get biased TOX results.

Method	Working solution concentration	Rinsing volume	Nitrate loading[a]
Euroglas	1,240 mg NO_3^-/l[a]	25 ml	31 mg NO_3^-/ sample
Dohrmann	5,000 mg NO_3^-/l	2 ml	10 mg NO_3^-/ sample
Standard method	5,000 mg NO_3^-/l	2–5 ml	10–25 mg NO_3^-/ sample

[a]Values were calculated based on information from operational manual and standard method

HAA recovery

- 30 mL nitrate wash
- 100, 300 and 500 ug/L
- Higher MW compounds, higher recovery
- Decreased ratio, higher recovery



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DCAA recovery with Euroglas

Standards	Washing volume	1st column (µg Cl/l)	2nd column (µg Cl/l)	Total (µg Cl/l)	Recovery
DCAA	30 ml	108	125	233	78%
300 µg	25 ml	141	112	253	85%
Cl/l	13 ml	208	77	285	95%

- DCAA 300 ugCl/L used
- Highest recovery with 13 mL of washing solution
- Higher washing volumes caused washing out of the Cl

Halide rejection by different carbon columns

Halide	Concentration (mg/L)	CPI-002	CPI-001	F-600
Cl^-	1000	500,000	500,000	200,000
Br^-	500	250,000	250,000	45,000
I^-	1	>100	>100	12
	5	30	>100	3

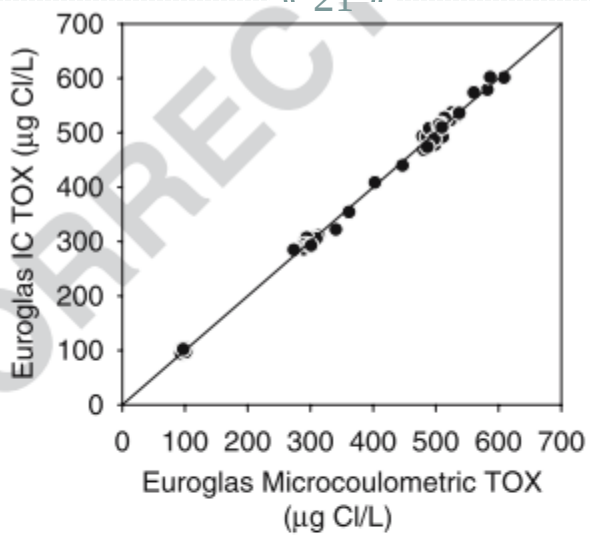
- Excessive inorganic I retention using F-600
- Rejection: Cl>Br>I

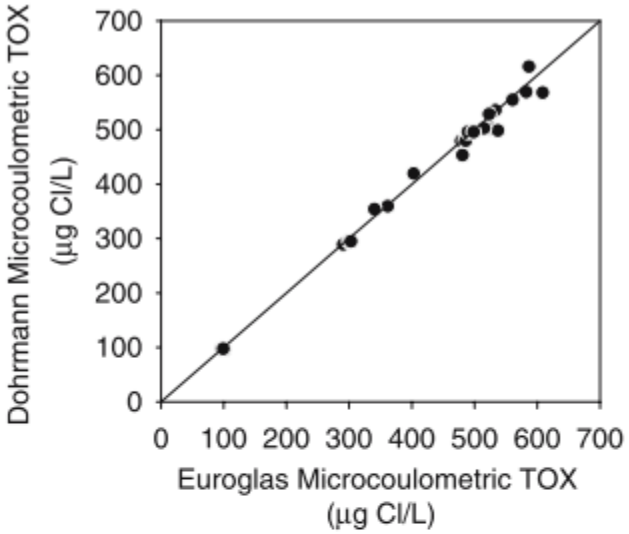
Euroglas analyzer/IC versus Euroglas/Microcoulometry

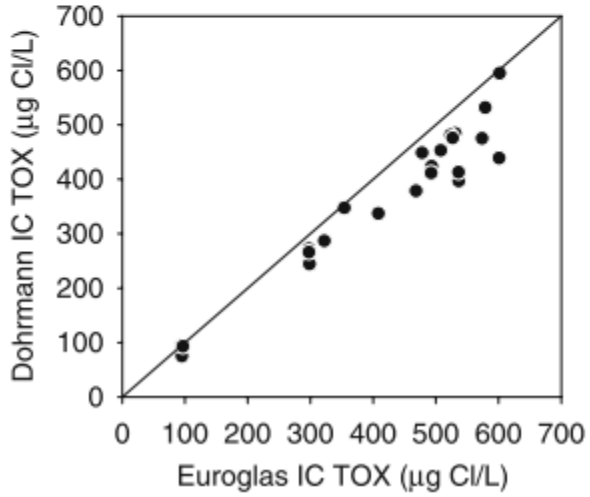
Compound	Recovery (%)	
	Microcoulometric	IC
Dibromochloromethane	103	104
Dichlorobromomethane	102	101
Bromoform	98	98
Triboromoacetic acid	98	98
Trichloroacetic acid	100	97
Dibromoacetic acid	102	101
Dichloroacetic acid	98	101
Bromochloroacetic acid	97	100
Monoiodoacetic acid	99	94
Monobromoacetic acid	96	95
Monochloroacetic acid	91	92

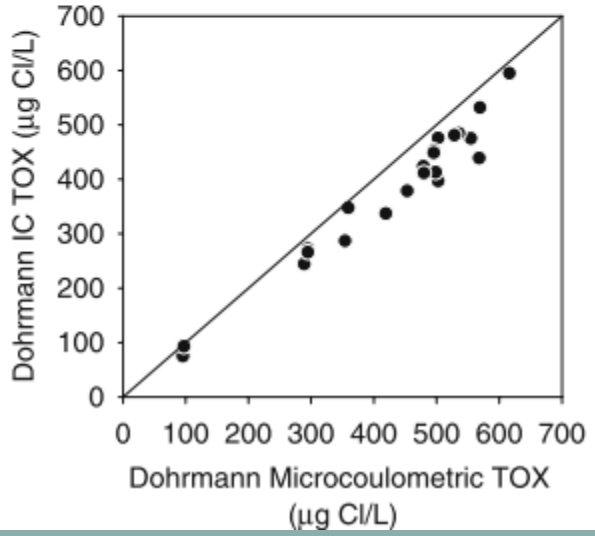
General comparisons

- All data from model compounds and real water samples
- No real difference for Euroglas IC versus Euroglas Microcoulometry or in Dohrmann and Euroglas Microcoulometry
- Better performance of Euroglas IC TOX verus Dohrmann IC TOX









Iodinated compounds in the literature

Compound Name	Goslan et al., 2009	Ye et al., 2012	Pan and Zhang, 2013	Hua et al., 2006	Richardson et al., 2008
Dichloroiodomethane	USEPA 551.1	-	-	Pentane extraction GC/ECD	USEPA 552.3
Bromochloroiodomethane	USEPA 551.1	-	-	Pentane extraction GC/ECD	USEPA 552.3
Iodoform	-	USEPA 551.1	-	Pentane extraction GC/ECD	-
Iodoacetic acid	-	USEPA 551.1	UPLC/ESI-MS/MS	-	USEPA 552.3
Triiodoactic acid	-	USEPA 551.1	-	-	-
3-iodo-4-hydroxybenzoic acid	-	-	UPLC/ESI-MS/MS	-	-
Diiodoacetic acid	-	-	UPLC/ESI-MS/MS	-	-
3,5-diiodo-4-hydroxybenzaldehyde	-	-	UPLC/ESI-MS/MS	-	-
2,6-diiodo-4-nitrophenol	-	-	UPLC/ESI-MS/MS	-	-
2,4,6-triiodophenol	-	-	UPLC/ESI-MS/MS	-	-
Chloroiodomethane	-	-	-	Pentane extraction GC/ECD	
Dibromoiodomethane	-	-	-	Pentane extraction GC/ECD	
Bromoiodomethane	-	-	-	Pentane extraction GC/ECD	
Dichlorodiiodomethane	-	-	-	-	USEPA 552.3
Bromoiodoacetic acid	-	-	-	-	USEPA 552.3

Method improvement

- Still use of adsorption, pyrolysis and collection of off-gas, with or without nitrate wash.
- Use of off-line inductively coupled plasma-mass spectrophotometer (ICP-MS) for Iodine and Bromine quantification in place of the IC.

ICP-MS

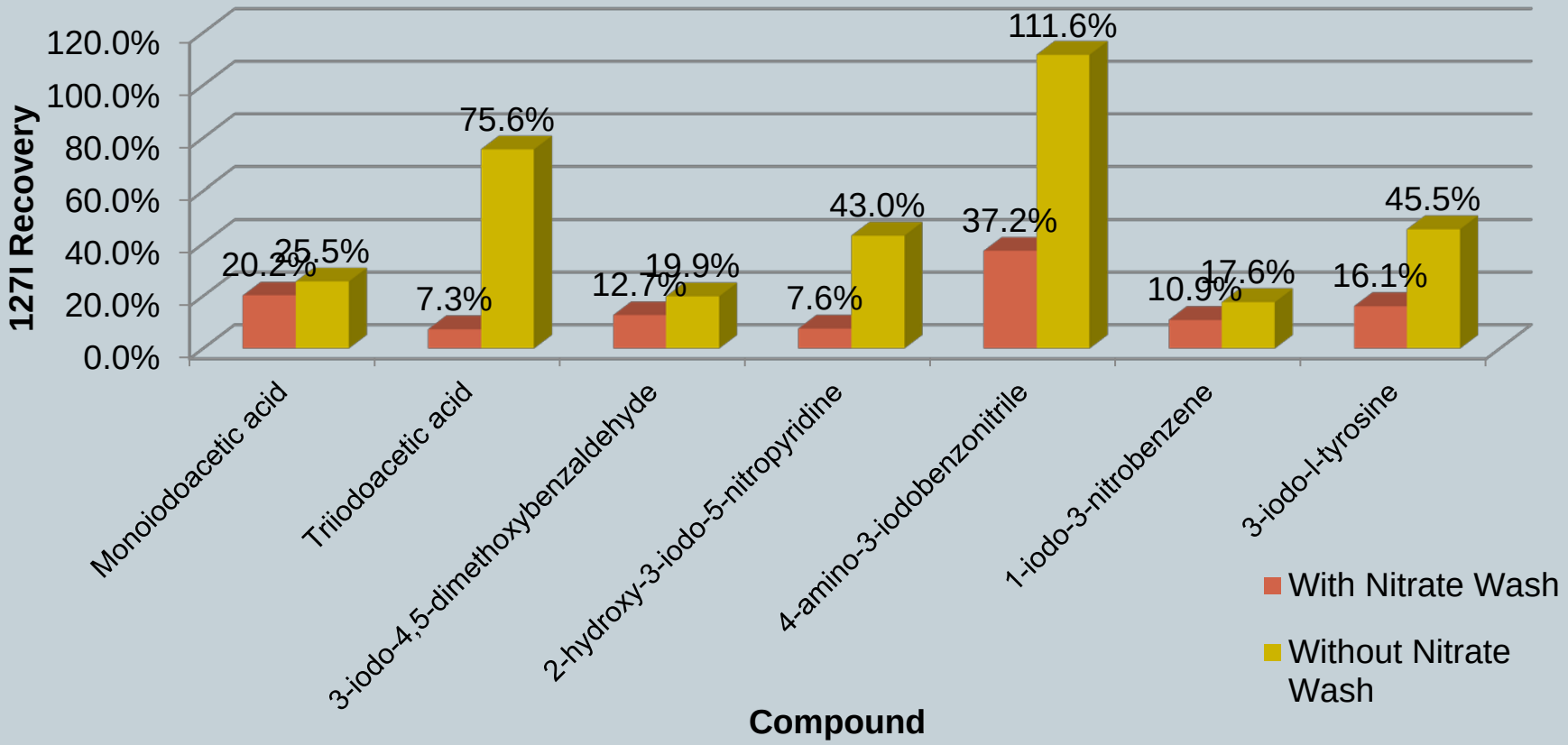
- Sensitive analytical machine for Bromine and Iodine detection
- Low method detection limits
- Carrier gas is Ar(g)
- Look for multiple analytes at the same time
- Fast (2-3 minutes per sample) and precise
- Famous for detecting metals and several non-metals at very low concentrations
- Sample is injected and ionized in the ICP part then the MS is used to separate and quantify the ions
- Drawbacks:
  - Ar interferes with some analytes
  - Uses a lot of gas
  - High maintenance in case it broke

ICP-MS Results

- Method detection limit (MDL)
  - The mean concentration and the standard deviation of this mean between seven replicates were calculated
  - The student t-value at 99% confidence interval and n-1 degrees of freedom (3.143 for seven replicates) was then multiplied by this standard deviation to yield a statistical estimate of the MDL.
- Limit of quantitation (LOQ)
  - The minimum concentration that can be reported with a specified degree of confidence
  - Calculated as the MDL multiplied by a factor of 3.182.

- Iodine: the MDL and LOQ were 0.19 and 0.61 µgI/L, respectively
- Bromine: the MDL and LOQ were 0.98 and 3.13 µgBr/L

Recovery of iodinated compounds with/without nitrate wash



Method development

- Initial pH of sample prior to adsorption
  - pH<2 for chloride and bromide
  - pH<1 for iodide
- Addition of H2O2 in absorber cell
  - If the absorber cell contained not only hydrogen halides (HX), but also halide gas (X_2) ➔ need to be converted to X^- in order to be detected by the ICP/MS
- Addition of tetramethyl ammonium hydroxide (TMAH) prior to ICP-MS
  - 0.1% for bromide
  - 2% for iodide
  - Reduces memory effect on glassware in ICP-MS
- Use of HNO3 (2%) versus TMAH (0.1%) wash as rinse solution in ICP-MS
  - TMAH for Br
  - HNO3 for HNO3

To find best combination

- Verify “optimal” combination of steps to achieve highest recovery of compounds (e.g., IAA or BAA)
  - ANOVA (full-factorial, duplicates)
    - Study of the effects of multiple factors
    - Useful for comparing response across multiple combinations of independent variables

- To next lecture