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CEE 697z
Organic Compounds in Water and Wastewater

Measuring NOM

Lecture #2

NOM: Modern Engineering Concerns

- **Coagulant demand**
- **Disinfectant demand**
- **Major DBP precursors**
- **Source of color**
- **Fouling of membranes and GAC adsorbers**
- **Coats clay particles and affects behavior**
- **Elevates solubility of hydrophobic pollutants and heavy metals**
- **Provides buffering in waters of low alkalinity**
- **Can affect mineral dissolution and precipitation**
- **Carbon source for biofilm growth in distribution systems**
- **Can affect corrosion**
- **Source of tastes and odors**

NOM in Source Waters: Some definitions

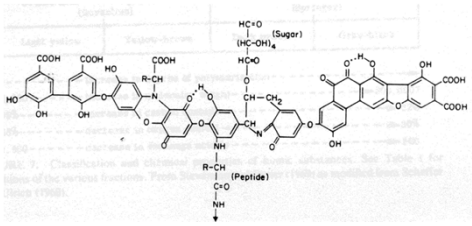
Groupings Based on Origin

- **autochthonous** material is formed within the water body
- **allochthonous** material can originate from either the soil or from upstream water bodies

- **aquagenic**, substances originating from any water body
- **pedogenic** for substances originating from soil

Types of NOM

- **Terrestrial/watershed sources; runoff; vegetative debris; humic substances**



- ***In situ* sources (algae); extracellular and intracellular AOM; macromolecules and cell fragments**

Microbial Origin

- **"Background" (drinking water) NOM + soluble microbial products (SMPs) from biological treatment**

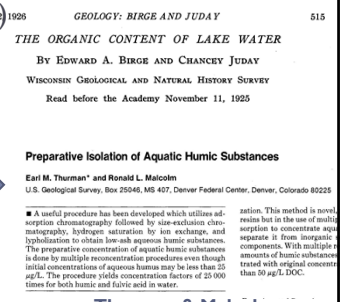
from: Krasner & Amy

II. NOM Structure (cont.)

- NOM from specific source types
  - allochthonous or pedogenic
    - lignins & non-humics
  - autochthonous or aquogenic
    - algal (AOM)
  - wastewater effluent organics (EfOM)
    - soluble metabolic products
  - Major biochemical consitutents
    - lignin, proteins, terpenoids, tannins, others

How to quantify NOM?

- Isolation with hydrophobic resins and solvents
  - Requires drying and weighing of the final residue
  - Some choices for solvents (LLE) and resins (SPE)
    - Ether
    - GAC & Chloroform extraction
    - XAD & alkali/organic extraction
- Elemental analysis for Carbon
  - Requires separation from carbonates and oth inorganic forms
  - Extensive bond breakage (mineralization) follc by conversion on the carbon atoms to a common form (usually CO_2 or CH_4)
  - Detection of the resulting carbon compound



1926 GEOLOGY: BIRGE AND JUDAY 515

THE ORGANIC CONTENT OF LAKE WATER

By Edward A. Birge and Chancey Juday

Wisconsin Geological and Natural History Survey

Read before the Academy November 11, 1925

Preparative Isolation of Aquatic Humic Substances

Earl M. Thurman* and Ronald L. Malcolm

U.S. Geological Survey, Box 25046, MS 407, Denver Federal Center, Denver, Colorado 80225

■ A useful procedure has been developed which utilizes adsorption chromatography followed by size-exclusion chromatography, hydrogen saturation by ion exchange, and lyopholization to obtain low-ash aqueous humic substances. The preparative concentration of aquatic humic substances is done by multiple reconcentration procedures even though initial concentrations of aqueous humus may be less than 25 µg/L. The procedure yields concentration factors of 25 000 times for both humic and fulvic acid in water.

zation. This method is novel resins but in the use of multi sorption to concentrate aqu separate it from inorganic components. With multiple amounts of humic substance trated with original concentr than 50 µg/L DOC.

Thurman & Malcolm (1981) ES&T 15(4)463-466

Carbon Chloroform Extract

Tentative Method for

Carbon Chloroform Extract (CCE) in Water

A method prepared by the Subcommittee on Organic Chemicals of AWWA Committee 8930 P—Standard Methods for the Examination of Water and Wastewater. The members of the subcommittee were: Francis M. Middleton (Chairman), Arnold E. Greenberg, and G. Fred Lee. In accordance with the procedure agreed upon by the three sponsoring associations—American Public Health Association, American Water Works Association, and Water Pollution Control Federation—this method has been submitted to the Joint Editorial Board for the Twelfth Edition of Standard Methods for the Examination of Water and Wastewater and has been adopted as a "Tentative" method by that body, effective Mar. 1, 1962.

ORGANIC contaminants—in natural substances, insecticides, herbicides, and other agricultural chemicals—enter water supplies from runoff. Domestic sewage and industrial wastes, depending on the degree of treatment, contribute contaminants in various amounts. As a result of accidental spills and leaks, industrial organic wastes also enter streams. Some of the contaminants, extremely persistent and only partially removed by treatment, reach the consumer in drinking water.

Contaminants, both natural and manmade, can conceivably have undesirable effects on health. Some of the materials interfere with water quality, and kill fish. A few micrograms per liter may be significant. Where concentrations of 200 μg/l have been found, the taste and odor of the water have nearly always been poor. The isolation and recovery of DDT, nitriles, orthonitrochlorobenzene, aromatic ethers, and many other synthetic chemicals suggest that a method for assessing these materials in water is desirable.

General Discussion

1.1. *Principle.* Activated carbon is a remarkable adsorption media for many types of organic materials. As used in a carbon adsorption unit (Fig. 1), it aids in the detection of low, but significant, quantities of organic contaminants in large volumes of water.

When a sufficient quantity of water has been run through the unit, the carbon containing the adsorbed sample is removed, dried, and extracted with chloroform. The removal of the chloroform by distillation leaves a weighable residue of contaminants. Other solvents, such as ethyl alcohol, will remove additional organics, but for monitoring and control purposes the chloroform extraction is considered adequate.

This method does not determine the total organic content of water. Although it is very effective, the carbon does not adsorb all the organics, and the solvent does not recover all of the materials adsorbed. Synthetic detergents are not measured by this procedure.

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- Published Feb 1962
- Steps
  - Adsorption to GAC
  - Dry
  - Extract GAC with chloroform
  - Evaporate chloroform
  - Weigh residue
- Problems
  - Requires 10,000 liters of sample
  - Subject to many errors
  - May only recover a few percent of NOM
    - Typical clean waters are 25-50 μg/L CCE

JAWWA 50(2)223-227

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 (*9*), or the quantity of carbon dioxide evolved may be determined by manometric (*18*), 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.

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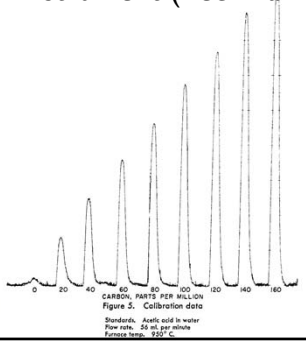


Figure 5. Calibration data

Standards. Acetic acid in water
Flow rate. 56 ml. per minute
Furnace temp. 930° C.

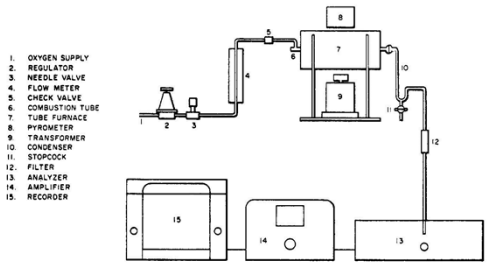


Figure 1. Schematic diagram of combustion apparatus

Dave Reckhow - Organics in Water

Great Recovery

- TOC

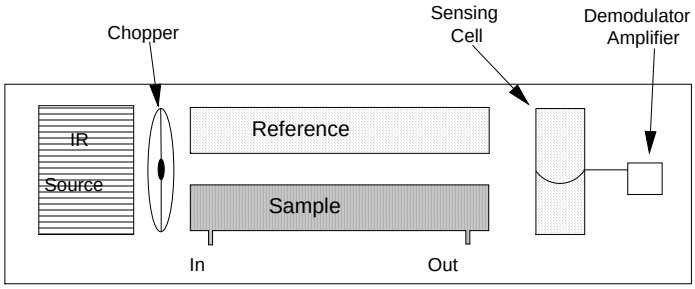
Table I. Analyses of Standard Solutions

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.

CO_2 Analyzer

Arnold Beckma



- 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

Dave Reckhow - Organics In W & WW

Filter

NOM Quantification: TOC & DOC

Principle: oxidize all organic matter to Carbon dioxide and water. Then measure the amount of carbon dioxide produced

$$C_aH_bN_cO_d + (a + \frac{b}{4} - \frac{d}{2})O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O + \frac{c}{2}N_2$$

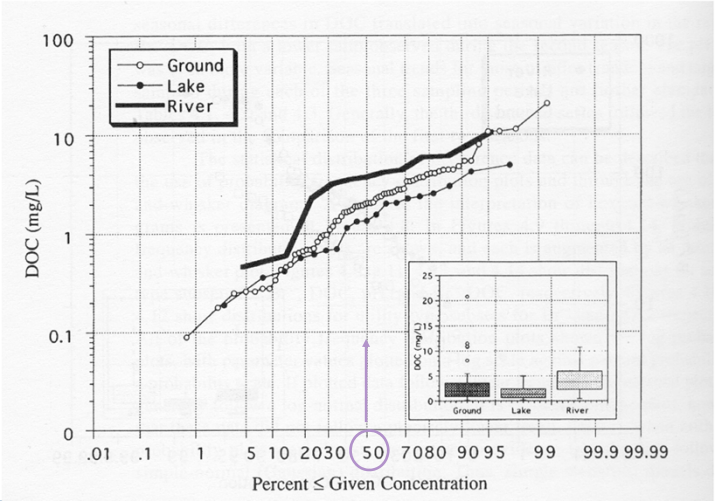
Oxidation

- High Temperature Pyrolysis
- UV Irradiation
- Heated Persulfate
- UV/Persulfate

Current state of NOM quantification

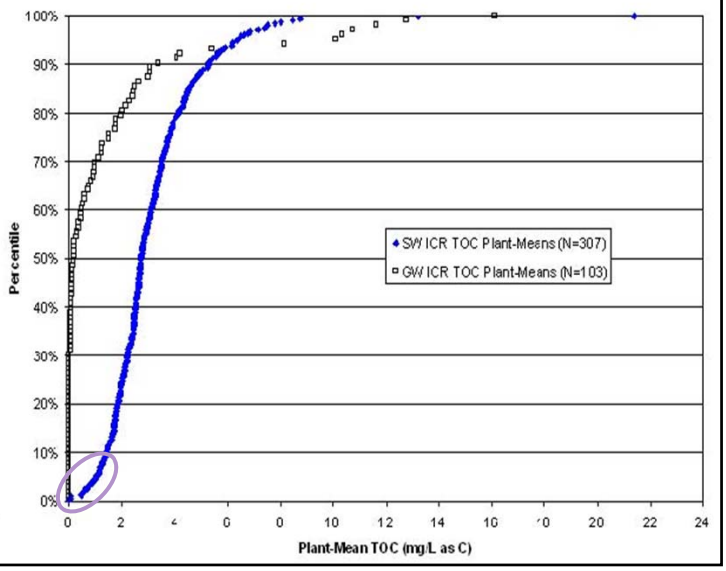
- The total (or dissolved) organic carbon method is the standard
  - Most use combustion with IR detection
- Resin isolation is still used but mostly for:
  - Affinity-based characterization
    - XAD-8 & XAD-4 methods
      - Hydrophobic/mesophilic/hydrophilic
  - Preparative-scale isolation of major fractions for subsequent analysis
    - XAD resins, sometimes with ion exchange resins

DOC Frequency Distribution: North American Drinking Water Sources



from: Krasner & Amy

- Source: ICR AUX1 database (USEPA 2000)



- To next lecture