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WHITEPAPER

Analytical and Measuring Instruments

Introduction to Environmental Testing in the USA

■ What is Environmental Chemistry?

Environmental laboratories practice "applied analytical chemistry" by analyzing samples using a list of potential contaminants to determine how much, if any, of the contaminant is present. These contaminants, the methods used to analyze for them, and the maximum amount of contaminant allowed in the sample is defined by regulation.

Table 1 is a timeline that highlights major events in history in regards to the environment and correlates them with the invention of laboratory instruments. Only with the invention of instrumentation that allowed the measurement of pollutants was it possible to know that many of the pollutants were present. As instrumentation became more sensitive, it became possible to detect trace contaminants in soil, air, and water. The discovery of these pollutants in the environment led Congress to establish the Environmental Protection Agency (EPA).

After the creation of the EPA, Congress began to pass legislation to regulate and limit pollution. First was the Clean Air Act, followed by the Clean Water Act, Safe Drinking Water Act, and the Resource Conservation and Recovery Act. These four major pieces of legislation and their enforcement by the EPA were responsible for a boom in the environmental laboratory testing industry.

■ Discussion

In the first few years of the environmental laboratory industry, there were multiple methods of analysis and virtually no set guidelines on data acquisition criteria, record keeping, and quality control procedures. Data produced at different laboratories was not very comparable. This led the EPA to establish prescription style methodology and force their use by laboratories that were generating data for regulatory compliance purposes. Many of these first test methods are still in use today and are listed in the applicable sections of the Federal Code.

The Federal Regulations that require water testing are:

1. Safe Drinking Water Act (SDWA) – regulates public drinking water supplies. Approved Methods are in 40 CFR Part 141.
2. Clean Water Act (CWA) – regulates pollutants from industrial discharge. Requires anyone discharging significant amounts of wastewater into US waterways to obtain a NPDES permit. Approved methods are in 40 CFR Part 136.
3. Resource Conservation and Recovery Act (RCRA) – regulates the generation and disposal of solid waste. Approved methods are consolidated in the EPA SW 846.

Each regulatory act also requires that methods used for compliance with the act be approved for that purpose. In other words, to analyze a wastewater for a pollutant the laboratory must use a 40 CFR Part 136 approved method. The laboratory cannot use another method, even if it is an official method, if it is not listed as approved for wastewater testing.

The Clean Water Act was established in response to public outcry at visible pollution caused by industrial discharges, sewage treatment plant effluents, and oil spills. The initial parameters tested under the Clean Water Act were what we now term "Conventional Pollutants".

Conventional Pollutants are parameters such as Oil & Grease, pH, BOD, TSS, ammonia nitrogen, phosphate, and nitrate nitrogen. These parameters were chosen because they were relatively easy to measure, and are adequate indicators of the level of pollution. They were also chosen because they measure the types of pollution that had occurred in the various "environmental incidents" that led to the establishment of the EPA. Oil & Grease could accurately measure oil in water and soil from oil spills; pH could measure acid rain, and mine water runoff, BOD & TSS could measure the sewage

effluents that had caused fish kills; and ammonia, nitrate, and phosphate were the nutrients responsible for algal blooms in coastal waters.

■ EPA-approved methods, Environmental Matrices, and Corresponding Shimadzu Instruments

Safe Drinking Water Act (SDWA)

The Safe Drinking Water Act (SDWA) ensures the quality of Americans' drinking water. Under SDWA, the EPA sets standards for drinking water quality and oversees the states, localities, and water suppliers who implement those standards.
The United States Environmental Protection Agency (US EPA) is authorized under the SDWA to set national health-based standards for drinking water to protect against both naturally-occurring and man-made contaminants. The US EPA, states, and water systems then work together to make sure that these standards are met.

Water systems must use EPA-approved analytical methods when analyzing samples in order to meet federal monitoring requirements or to demonstrate compliance with drinking water regulations. Approved methods are listed in the Code of Federal Regulations Title 40 Parts 141 - 143. Approved methods are developed by the EPA, other government agencies, universities, consensus methods organizations, water laboratories, and instrument manufacturers.

Laboratories must be certified by the EPA or the State to analyze drinking water samples for compliance monitoring.

Inorganics Lab - EPA Approved Methods for the Analysis of Multiple Metals in Drinking Water

Method	Instrumental Technique	Shimadzu Model
EPA 200.5	ICP Axial	ICPE-9800
EPA 200.7	ICP Radial	ICPE-9800
EPA 200.8	ICPMS	NA
EPA 200.9	GFAAS	AA-7000G

Wet Chemistry Lab - EPA approved Methods for Anions in Drinking Water

Anions	Method	Instrumental Technique	Shimadzu Model
Cyanide	Standard Methods 4500 CN	Manual Spectrophotometry	UV-1280
Nitrate	Standard Methods 4500 NO3	Manual Spectrophotometry	UV-1280
Nitrite	Standard Methods 4500 NO2	Manual Spectrophotometry	UV-1280
Phosphate	Standard Methods 4500 P	Manual Spectrophotometry	UV-1280
Sulfate	Standard Methods 4500 SO4	Manual Spectrophotometry	UV-1280

Wet Chemistry Lab - Disinfection by Products Monitoring

Contaminant of Concern	Method	Shimadzu Instrument
Total Organic Carbon (TOC)	Standard Methods 5310B	TOC-L

Volatile Organics Lab - EPA Approved Methods for Organics in Drinking Water

Contaminant Group	Method	Instrumental Technique	Shimadzu Model
Volatiles	EPA 524.2	Purge & Trap GCMS (original method – no flexibility allowed)	GCMS-QP2010SE with EST
	EPA 524.3	Purge & Trap GCMS (flexibility allowed, SIM allowed, requires sample cooling)	GCMS-QP2010SE with EST
	EPA 524.4	Purge & Trap GCMS (Nitrogen as purge gas, flexibility allowed, SIM allowed, requires sample cooling)	GCMS-QP2010SE with EST
1,4-Dioxane	EPA 522	Purge & Trap GCMS (Nitrogen as purge gas, flexibility allowed, SIM allowed, requires sample cooling)	GCMS-QP2010SE with EST

Semi-Volatile Organics Lab – EPA Approved Methods (and some not yet) for Organics in Drinking Water

Contaminant Group	Method	Instrumental Technique	Shimadzu Model
Semi volatiles	EPA 525.2	Liquid-Solid Extraction Direct Injection GCMS	GCMS-QP2010SE or GCMS-QP2010 Ultra
	EPA 525.3	SPE Direct Injection GCMS (SIM and some flexibility allowed)	GCMS-QP2010SE or GCMS-QP2010 Ultra
Organochlorine Pesticides and PCBs	EPA 508	Liquid-Liquid Extraction Direct Injection GC with ECD	GC-2010 Plus
	EPA 508A	Liquid-Liquid Extraction Direct Injection GC with ECD	GC-2010 Plus
	EPA 508.1	Liquid-Solid Extraction Direct Injection GC with ECD	GC-2010 Plus
Organophosphorus and organonitrogen pesticides	EPA 507	Liquid-Liquid Extraction Direct Injection GC with NPD	GC-2010 Plus
Triazine pesticides	EPA 536	HPLCMSMS	LCMS-8050
	EPA 523	Liquid-Solid Extraction GCMS	GCMS-QP2010SE or Ultra
Carbamate Pesticides	EPA 531.1	Direct Injection HPLC with Post Column Derivatization	Carbamate Pesticide Analysis System
	EPA 531.2	Direct Injection HPLC with Post Column Derivatization	Carbamate Pesticide Analysis System
Chlorinated Acids (Herbicides)	EPA 515.4	Liquid-Liquid Extraction, Derivatization and GC with ECD	GC-2010 Plus
Haloacetic Acids and Dalapon	EPA 552.3	Liquid-Liquid Extraction, Derivatization and GC with ECD	GC-2010 Plus
	EPA 557	Ion Chromatography ESI MSMS	LCMS-8050
Glyphosate	EPA 547	Direct Injection HPLC, Post Column Derivatization, and Fluorescence Detection	Prominence HPLC
Hormones	EPA 539	SPE HPLCMSMS	LCMS-8050
PFC's	EPA 537	SPE HPLCMSMS	LCMS-8050

Clean Water Act (CWA)

The Clean Water Act (CWA) regulates discharge of pollutants into the waters of the United States and regulates water quality standards for surface water.

Under the CWA, it is unlawful to discharge any pollutant from a point source into navigable waters without a permit. The National Pollutant Discharge Elimination System (NPDES) issues permits to industrial, municipal, and other facilities that discharge directly to surface waters.

The EPA publishes laboratory analytical methods, or test procedures, that must be used by industries and municipalities to analyze regulated pollutants in wastewater and other environmental samples. Most of these methods are published as regulations in the Code of Federal Regulations (CFR) at Title 40 Part 136.

Inorganics Lab – EPA Approved Methods for the Analysis of Multiple Metals in Waste Water

Method	Instrumental Technique	Shimadzu Model
EPA 200.5	ICP Axial	ICPE-9800
EPA 200.7	ICP Radial Axial allowed at Part 136.6	ICPE-9800
EPA 200.8	ICPMS Collision cells allowed at Part 136.6	NA
EPA 200.9	GFAAS	AA-7000G

Wet Chemistry lab - EPA approved Methods for Anions and in Waste Water

Anions	Method	Instrumental Technique	Shimadzu Model
Cyanide	Standard Methods 4500 CN	Manual Spectrophotometry	UV-1280
Nitrate	Standard Methods 4500 NO3	Manual Spectrophotometry	UV-1280
Nitrite	Standard Methods 4500 NO2	Manual Spectrophotometry	UV-1280
Phosphate	Standard Methods 4500 P	Manual Spectrophotometry	UV-1280
Phenolics	EPA 420.1	Manual Spectrophotometry	UV-1280
Sulfate	Standard Methods 4500 SO4	Manual Spectrophotometry	UV-1280
Total Organic Carbon	Standard Methods 5310B	High Temperature Catalytic Oxidation	TOC-L

Volatiles Lab - EPA Approved Methods for Organics in Waste Water

Contaminant Group	Method	Instrumental Technique	Shimadzu Model
Volatiles	EPA 624	Purge & Trap GCMS (See Part 136.6 for allowed Flexibility)	GCMS-QP2010SE with EST
	EPA 1624B	Purge & Trap isotope dilution GCMS	GCMS-QP2010SE with EST

Semi-Volatiles Lab - EPA Approved Methods for Organics in Waste Water

Contaminant Group	Method	Instrumental Technique	Shimadzu Model
Semi volatiles	EPA 625	Liquid-Liquid Extraction Direct Injection GCMS	GCMS-QP2010SE or GCMS-QP2010 Ultra
	EPA 1625B	Liquid-Liquid Extraction Direct Injection Isotope Dilution GCMS	GCMS-QP2010SE or GCMS-QP2010 Ultra
Dioxins	EPA 1613 modified	Solvent Extraction direct injection HRGC/HRMS	GCMS-TQ8040 Not for compliance
Organochlorine Pesticides and PCBs	EPA 608	Liquid-Liquid Extraction Direct Injection GC with ECD	GC-2010 Plus
Organophosphorus and organonitrogen pesticides	EPA 507	Liquid-Liquid Extraction Direct Injection GC with NPD	GC-2010 Plus

Organophosphorus Pesticides	EPA 614	Liquid-Liquid Extraction Direct Injection GC with FPD	GC-2010 Plus
	EPA 622	Liquid-Liquid Extraction Direct Injection GC with NPD	GC-2010 Plus
Triazine pesticides	EPA 619	Liquid-Liquid Extraction Direct Injection GC with NPD	GC-2010 Plus
Carbamate Pesticides	EPA 632	Direct Injection HPLC with Post Column Derivatization	Carbamate Pesticide Analysis System
Chlorinated Acids (Herbicides)	EPA 615	Liquid-Liquid Extraction, Derivatization and GC with ECD	GC-2010 Plus

Resource Conservation and Recovery Act (RCRA)

Under the Resource Conservation and Recovery Act (RCRA), the EPA has the authority to control hazardous waste. This includes the generation, transportation, treatment, storage, and disposal. RCRA also enables the EPA to address environmental problems that could result from underground tanks storing petroleum and other hazardous substances.

The solid waste program encourages states to develop comprehensive plans to manage nonhazardous industrial solid waste and municipal solid waste, sets criteria for municipal solid waste landfills and other solid waste disposal facilities, and prohibits the open dumping of solid waste. The hazardous waste program establishes a system for controlling hazardous waste.

The underground storage tank (UST) program regulates underground storage tanks containing hazardous substances and petroleum products.

The SW-846

The EPA publication SW-846, entitled *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, is a compendium of analytical and sampling methods that have been approved for use in complying with the RCRA regulations. SW-846 functions primarily as a **guidance document** setting forth acceptable, although not required, methods for the regulated and regulatory communities to use in responding to RCRA-related sampling and analysis requirements.

Inorganics Lab - SW846 Methods for the Analysis of Multiple Metals in Solid Waste

Method	Instrumental Technique	Shimadzu Model
6010C	ICP Axial or Radial	ICPE-9800
6020A	ICPMS	NA
7000B	Flame AAS	AA-7000F
7010	GFAAS	AA-7000G

Wet Chemistry Lab - SW846 Methods for Anions in Solid Waste

Anions	Method	Instrumental Technique	Shimadzu Model
Cyanide	9012B	Manual Spectrophotometry	UV-1280
Phenolics	9065	Manual Spectrophotometry	UV-1280
Total Organic Carbon (TOC)	9060	High Temperature Catalytic Oxidation	TOC-L

Volatile Organics lab - SW846 Methods for Organics in Solid Waste

Contaminant Group	Method	Instrumental Technique	Shimadzu Model
Volatiles	8260C	Purge & Trap GCMS	GCMS-QP2010SE with EST

Semi-Volatile Organics lab - SW846 Methods for Organics in Solid Waste

Contaminant Group	Method	Instrumental Technique	Shimadzu Model
Semi volatiles	8270D	Extraction Direct Injection GCMS	GCMS-QP2010SE or GCMS-QP2010 Ultra
Organochlorine Pesticides and PCBs	8081B	Liquid-Liquid Extraction Direct Injection GC with ECD	GC-2010 Plus
	8082A	Liquid-Liquid Extraction Direct Injection GC with ECD	GC-2010 Plus
Organophosphorus and organonitrogen pesticides	8141A	Liquid-Liquid Extraction Direct Injection GC	GC-2010 Plus
Carbamate Pesticides	8315A	Direct Injection HPLC with Post Column Derivatization	Carbamate Pesticide Analysis System
Toxaphene and Toxaphene Congeners	8276	Extraction Direct Injection GC-NICI/MS	GCMS-QP2010 Ultra
Polycyclic Aromatic Hydrocarbons (PAH)	8272	SPME GCMS/SIM	GCMS-QP2010 Ultra
Chemical Agents	8271	Direct Injection or Thermal Desorption GCMS	GCMS-QP2010 Ultra
Perchlorate	6850	HPLC/ESI/MS or HPLC/ESI/MS/MS	LCMS-2020 or LCMS-8050
Nitroaromatics, nitramines, nitrate esters	8330B	HPLC	Prominence

You may have noticed when observing the above charts that there is significant repetition of instrumentation and analytes between the three main USEPA divisions. With the exception of organics in drinking water, most laboratories will group all samples and run essentially only one method for all matrices whether being reported for drinking water, wastewater, or hazardous waste compliance. Often, for organics, the method used is the SW-846 method, and for metals, the wastewater methods. As long as the quality control criteria are met for both methods, it is acceptable to analyze wastewater, solid waste, and drinking water samples in one batch. Since there is a risk of contamination when attempting the analysis of organics from wastewater or solid waste in the same batch as drinking water, many laboratories segregate drinking water organics analysis to instrumentation reserved specifically for drinking water.

■ Shimadzu Instruments Fill the Needs of Modern Environmental Laboratory Testing

Laboratory and on-line analyzers available from Shimadzu Scientific Instruments are capable of rapid, accurate, and precise measurements of virtually all pollutants required for testing under the Clean Water Act, Safe Drinking Water Act, and the Resource Conservation and Recovery Act. Shimadzu instruments are easy to use, rugged, with more than enough of the required sensitivity necessary to meet or exceed all EPA regulatory methods for which they are applied.

For instance, a Shimadzu GCMS-QP2010 SE Gas Chromatograph Mass Spectrometer (Figure 1) coupled with a Purge and Trap sample concentrator is capable of analyzing air, drinking water, wastewater, and solid waste for hundreds of trace organic compounds. The Shimadzu LCMS-8050 HPLC MSMS (Figure 2) and/or the Shimadzu GCMS TQ8040 GCMSMS are capable of accurately determining trace concentrations of halogenated hydrocarbons, pesticides, pharmaceuticals, and personal care products in even the most complex matrices.

Figure 1: Shimadzu GCMS-QP2010 SE Single Quadrupole GCMS

Figure 2: Shimadzu LCMS-8050 Triple Quad LC/MS/MS

Analysis of metals is easily made using the Shimadzu AA-7000 Flame Atomic Absorption Spectrophotometer with capability of adding electro thermal atomization for even lower detection limits. For highly sensitive simultaneous analysis of multiple elements many laboratories turn to Inductively Coupled Plasma Atomic Emission Spectrometers (ICP), such as the Shimadzu ICPE-9000.

Conventional pollutants such as TKN, cyanide, total phenolics, and total nitrogen can be analyzed using a visible spectrophotometer, such as the Shimadzu UV-1800, Oil and Grease measurements can be made by a new measurement technology using the Shimadzu IRTracer-100 FTIR, and labor- intensive sample collection and manual digestions for TKN and Total Phosphorus can be automated and measured simultaneously with Total Organic Carbon (TOC) using the Shimadzu TNPC-4110C on-line analyzer (Figure 3).

Figure 3: Shimadzu TNPC-4110C Analyzer

■ Conclusion

Shimadzu laboratory instruments can be used to analyze nearly all of the pollutants listed for drinking water, wastewater, groundwater, and solid waste. Shimadzu instruments typically achieve lower detection limits and have less interference than comparable instruments that were used to generate the original EPA-approved methods. Laboratory and on-line instruments from Shimadzu are accurate and precise, and are designed to meet or exceed EPA method criteria.

Table 1: Major historical events and introduction of laboratory instruments

Year	Major Instrument	Significance	Environmental Movement	Environmental Regulation
Prior to 1850	Gravimetric analysis		George Perkins Marsh advocates conservation to management of forest	
1850	Titrimetric analysis	Speeds testing		
1864			Henry David Thoreau's *The Maine Woods* calls for establishment of National Preserves	Yosemite Valley becomes a park
1872				Yellowstone becomes National Park. Congress passes Mining Law allowing mining on public land.
1891				Forest Reserve Act, foundation of National Forest System
1892			Sierra Club Founded	
Early 1900's	Colorimeter	Measurement of low levels of analyte becomes possible		
1910			Lakeview Gusher in California releases an approximate 9.4 million barrels of oil over 18 months. About half flowed into rivers, and farmland	
1916				National Park System
1935	PH meter	First chemistry use of electronics	Wilderness Society Founded	
1941	Model DU Spectrometer	First commercial spectrometer, allows accurate low level testing		
1942	Grating Spectrograph	Semi-quantitative metals		
1943	Oxygen Analyzer	First instrument to measure D.O.		
1944	Commercial IR	Allows rapid analysis of organics such as rubber and pesticides		
1948			Atmospheric inversion in Donora. Town is held under cloud of gas from Donora Zinc Works. People begin to study air pollution	
1949	Flame photometer	Rapid analysis of alkali metals		
1954	Spectronic 20	Spectrophotometer becomes widely used		
1957	Auto-Analyzer	First instrument to automate lab processes		

Year	Major Instrument	Significance	Environmental Movement	Environmental Regulation
1959	Gas Chromatograph	Commercial GC with FID and ECD, allows determination of pesticide residues		
1961	Atomic Absorption	Simplifies determination of metals, speeds determination of trace metals		
1962			*Silent Spring* is published. People become concerned with the use of pesticides	
1963	HPLC	Commercial HPLC		
1964				Wilderness Act is passed
1967	GC/MS	First computerized GC/MS, becomes primary method of organic analysis		
1969			Santa Barbara Oil Spill fouls beaches in Southern California and arouses public anger against pollution	**National Environmental Policy Act creates the EPA**
1970			First Earth Day	Clean Air Act is passed. Sets auto emission and air pollution standards
1971				Congress restricts use of lead based paint
1972				Water Pollution Control Act is passed. DDT is banned in US, and Congress requires extensive review of pesticides
1973			OPEC triggers energy crisis	Endangered Species Act is passed. Phase out of leaded gasoline. EPA issues first NPDES permit
1974				Congress passes Safe Drinking Water Act allowing EPA to regulate Drinking Water
1975	Ion Chromatograph	Automates the determination of anions in water		Congress establishes fuel economy standards, tail pipe emission standards
1976	Bench top GC/MS	GC/MS becomes tool in almost every laboratory		Congress passes RCRA regulating hazardous waste production and disposal
1977			Supreme Court upholds the Endangered Species Act and stops construction of Tellico Dam in Tennessee.	Clean Air Act amendments strengthen air quality standards
1978			President Carter declares emergency at Love Canal	CFC's are banned in aerosol cans
1979	Capillary Column	Improves analysis of organics by GC and GC/MS	Three Mile Island Nuclear plant almost has meltdown.	Scrubber technology on coal-fired plants demonstrated by EPA

Year	Major Instrument	Significance	Environmental Movement	Environmental Regulation
1980				Alaska National Interest Lands Conservation Act is passed. Congress creates Superfund to clean up hazardous waste sites
1981	IBM PC	Computers become widely available		National Research Council reports on acid rain
1982			Dioxin contamination forces government to purchase homes in Missouri. A PCB landfill protest begins the environmental justice movement	Congress enacts laws for save disposal of nuclear waste
1983			Cleanup actions begin to rid Chesapeake Bay of pollution from sewage, city runoff, and farms.	EPA encourages testing for Radon gas
1984	HP 5890			
1985			Scientists report hole in ozone layer	
1986			Chernobyl Reactor suffers explosion and fire. Thousands are subjected to radiation	Congress declare public has the right to know when toxic chemicals are released to air, land, and water
1987			Medical waste washes up on north eastern beaches	United States pledges to phase out CFC's
1988				Congress bans ocean dumping
1989			Exxon Valdez spills 11 million gallons of oil in Alaska	
1990				Congress requires states to demonstrate progress in improving air quality
1993			A cryptosporidium outbreak in drinking water kills more than 100 people	
1995				EPA launches incentive based acid rain program to reduce SO2 emissions
1996				Drinking water suppliers are required to inform public about pollution in water. Food Quality Act tightens restrictions on pesticides.
1997				EPA issues tougher air quality standards
1999				New emission standards on cars
2000				Tougher regulations on diesel engines and fuel

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SHIMADZU Corporation
www.shimadzu.com/an/

SHIMADZU SCIENTIFIC INSTRUMENTS
7102 Riverwood Drive, Columbia, MD 21046, USA
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222
URL: www.ssi.shimadzu.com

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