Evolution of Drinking Water Analysis During EPA's First 50 Years

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Pre-EPA

- Prior to late 1800's, drinking water treatment focused on taste/odor, not illness
- Early 1900's recognition of link between waterborne illnesses (e.g., cholera and typhoid fever) and contaminated water supplies
- Treatment initiated at state/local levels
    - Water supply pollution control
    - Filtration/disinfection

Pre-EPA: U.S. Public Health Service

- First federal drinking water standards adopted in 1914
  - Only applied to interstate carriers
  - Bacteriological quality standards
- 1925 standards addressed some physical and chemical parameters (Pb, Cu, TDS)
- By 1960's greater interest in coordination at federal level
  - Industrial production/agricultural activities and more contamination of source waters

U.S. EPA Established

- 1970
- Independent agency
  - Federal research
  - Monitoring
  - Setting standards
  - Enforcement
- Public Health Service drinking water program merged into EPA

Drinking Water Quality Survey

- Conducted in the early 1970s
  - contamination on a national scale, particularly with synthetic organic chemicals.
- Prompted Congress to enact the Safe Drinking Water Act (SDWA)

Safe Drinking Water Act

- **July 10, 1974: Safe Drinking Water Act**
  - Purpose: Assure that water supply systems serving the public meet minimum national standards for protection of public health
    - Authorizes EPA to set federal enforceable health standards for contaminants that apply to all public water systems
      - PWS defined as serving at least 25 people or with at least 15 service connections at least 60 days/year
    - Establishes a joint Federal-State system for assuring compliance (primacy)
  - Amended in 1977, 1979, 1980, 1986, 1996 (reauthorized and amended), 2018, 2019

Safe Drinking Water Act

- EPA to regulate drinking water by:
  - Establishing National Interim Primary Drinking Water Regulations (NIDWRs)
    - RMCLs - **Recommended Maximum Contaminant Levels**
    - MCLs - **Maximum Contaminant Levels**
    - Monitoring requirements
    - Analytical requirements
    - Treatment techniques
  - Revise the interim standards as necessary

National Interim Primary DW Regulations (12/24/75, 7/9/76)

- 22 regulated contaminants
- At least one test method promulgated with each regulation to confirm compliance with MCL
- Analytical methods based on existing technical capability
  - 13th edition of Standard Methods

1986 SDWA Amendments

- Established regulations for 83 specific contaminants
  - Promulgated methods/treatment techniques with regs.
- ***25 additional contaminants to be regulated every 3 years***
- Required disinfection for all public water supplies
  - Filtration for most surface water systems
- Developed programs to protect ground water
- Established monitoring requirements for unregulated contaminants (implemented by states)
- Banned lead in distribution systems for new installations
- Specified a "best available technology" for each contaminant

1996 SDWA Amendments

- Improved on the 1986 SDWA Amendments regulatory framework
  - Contaminant regulation priorities based on
    - Adverse health effects
    - Occurrence
    - Estimated reduction of health risk
    - Cost benefit analysis

1996 SDWA Amendments

- Strengthen protection from microbial contaminants and disinfection byproducts
- Established Contaminant Candidate List (CCL) and Unregulated Contaminant Monitoring Rule (UCMR) to assess occurrence for potential regulation
  - Five-year cycle and need for test methods
  - Engagement with suppliers of certified reference material to ensure availability of analytical reference standards for emerging contaminants
  - Critical collaboration with instrument vendors and laboratories on method development and validation.

Evolution of Regulations and Methods

- To support regulatory monitoring, an analytical method is EPA approved for use, if an effective technique is available
  - Limited to best available science at the time
  - With the exception of a few parameters (e.g., temperature, pH, turbidity), drinking water compliance samples must be analyzed in a certified lab
    - Incorporate consistent quality control in methods (still an issue with older methods)
  - Technological advancements have allowed measurement at lower levels with greater accuracy and precision

NPDWR – VOCs (1987)

- Promulgated methods 502.1, 503.1, 524.1, 524.2
  - Purge-and-trap with GC/ECD, GC/PID or GC/MS
  - Manually load purge-and-trap concentrator
  - Typical processing: 32K ROM, 2K RAM
  - Tenax/silica gel sorbent trap
  - Prescriptive parameters

Reference: Teledyne Tekmar

NPDWR – VOCs

- New methods 524.3, 524.4
  - Purge-and-trap with GC/MS
  - Fully automated operation
  - Flexible parameters for optimized performance
  - Improved moisture control/sorbent traps

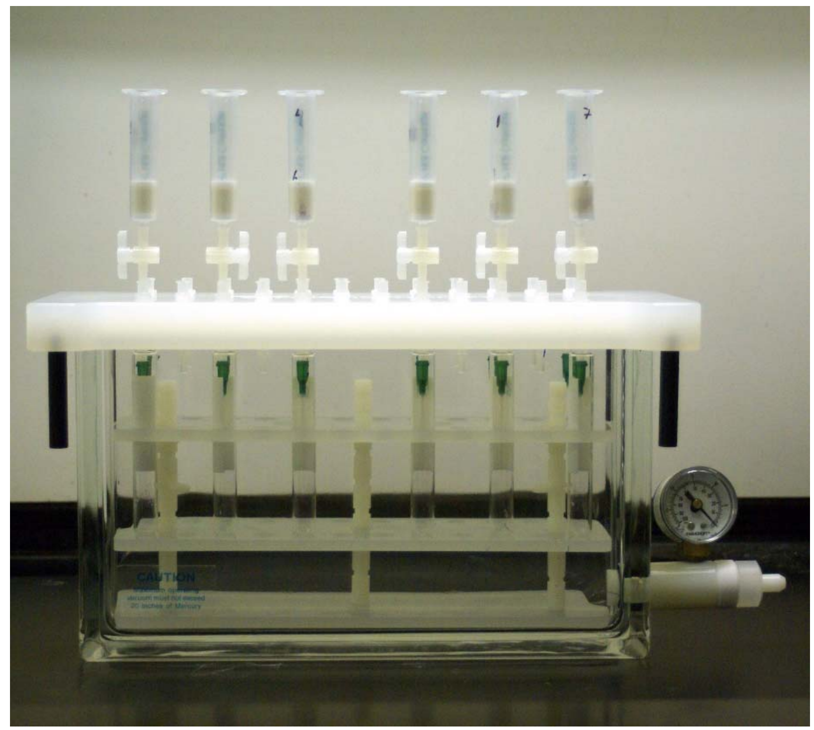
Reference: Teledyne Tekmar

Separation/Extraction

- SOCs/Pesticides
  - Liquid/liquid extraction (methylene chloride)
  - Kaderna-Danish concentration

Separation/Extraction

- SOCs/Pesticides
  - Newer methods: Solid Phase Extraction (SPE)
  - Sorbents allow more selective extraction
  - Require less organic solvent



Analysis – Gas Chromatography

- Early GCs
  - Manual injection
  - Packed columns
  - Non-specific detectors (TCD, FID)

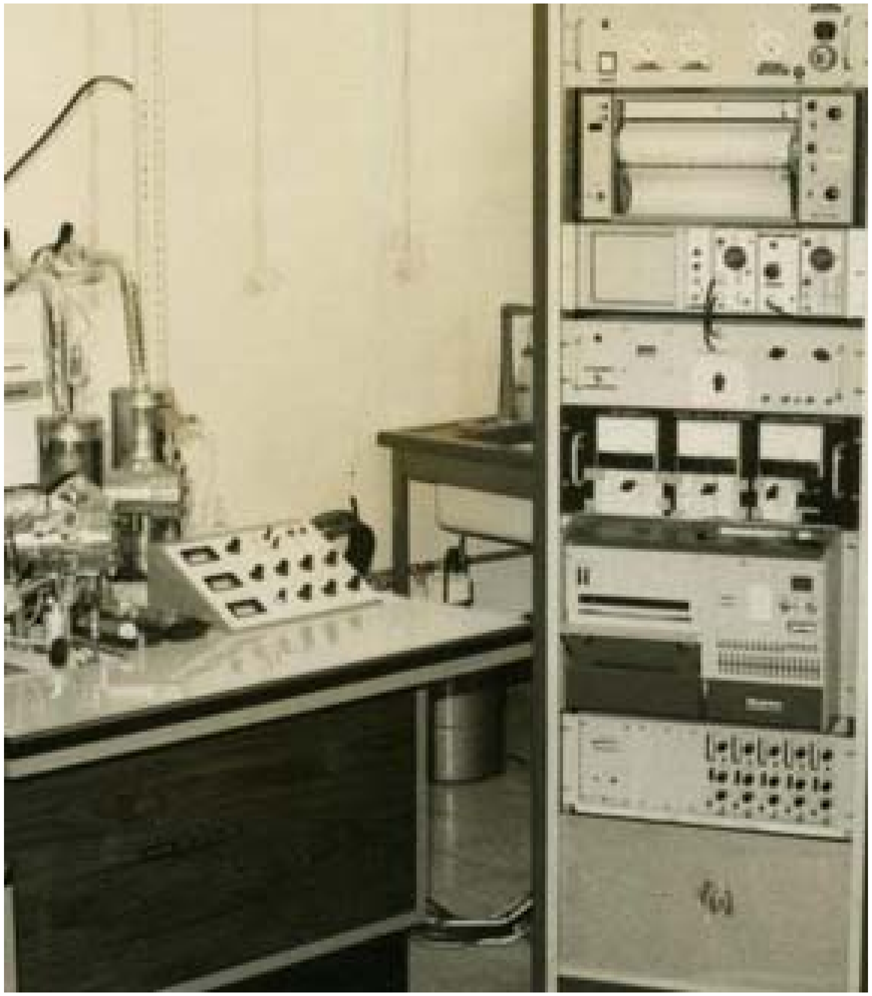
Analysis – Gas Chromatography

- Organics
  - Earliest methods: packed columns, non-specific detectors (e.g. ECD, NPD)
  - Mid-1980’s introduced fused silica capillary columns
  - Mid-1990’s removed packed column methods

Gas Chromatography-Mass Spectrometry

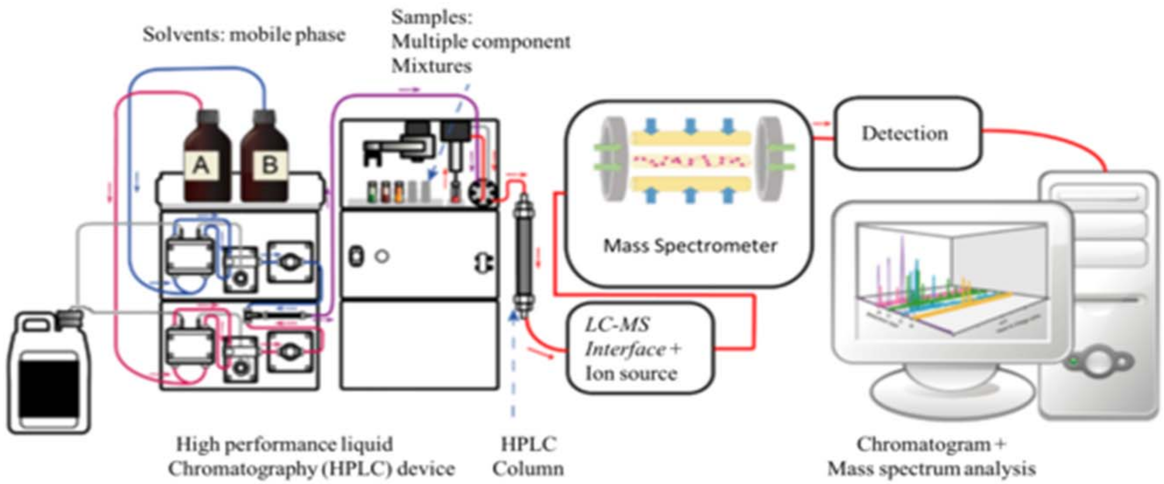
Mass spectrometry offers analytical specificity not attainable with other GC detectors.

Early MS detector systems were large, expensive, required frequent tuning, and more suited to research



Liquid Chromatography-Mass Spectrometry

- GC/MS
  - Volatile contaminants
  - Cannot be used for thermally labile compounds
- MS operates under high vacuum
  - Must be able to mitigate water load when coupled to HPLC



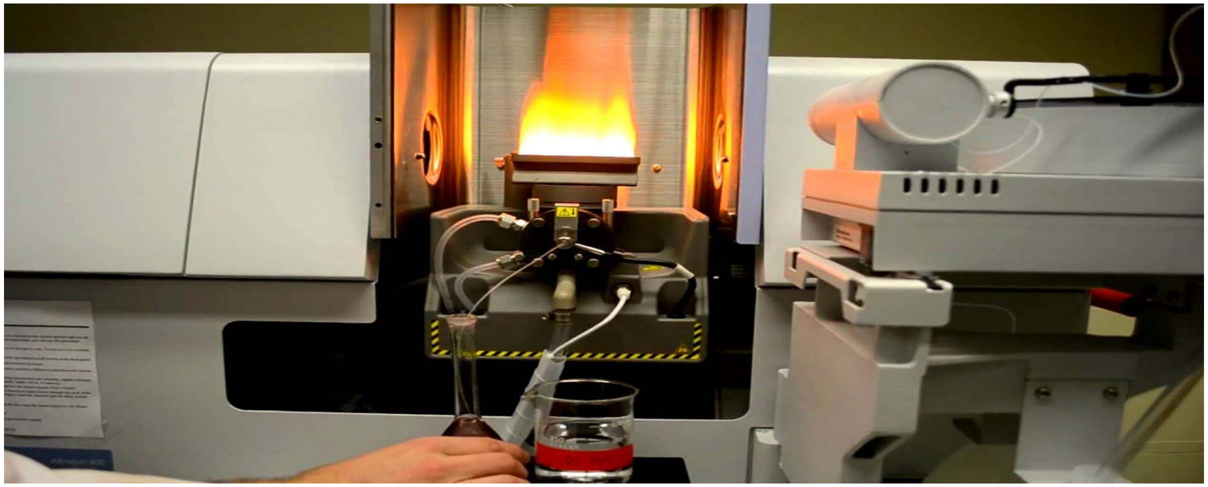
HPLC-MS/MS

- Unregulated Contaminant Monitoring Rule (UCMR)
  - UCMR 2
    - Acetanilide degradates (EPA Method 535)
  - UCMR 3
    - Perfluorinated Compounds (EPA Method 537)
    - Hormones (EPA Method 539)
  - UCMR 4
    - Cyanotoxins (EPA Methods 544 and 545)

Reference: Mercyhurst University

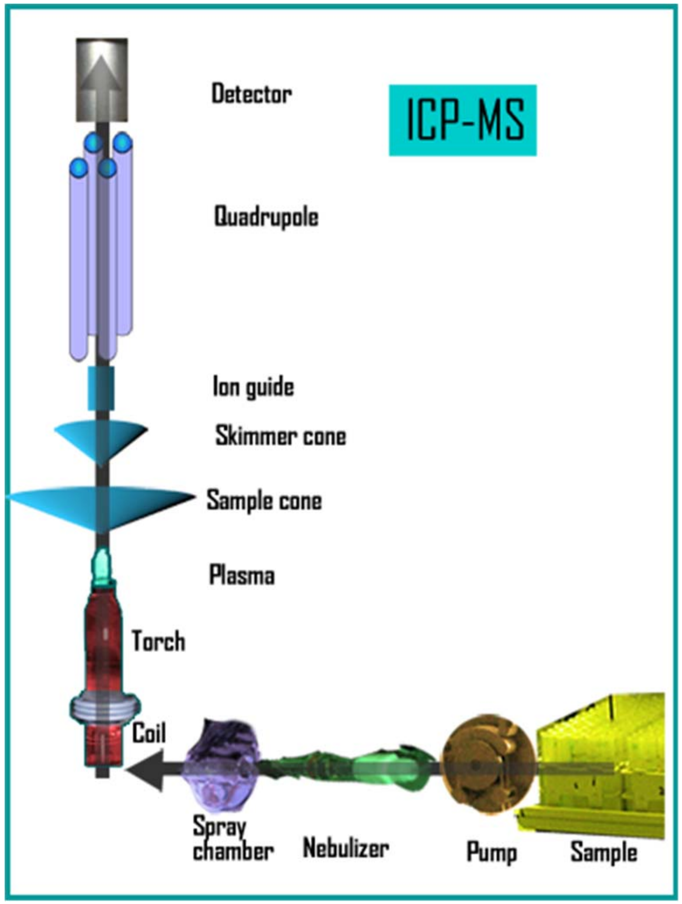
Metals Analysis

- Atomic Absorption
  - Single element determination
  - Inexpensive
  - Burner nebulizers are relatively inefficient
    - Sensitivity limited: ppm to ppb levels



Metals Analysis

- Inductively Coupled Plasma (ICP)-Mass Spectrometry
  - Multi-element determination
  - Expensive
  - Faster; wider analytical working range
    - Sensitivity: ppb to ppt levels



Turbidity

- Measure of clarity of a liquid
  - Aesthetic quality
  - Pathogens (e.g. Crypto oocysts)
- EPA Method 180.1
  - White light (incandescent) source

Turbidity

- New sources
  - Lasers
  - LEDs
- Online, benchtop and field portable

Reference: Hach Company

On-Line Monitoring/Sensors

Approved for water quality parameters (disinfectant residuals)

- EPA Method 334.0: Online free/total chlorine analyzers calibration and quality control requirements
- ChloroSense: Amperometric sensors for free/total chlorine
- ChlordioX Plus: Amperometric sensors for chlorine dioxide
- Water quality parameters do not have to be measured in certified labs

Compliance parameters?

- Drinking water regulations require analysis in certified labs (40 CFR 141.28)
- How could water system incorporate a TTHM sensor for compliance?

Quality Assurance/Quality Control Status

- Working to specify QC elements and criteria as part of methods
- Establish consistent Data Quality Objectives across methods
- Identifying how methods compare and contrast across multiple matrices: drinking water and wastewater
- Evaluating how QC impacts laboratory certification decisions

Quality Assurance/Quality Control

Example:

Revising 900-series Radiochemistry Methods

- Original methods have limited QC

EPA Method 900.0, Rev. 1.0: *Gross Alpha and Gross Beta*

Published Feb. 2018; approved for DW compliance October 12, 2018 (83 FR 51636)

- Updated for newer instruments with simultaneous alpha/beta counting capability and addresses spillover (crosstalk)
- Details efficiency calibration
- Incorporates QC specifications and criteria

Quality Assurance/Quality Control

Example:

EPA Methods 150.1 and 150.2 for pH

- Older pH technology

EPA Method 150.3: Determination of pH in Drinking Water

Published February 2017; approved for DW compliance July 27, 2017(82 FR 34861)

- Updated for newer pH technologies (both at bench level and continuous online monitoring)
- Calibration frequency and verification
- Incorporates QC specifications and criteria

Future

How do we continue to evolve?

Alternate Test Procedures (ATP) Program

- Evaluate new technologies

Drinking Water Expedited Methods Approval Process

- SDWA provision: After promulgation of “reference method,” “equally effective” alternate methods can be approved in *Federal Register* notice
- Method approval in as little as one year following completion of method evaluation (as opposed to formal notice-and-comment rulemaking)
- Alternate methods found in Appendix A to Subpart C of Part 141

Revisit status of ‘old’ methods

Summary

- Drinking water compliance methods have evolved as a function of regulatory requirements and technological advancements
  - Technology advancements will provide opportunities to continuously improve monitoring programs.
- Increasing expectation for QC incorporation within methods to enhance data reliability and comparability