

Review

Environmental chromatographic methods and regulations in the United States of America

Zoe A. Grosser, James F. Ryan and Michael W. Dong*

The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0250 (USA)

ABSTRACT

The five major monitoring programs and the pesticide program administered by the US Environmental Protection Agency (EPA) are reviewed. Gas chromatographic (GC) and high-performance liquid chromatography (HPLC) methods used by each EPA program for organic analysis are described. Quality control is the major difference among methods in different programs. Trends for the future of environmental analyses in the US are discussed.

CONTENTS

1. Introduction	76
2. Environmental legislation and the five major monitoring programs	76
2.1. Wastewater	76
2.2. Drinking water	77
2.3. Solid and hazardous waste	77
2.4. Air	78
2.5. Pesticides	79
3. EPA gas chromatography methods	79
3.1. Sample introduction and concentration techniques	79
3.2. Detection techniques	82
4. EPA high-performance liquid chromatography methods	82
4.1. Detection techniques	82
5. Quality assurance and quality control for EPA methods	84
6. EPA chromatographic method trends	84
6.1. Method integration	85
6.2. Air methods	85
6.3. Trends towards automation, more efficient sample preparation techniques, and HPLC	85
7. Discussion	86
8. Acknowledgements	86
References	86

* Corresponding author.

1. INTRODUCTION

The US Environmental Protection Agency (EPA) interprets legislation enacted by the US Congress and drafts regulations to implement and enforce the perceived intent. The EPA was created in 1969 by the US Congress to consolidate all environmental functions, previously performed by diverse agencies, under one regulatory body. Since the EPA's inception, over 25 major environmental acts, or amendments to existing acts, have been passed by the US Congress. While some environmental programs are administered directly by the EPA, others can be administered through individual states. Individual states may accept "primacy" for a particular EPA program, which means they have demonstrated analytical proficiency and accept responsibility for implementation and enforcement.

The EPA organizational structure has grown out of the needs of the agency to comply with Congressional mandates [1]. Fig. 1 shows a simplified schematic of the current structure of the EPA. The different EPA Offices are centered around types of sample media: water, solid waste, air, and pesticides. Each Office has set up its own research programs and developed its own analytical methodology. This has led to a proliferation of methods, many of which differ only slightly in the sample preparation or analytical methodology [2]. Table 1

lists the relevant legislative acts and the resulting series of analytical methods by each type of medium. Consider the determination of chlorobenzene for which 13 gas chromatographic (GC) methods are available. In the USA, where the bulk of the environmental analytical work is performed by private laboratories, this has led to confusion over the proper method to use with a specific sample.

This paper reviews the five major EPA monitoring programs for drinking water, wastewater, solid and hazardous materials, and air. This paper also reviews the EPA's pesticide registration program, which is heavily dependent on chromatographic techniques. The chromatographic methods for each program are listed and their commonalities and differences highlighted. Sampling techniques, column requirements, and detection systems are reviewed. The unique performance characteristics of GC and high-performance liquid chromatography (HPLC) are described. Quality assurance and control (QA/QC) procedures necessary for accurate environmental analyses are discussed.

2. ENVIRONMENTAL LEGISLATION AND THE FIVE MAJOR MONITORING PROGRAMS

2.1. Wastewater

The Clean Water Act of 1977 gave the EPA the responsibility to regulate industrial discharges into

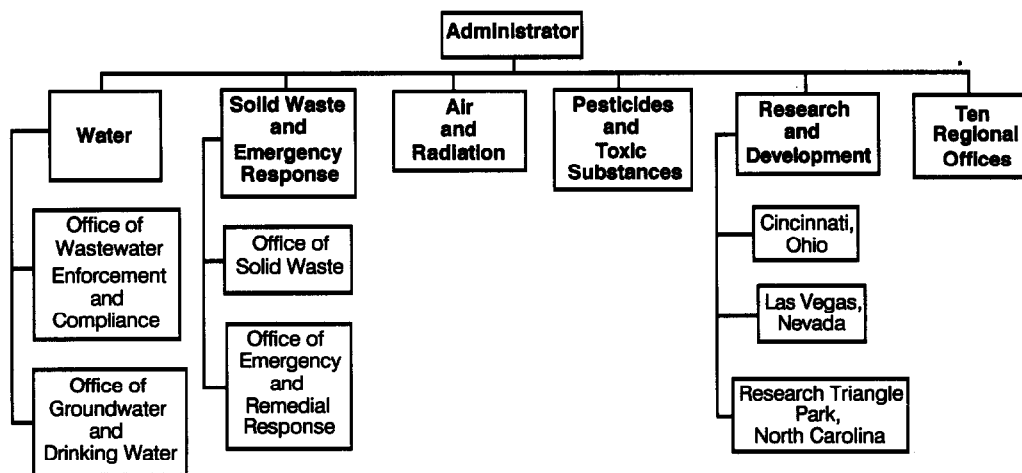


Fig. 1. Simplified structural diagram of the US EPA, showing the major monitoring program offices and regional research and development offices.

TABLE I
KEY ENVIRONMENTAL LEGISLATION AND OFFICIAL ANALYTICAL METHODS FOR ORGANICS

Sample	Legislation and year of enactment	Methods
Wastewater	Federal Water Pollution Control Act (FWPCA) 1972, 1977 or Clean Water Act	EPA 600-Series
Drinking water	Safe Drinking Water Act (SDWA) 1974, 1977, 1986	EPA 500-Series
Solid waste	Resource Conservation and Recovery Act (RCRA) 1976, 1980, 1984 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) 1980 Superfund Amendments Reauthorization Act (SARA) 1986	SW-846 Methods (8000-Series) Statement of Work (SOW)
Air	Clean Air Act (CAA) 1970, 1990	Toxic Organic Series (TO)
Pesticides	Toxic Substances Control Act (TSCA) Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)	Company proprietary

surface waterways to maintain their quality. The EPA Office of Wastewater Enforcement and Compliance created the National Pollution Discharge Elimination System (NPDES) to permit the regulation of individual point sources. Guidelines have been established for the discharges of over 50 types of industries, and specific permits are negotiated between the wastewater generator and the regional EPA office or state, when state primacy applied. The 600-series of analytical methods [3] using GC, GC-MS, and HPLC have been developed by the Environmental Monitoring Support Laboratory in Cincinnati, OH, USA to aid in setting guidelines and enforcing permit requirements. Wastewater typically requires extraction, concentration, and cleanup with silica or florisil before introduction into the instrument.

2.2. Drinking water

Drinking water regulations [4] arise from the Safe Drinking Water Act passed by Congress in 1974. The EPA Office of Ground Water and Drinking Water protects public health through the National Primary Drinking Water Regulations. These regulatory limits are based on health criteria. As with all federal regulations, they are published in the Federal Register and set the maximum amount of organic and inorganic contaminants allowed in a drinking water supply. The National Secondary Drinking Water Regulations set contaminant levels which, if

exceeded, will affect the aesthetic quality of a water supply. Secondary levels are EPA guidance, and as such, are not enforceable at the federal level. The EPA's Office of Drinking Water and Ground Water Protection adopted the 500-series of methods [5,6] for the determination of organic compounds in drinking water because the 600-series methods developed for wastewater analysis lack the sensitivity necessary to enforce the drinking water maximum contaminant levels (MCLs). The 200-series of methods [7] are used to determine inorganic components in both drinking water and wastewater.

Drinking water is a simple matrix, and filtration may be the only sample preparation step required. However, sample concentration is often needed, using either solid-phase extraction or methylene chloride extraction, to obtain the trace level (part-per-billion to part-per-trillion) required in the regulations. Direct injection is possible for some HPLC methods, such as the methods for the analysis of carbamate pesticides or the herbicide glyphosate, utilizing extremely sensitive and selective detection techniques (post-column reactions with fluorescence detection).

2.3. Solid and hazardous waste

There are two EPA programs with jurisdiction over solid and hazardous waste. The first program covers the more routine aspects of toxic transportation, storage and disposal (TSD) of hazardous ma-

terials. The second program establishes procedures to handle emergency releases of hazardous materials as well as dealing with hazardous waste sites that have been abandoned and require cleanup.

The Resource Conservation and Recovery Act (RCRA) of 1976, updated by the Hazardous and Solid Waste Amendments of 1984, directed the EPA to take “cradle to grave” responsibility for hazardous materials. This includes management of wastes through transportation, storage, and disposal. Most waste materials generated by the USA population are disposed of in municipal landfills or by incineration in waste disposal furnaces. However, hazardous waste must be treated separately (and more expensively). Determining whether a waste is hazardous has a great effect on the cost of disposal. Wastes are either listed as hazardous because of known hazardous compounds or are characterized to determine whether they are hazardous through four tests. Characterization tests determine reactivity, ignitability, corrosivity, and toxicity. The toxicity test is the most quantitative; it employs the Toxicity Characteristic Leaching Procedure (TCLP) to extract potentially toxic components into an acetic acid buffer solution. The solution is then analyzed for 31 organic components, using mostly GC–MS techniques.

The Office of Solid Waste has created four volumes of analytical methods covering a variety of analytes in soil, solid waste, oily matrices, and groundwater. The method compendium, entitled Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, known colloquially as the SW-846 set of methods [8], contains the 8000-series methods for GC, GC–MS, HPLC, and HPLC–MS. Complex soil, sludge, and waste matrices are commonly analyzed by this program; some of the sample extraction and clean-up methods are listed in Table 2. Other programs often incorporate the sample preparation steps into the specific analytical method.

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980, updated by the Superfund Amendments and Reauthorization Act (SARA) of 1986, prompted the EPA to create a unique program known as “Superfund” to clean up abandoned hazardous waste sites using funds derived from a special petrochemical tax. The EPA’s Office of Emergency and

TABLE 2

EPA EXTRACTION AND SAMPLE CLEANUP METHODS USED IN TEST METHODS FOR EVALUATING SOLID WASTE (SW-846)

3510	Methylene chloride extraction
3520	Continuous liquid–liquid extraction
3540	Methylene chloride–acetone soxhlet extraction
3541	Automated soxhlet extraction
3550	Methylene chloride–acetone ultrasonic extraction
3580	Waste dilution
3610	Sample cleanup (alumina)
3620	Sample cleanup (florisil)
3630	Sample cleanup (silica gel)
3640	Sample cleanup (gel-permeation chromatography)
3650	Sample cleanup (acid–base partition)
3660	Sample cleanup (sulfur)
3665	Sample cleanup (sulfuric acid–permanganate)

Remedial Response administers the program. Analytical methods used for contamination assessment and cleanup monitoring are derived from other programs and modified to suit the special needs of Superfund. Generally, the quality assurance and control measures required by Superfund are more stringent, because data may be used in a court of law to help prove the source of pollution and recover cleanup costs for a contaminated site. Methods developed for this program are published in a contractual statement of work (SOW), which details the sample preparation, analysis, and QA/QC requirements to be used by analytical labs who work for the EPA under contract. Sample lots are awarded to various contract laboratories through a competitive bid process. Routine analyses are performed using GC–MS for 33 volatile organic compounds and 64 semivolatiles, and GC with an electron-capture detector for 28 target pesticides.

2.4. Air

The Clean Air Act of 1983, amended in 1990 (CAA), governs ambient air, stack sources, and moving sources of chemical contamination. To date, ambient air quality standards have been established for six components (NO_x, SO₂, ozone, CO, lead, and particulate matter smaller than 10 μm) using methods published in the US Code of Federal

Regulations. New Source-Performance Standard (NSPS) regulations for new sources suggest use of the toxic organic (TO) series of methods [9] for organics to verify compliance with individually negotiated permits, in much the same fashion as the wastewater NPDES program. The EPA Office of Air and Radiation is quickly moving to implement regulations to limit and additional 189 compounds in stack sources, moving sources, an ambient air as required by the recent CAA. New methods will need to be developed or adapted from other programs to determine the newly regulated contaminants.

2.5. Pesticides

From the EPA standpoint, pesticide analytical methods have been developed in support of registration petitions to the EPA under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and the Toxic Substances Control Act (TSCA). The methods used can be company-proprietary and thus not widely available. This is in contrast to the published methods readily available for the other programs.

Pesticide determinations are made for samples such as drinking water, wastewater, and solid waste using EPA methods and in residual analysis of foodstuff (regulated by FDA) using American Society for Testing and Materials (ASTM), Association of Official Analytical Chemists (AOAC), and National Pesticides Survey (NPS) methods [10,11]. In addition, TSCA requires chemical manufacturers to notify the EPA using a Premanufacture Notice (PMN) describing structure, impurities, by-products, environmental fate, and toxicology data. Company-proprietary methods (mostly HPLC) are used to generate assay, stability, residue, and metabolism data under the guidelines of Good Laboratory Practices (GLP).

3. EPA GAS CHROMATOGRAPHY METHODS

In the previous section, legislation was described as the driving force to develop different EPA programs, which in turn, developed different methods. In this section we review the instrumentation specified by the EPA methods. The sample introduction systems, sample concentration devices, and detec-

tors generally used are described. The EPA methods are segmented by program and the detection technique specified in the method to show the diversity and commonality of program analyte requirements.

3.1. Sample introduction and concentration techniques

EPA GC methods utilize common sample introduction and concentration techniques for liquid and volatile samples. For liquid samples (*e.g.*, semi-volatiles in extracts from water, air, and soil), the conventional flash vaporization injectors are used with packed columns. Both split and splitless injectors are also used with narrow and wide-bore fused-silica capillary columns specified in the newer EPA methods [12]. For compounds which might decompose under flash vaporization injection conditions, cold direct liquid injection or temperature-programmed vaporization techniques are preferred.

For volatiles and gaseous compounds, pneumatic sampling valves with cryogenic trapping are commonly used with several novel sample concentration devices developed specifically for water or air samples. Purge-and-trap devices are designed as on-line sample extraction and concentration systems for purgeable organics in water samples. First introduced in the late 1970s, they have become rugged and automated for routine determination of volatile compounds which are otherwise easily lost in the conventional liquid extraction process.

Headspace analysis is used as a quick turnaround method (CERCLA program) for evaluation of contaminated soil and groundwater at cleanup sites. Headspace sampling eliminates sample cleanup by using heat to desorb organics from a solid or liquid matrix into the headspace of an enclosed vial. The technique can be automated and is quantitative after appropriate calibration. Quick turnaround methods are used during cleanup of contaminated waste disposal sites where analytical data direct the cleanup efforts in progress. The same technique is particularly useful for screening purgeables in soil samples that often plague purge-and-trap systems due to cross-contamination problems [13].

For the determination of volatile organics in ambient air, adsorption systems using Tenax (Method TO-1) or carbon molecular sieves (Method TO-2),

TABLE 3
EPA GC METHODS

Method	Wastewater	Drinking water	Air	
GC-FID	603	Acrolein and acrylamide	TO-3 Volatile organic compounds (VOC)	
	604	Phenols	TO-12 Non-methane organic compounds	
	609	Nitroaromatics and isophorone	TO-13 Benzo[a]pyrene and PAHs	
	610	PAHs		
GC-ECD	606	Phthalate esters	501.2 Trihalomethanes (liquid-liquid extraction)	
	608	Organochlorine pesticides and PCBs	504 EDB and DBCP	
	608.2	Organochlorine pesticides and PCBs	505 Organohalide pesticides and PCBs	
	612	Chlorinated hydrocarbons	508 Chlorinated pesticides	
	627	Dinitroaniline pesticides	508A Chlorinated pesticides and PCBs (derivatized)	
			515.1 Chlorinated acids	
		548 Endothall	TO-3 Volatile organic compounds	
			TO-4 Organochlorine pesticides and PCBs	
			TO-10 Organochlorine pesticides	
GC-PID	602	Purgeable aromatics	503.1 Volatile aromatics (purge and trap)	
GC-ELCD	601	Purgeable halocarbons	502.1 Volatile organic compounds (purge-and-trap)	
	611	Haloethers	502.2 Volatile organic compounds (purge-and-trap, ELCD and PID)	
			501.1 Trihalomethanes (purge-and-trap)	
GC-NPD	607	Nitrosamines	507 Nitrogen and phosphorus pesticides	
	645	Amine pesticides		
	633	Organonitrogen pesticides		
GC-FPD				
GC-MS	624	Purgeables	524.2 Purgeables (purge-and-trap, capillary column)	TO-1 Volatile organic compounds (capillary)
	625	Base/Neutrals (packed)		
	625.1	Base/Neutrals (capillary)	525 Organics (liquid-solid extraction, capillary column)	TO-2 Highly volatile organic compounds
	680	Pesticides and PCBs		
	613	Dioxin	501.3 Trihalomethanes (SIM) ^a	TO-14 Volatile organic compounds (GC-MS and other detectors)
	1624	Volatile organic compounds (isotope dilution)		TO-13 Benzo[a]pyrene and PAHs by GC-MS and GC-FID
	1625	Semi-volatile compounds (isotope dilution)		TO-9 Dioxin (GC-HRMS) ^a
				TO-7 N-Nitrosodimethylamine
GC-FT-IR				

^a Abbreviations: SIM = single ion monitoring; HRMS = high-resolution mass spectrometry.

RCRA	CERCLA
8030 Acrolein, acrylamide, acetonitrile	
8040 Phenols	
8060 Phthalate esters	
8090 Nitroaromatics	
8015 Non-halogenated volatile organics (purge-and-trap)	
8060 Phthalate esters	Pesticides/Arochlors, Routine Analytical
8061 Phthalate esters (capillary)	Services Statement of Work,
8080 Organochlorine pesticides	OLMO1.8, 8/91
8081 Organochlorine pesticides (capillary)	Pesticides, Special Analytical Services,
8090 Nitroaromatics and cyclic ketones	Low Concentration Water SOW, 9/90
8120 Chlorinated hydrocarbons	
8121 Chlorinated hydrocarbons (capillary)	
8150 Chlorinated herbicides	
8151 Chlorinated herbicides (capillary)	
8100 PAHs	
8085 PCBs (derivatized)	
8032 Acrylamide	
8011 EDB and DBCP	
8045 Endothall	
8020 Volatile aromatics (purge-and-trap)	
8021 VOCs (purge-and-trap, ELCD–PID in series)	
8010 Halogenated VOCs (purge-and-trap)	
8021 VOCs (purge-and-trap, ELCD–PID in series)	
8080 Organochlorine pesticides and PCBs	
8150 Chlorinated herbicides	
8151 Chlorinated herbicides (capillary)	
8110 Haloethers	
8070 Nitrosamines	
8141 Organophosphorus compounds (capillary)	
8031 Acrylonitrile	
8145 Alkylphosphates	
8140 Organophosphorus pesticides	
8141 Organophosphorus compounds (capillary)	
8240 VOCs (purge-and-trap)	Volatile Organic Compounds, Routine Analytical
8260 VOCs (purge-and-trap, capillary)	Services Statement of Work,
8266 VOCs (isotope dilution)	OLMO1.8, 8/91
8250 Semi-volatile organics	Semi-volatile Organic Compounds, Routine
8270 Semi-volatile organics (capillary)	Analytical Services Statement of
8276 Semi-volatile organics (isotope dilution)	OLMO1.8, 8/91
8280 Dioxin	Volatile Organic Compounds, Special
8275 TC–MS for semivolatile screening	Analytical Services Statement
8290 PCDDs and PCDFs by HRGC–HRMS	of Work for Low Concentrations in
	Water, 9/90
	Volatile Organic Aromatics, Special
	Analytical Services Statement of
	Work for Low Concentration in
	Water (based on 524.2), 9/90
8410 Semivolatile organics (capillary)	
8415 Tris-2,3-dibromopropyl phosphate	
8430 Bis(2-chloroethyl)ether	

as well as cryogenic preconcentration trapping (Method TO-3) or SUMMA canister sampling techniques (Method TO-14) are used. These devices are used off-line or on-line with a GC or GC–MS system.

3.2. Detection techniques

Table 3 lists the EPA methods using gas chromatography with various detectors, and are categorized by the major EPA programs.

Gas chromatography is the traditional analytical technique for volatile organics. Because EPA methods often target trace levels of specific compound types in complex matrices, selective detection offers the most effective approach. Thermal conductivity detection (TCD) is not generally used in EPA methods because of its low sensitivity. Flame ionization detection (FID) is used, typically after extensive sample cleanup, and only if a more specific detector is not available.

Electron-capture detection (ECD) is used extensively for pesticides, chlorinated compounds, and phthalates in all five EPA programs. Nitrogen-phosphorous detectors are used for the analysis of nitrosamines, amines, acrylonitrile, and nitrogen and phosphorous-containing pesticides. Flame photometric detection (FPD) is used for organophosphorous pesticides in method 8140 and draft method 8141. Electrolytic conductivity detection (ELCD) and photoionization detection (PID), rarely used elsewhere, are employed often in tandem for purgeable organics (Methods 502.2 and 8021). ELCD is very selective for halogenated compounds, while PID, using a low-energy lamp, is selective for aromatics.

Mass spectrometry (MS) with confirmatory capability is the preferred detector for survey methods and for screening samples as evidenced by its predominance in all five monitoring programs. When operating in the scanning mode, MS functions as a universal detector with only moderate sensitivity. Both sensitivity and selectivity can be increased significantly by using the single-ion monitoring (SIM) mode (e.g., Method 501.3 for trihalomethanes in drinking water). Quite often, better detection limits can also be achieved by switching to a selective detector. For example, the detection limit for benzene using purge and trap and GC–MS can be lowered

from 0.03 $\mu\text{g/l}$ (in Method 8260) to 0.009 $\mu\text{g/l}$ (Method 8021) by photoionization detection.

With improvements in interface technology and detection sensitivity, use of Fourier transform infrared spectroscopy (FT-IR) is increasing as an ancillary technique for GC. FT-IR often complements MS data by providing additional information for isomer and structure identifications. Three RCRA methods using GC–FT-IR (8410, 8415, and 8430) are currently being proposed.

4. EPA HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY METHODS

The number of official EPA methods using HPLC has grown dramatically to more than 40 approved and draft methods [14–16]. In searching for more cost-effective methods, the EPA recognizes the applicability of HPLC for non-volatile, thermally labile, and polar materials. With the trend towards biodegradable pesticides, HPLC is becoming the preferred analytical method for most insecticides and their metabolites, herbicides, and plant growth regulators. Key target pesticides include carbamates, diquat and paraquat, triazine, phenylureas and glyphosate. In addition, HPLC is also amenable to acids, bases, surface active agents, dyes, and aromatic amines [17].

The advantages of HPLC include sensitive and selective detection for compounds with ultraviolet (UV) absorbance or natural fluorescence. HPLC also tolerates large-volume injections of aqueous samples, rendering it ideal for screening water samples. Reversed-phase chromatography is used almost exclusively in all EPA HPLC methods, with the exception of ion-exchange chromatographic methods for ion chromatography, glyphosate, and sulfonic acids. Gel-permeation chromatography (GPC) and liquid–solid chromatography are primarily used for sample cleanup.

4.1. Detection techniques

Table 4 lists the EPA HPLC methods segmented by detection system.

UV–Visible absorbance and fluorescence detectors are the primary detectors used. They are extremely sensitive for components with high molar absorptivity (ng levels) or fluorescence (pg levels).

TABLE 4
EPA HPLC METHODS

Method	Wastewater	Drinking water	Air	RCRA	CERCLA
HPLC-UV	610 PAHs	549 Diquat and paraquat	TO-5 Aldehydes and ketones	8310 PAHs	Pesticides/Aroclors, Routine Analytical Services Statement of Work, OLMOI.8 8/91, GPC cleanup
	631 Benomyl and carbendazim	550 PAHs	TO-6 Phosgene	8315A Aldehydes and ketones (2,4-DNPH derivatized)	
	632 Carbamates and urea pesticides	550.1 PAHs	TO-8 Phenols and cresols	8316 Acrylamide, acrylonitrile and acrolein	
	604.1 Hexachlorophene and dichlorophene		TO-11 Formadehyde	8317 4,4'-Methylene bis(2-chloroaniline) (MOCA)	
	629 Cyanazine		TO-13 PAHs	8321 Azo dyes, amines, organophosphorus compounds by HPLC-TSP-MS ^a	
	635 Rotenone			8330 Nitroaromatics and nitramine explosives	
	636 Bensulide			8331 Tetrazene	
	637 2,2'-Dithiobis-(benzothiazole)			8332 Nitroglycerine	
	639 Bendiocarb			8333 Nitro compounds	
	640 Mercaptobenzothiazole			8350 Aromatic sulfonic acids by ion exchange chromatography	
	642 Biphenyl and orthophenyl phenol				
	643 Bentazon				
	644 Picloram				
	HPLC-FL	610 PAHs	550 PAHs	TO-8 Phenols and cresols	8310 PAHs
641 Thiabendazole		550.1 PAHs	TO-13 PAHs	8318 N-Methylcarbamates (post-column reaction)	
		531.1 Carbamates (post-column reaction)			
HPLC-EC ^a	605 Benzidines	547 Glyphosate (post-column reaction)		8321 Azo dyes, amines, organophosphorus compounds by HPLC-TSP-MS	
				8325 Benzidines and nitrogen-containing pesticides by HPLC-PB-MS ^a	
HPLC-MS				8350 Aromatic sulfonic acids by ion-exchange chromatography	

^a Abbreviations: EC = electrochemical detection; PB = particle beam; TSP = thermospray.

The advent of diode array detection (used in draft method 547) increases the utility of absorbance detectors to include spectral confirmation capability required to eliminate false positives [18]. Its potential for determining a wide variety of analytes at low levels has yet to be fully exploited. Electrochemical detectors are used for electroactive compounds such as benzidines and certain pesticides. Refractive index detection lacks sensitivity for environmental applications.

Mass spectrometry (LC–MS) is becoming a powerful tool for rapid evaluation of solid wastes and for screening wastewater samples [19]. Currently, three LC–MS methods are proposed for hazardous waste analysis (8321, 8325 and 8350) for RCRA, currently the most HPLC-progressive program. Method 8321 is close to approval and uses HPLC with UV and MS detection for azo, anthraquinone, coumarin dyes, and organophosphorus pesticides. MS offers the possibility of a universal as well as selective and sensitive detector for HPLC, although its routine use is still hampered by the high system cost and operational difficulties. Rapid advances in LC–MS interface technology, in particular in electrospray and atmospheric pressure ionization (API), will improve the cost-effectiveness and applicability of this technique.

Carbamate and glyphosate analyses are currently performed routinely in many states. These EPA methods (531.1, 8318, and 547) utilize post-column reaction systems with fluorescence detection to provide sufficient sensitivity for direct injection of water samples at part-per-billion levels without concentration [20].

5. QUALITY ASSURANCE AND QUALITY CONTROL FOR EPA METHODS

Quality assurance (QA) and quality control (QC) is an important component for most methods developed by the EPA. Quality assurance programs cover all aspects of the laboratory process. The EPA defines QA as: *“The quality assurance process consists of management review and oversight at the planning, implementation, and completion stages of the environmental data collection activity, to ensure that data provided are of the quality required.”*

Typical guidelines for managing QA in environmental laboratories are adopted from Good Lab-

oratory Practices (GLP) and the ISO-9000 standards. The International Organization for Standardization (ISO) has developed a series of management standards (ISO 9000-9004) to assist manufacturing and service organizations in developing systems to ensure quality. The recently developed draft Good Automated Laboratory Practices (GALP) extend the GLP to data handling system [21]. Total quality management programs (e.g., Juran Program), once only applied to manufacturing operations, are being applied to laboratory production [22]. Common components of a QA program include standard operating procedures (SOP), operator training programs, and performance evaluation samples from outside evaluators. To avoid conflict of interest, it is important to have a QA Officer, who reports independently from laboratory operations.

The EPA defines quality control as: *“The Quality Control process includes those activities required during data collection to produce the data quality desired and to document the quality of the collected data.”* QC checks are performed at various points throughout the analysis to verify instrument and method performance. Many of the QC requirements are specified within the EPA method. One of the major differences between EPA methods that use the same technique for similar analyte lists in the QC requirements. Some programs have more intensive QC requirements because of the end use of the data. For example, the contract laboratory program (CLP) uses data to assign responsibility for cleanup costs at a contaminated site. Therefore, the data may have to stand alone in a court of law, long after the chemist who performed the analysis has left or the laboratory where the analysis was performed has ceased to exist. Table 5 compares the QC requirements of RCRA Method 8010 and drinking water Method 502.1 for halogenated volatile compounds. Although the analytes and technical aspects of the methods are very similar the QC checks and validation criteria are different, rendering it difficult to run both types of samples together in the same batch.

6. EPA CHROMATOGRAPHIC METHOD TRENDS

This section highlights a number of changes underway in regulations and technology that will im-

TABLE 5
COMPARISON OF METHOD PARAMETERS AND QC

Parameters	RCRA 8010 <i>Halogenated Volatile Organics</i>	Drinking Water 502.1 <i>Volatile Halogenated Organic Compounds in Water by Purge-and-Trap Gas Chromatography</i>
<i>Analytes</i>	39	50 (28 in common with 8010)
Sample introduction	Purge-and-trap	Purge-and-trap
Primary column	1% SP-1000 on Carbopack-B 60/80 mesh	Same
Detector	Halogen-specific	Same
Calibration	5 levels	3 levels (or more, depending on concentration range)
<i>Quality control</i>		
Initial response vs. subsequent standards	± 15%	± 20%
Spikes	5% or 1 per month	5%
Accuracy: Surrogate	± 3σ ^a	80–120%

^a 3σ determined from historical laboratory performance.

pact EPA chromatographic methods over the next few years.

6.1. Method integration

The EPA structure has developed in the present fashion because of the requirements placed on the EPA by the US Congress. The EPA has designed most regulations by the type of medium involved: soil, air, water, and solid and hazardous waste. Many methods have been created by the various agency programs that are technically redundant, but have different QC requirements. The EPA has recognized that the proliferation of methods is confusing and counter-productive [23]. It has created the Environmental Monitoring Management Committee (EMMC) to consolidate methods across program lines [24,25]. Three methods are targeted for initial efforts, including GC analysis of volatile organic compounds. Agreement on a method among so many participants may be difficult, but the eventual savings in analysis time and expense will make the effort worthwhile.

6.2. Air methods

The EPA Air program is poised for growth and change. Implementation of the Clean Air Act

amendments will require new methods and regulations [26]. Information on current contaminants and their pervasiveness will be required to assess the state of air quality. Routine monitoring will require the development of rugged methods suitable for a variety of skill levels.

Diffusive air sampling using prepacked adsorbents in sample tubes has been used extensively in industrial hygiene applications. It has been extended successfully to other environmental applications for air and water sampling in Europe. It is currently being evaluated in the USA for unattended ambient air sampling for toxic organics and for soil gas analysis. The advent of automated thermal desorption systems has rendered this technique extremely reproducible and cost-effective [27].

6.3. Trends towards automation, more efficient sample preparation techniques, and HPLC

The environmental laboratory of the future will emphasize automation and techniques that maximize sample throughput without sacrificing data quality. The EPA has recently drafted Good Automated Laboratory Practices to document guidelines in this regard. Trends to eliminate tedious and solvent intensive sample preparation techniques (such as soxhlet extraction, liquid–liquid extraction, etc.)

and to move towards more efficient techniques such as supercritical fluid extraction (SFE) [28], solid-phase extraction (SPE) using either cartridge or disk [29], and using HPLC (on-line through column switching or off-line using adsorption or GPC columns) are evident.

More HPLC methods are expected because of the advantages of the technique over GC for a large number of environmental pollutants. The EPA Office of Water must regulate an additional 25 compounds in drinking water every three years, and this may be an additional driving force to use HPLC for water testing. As requirements to monitor large numbers of compounds continue to grow, HPLC–MS will be preferred because of the broad-spectrum applicability and confirmatory nature of the technique.

7. DISCUSSION

Choosing an EPA method to match the analytical requirements can be a difficult task. Generally, the program areas require the use of their own methods or other well-established testing procedures such as ASTM methods or Standard Methods for the Examination of Water and Wastewater [30]. The RCRA program recently clarified in which cases the SW-846 methods must be used and the conditions under which more flexibility is allowed [31]. Generally the analyst must make a choice based on knowledge of the EPA program area involved and the concentration levels on which a decision might eventually be based. Until the EMMC is able to simplify the base of methods from which to choose, this will continue to be a task requiring careful consideration. This paper facilitates method selection by compiling all the methods for different programs under one cover, categorized by program and detection techniques.

In the past the EPA has been criticized for slow adoption of new technology. The EPA methods are well established and many have been in use for over 10 years, however the EPA moves slowly into new analytical technology because of the diversity of method users. Many private laboratories employ a variety of skill levels for sample preparation and instrument operation. Thus the methods, in addition to being accurate and precise, must be demonstrated to be rugged through time-consuming in-

terlaboratory studies before promulgation. However, changes in this regard are evident in recent years. Newer technologies, such as HPLC–MS, solid-phase extraction disks, and thermal desorption–GC are being added to the EPA's repertoire of methods in quickening pace, thus increasing the number of tools available to the environmental analyst.

8. ACKNOWLEDGEMENTS

The authors would like to thank the following people for many helpful discussions: Anneliese Lust and John Purcell of Perkin-Elmer, and David Friedman, Barry Lesnik and Dr. William Budde of the EPA.

REFERENCES

- 1 J. F. Ryan, *Am. Environ. Lab.*, 1 (1) (1989) 28–38.
- 2 Z. Grosser, *Environ. Test. Anal.*, 1 (5) (1992) 24–29.
- 3 *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*, Publication No. PB83-201798, National Technical Information Service (NTIS), US Department of Commerce, Springfield, VA, 1983.
- 4 US Environmental Protection Agency, *Fed. Regist.* 50 (1985) 46936; *Fed. Regist.*, 55 (1990) 30370–30373.
- 5 *Methods for the Determination of Organic Compounds in Drinking Water*, Publication No. PB89-220461, National Technical Information Service (NTIS), US Department of Commerce, Springfield, VA, 1989.
- 6 *Methods for the Determination of Organic Compounds in Drinking Water, Supplement 1*, Publication No. PB91-146027, National Technical Information Service (NTIS), US Department of Commerce, Springfield, VA, 1991.
- 7 *Methods for the Chemical Analysis of Water and Wastes*, Publication No. PB84-128677, National Technical Information Service (NTIS), US Department of Commerce, Springfield, VA.
- 8 *Test Methods for Evaluating Solid Waste (SW-846)*, Publication No. 955-001-00000-1, 3rd edition, Government Printing Office, Superintendent of Documents, Washington, DC, 1990.
- 9 *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, Publication No. PB90-127374, National Technical Information Service (NTIS), US Department of Commerce, Springfield, VA, 1988.
- 10 D. J. Munch, R. L. Graves, R. A. Maxey and T. M. Engel, *Environ. Sci. Technol.*, 24 (10) (1990) 1446–1451.
- 11 T. E. Fielding, W. A. Telliard, J. King, L. Riddick, S. Mitchell and D. R. Rushneck, *Environ. Lab.*, 4 (3) (1992) 18–24.
- 12 B. Lesnik, *Environ. Lab.*, 1 (2) (1989) 19–21.
- 13 A. Bianci, M. S. Varney and J. Phillips, *J. Chromatogr.*, 467 (1989) 111–128.
- 14 M. W. Dong, Z. A. Grosser, D. Hockman and J. T. Bychowski, *Environ. Lab.*, 3 (2) (1991) 13–16.

- 15 B. Lesnik, *Environ. Lab.*, 2 (2) (1990) 18–21.
- 16 B. Lesnik, *Environ. Lab.*, 4 (3) (1992) 40–43.
- 17 J. F. Lawrence (Editor), *Liquid Chromatography in Environmental Analysis*, Humana Press, Clifton, NJ, 1984.
- 18 M. W. Dong and A. Greenberg, *J. Liq. Chromatogr.*, 11 (1988) 1887–1905.
- 19 T. A. Bellar and W. L. Budde, *Anal. Chem.*, 60 (1988) 2076–2083.
- 20 Environmental Monitoring and Support Laboratory, *Measurement of N-methyl Carbamoyloximes and N-methyl Carbamates in Drinking Water by Direct Aqueous Injection HPLC with Post-Column Derivatization, EPA Method 531.1*, US Environmental Protection Agency, Cincinnati, OH, 1989.
- 21 *Good Automated Laboratory Practices, Recommendations for Ensuring Data Integrity in Automated Laboratory Operations, With Implementation Guidance*, Office of Information Resources Management, Environmental Protection Agency, Research Triangle Park, NC, 1990.
- 22 R. C. Splinter, *Environ. Test. Anal.*, 1 (3) (1992) 29–33.
- 23 R. A. Hites, *Environ. Sci. Technol.*, 26 (7) (1992) 1285–1287.
- 24 D. Friedman and J. Poppiti, *J. Chromatogr. Sci.*, 28 (1990) 450–452.
- 25 D. Friedman, *Environ. Lab.*, 4 (2) (1992) 20–30.
- 26 F. R. Dow, *Environ. Test. Anal.*, 1 (5) (1992) 38–42.
- 27 T. C. Voice and B. Kolb, *Environ. Sci. Technol.*, 27 (1993) in press.
- 28 V. Lopez-Avila, N. S. Dodhiwala and W. F. Beckert, *J. Chromatogr. Sci.*, 28 (1990) 468–476.
- 29 G. S. Junk and J. J. Richard, *Anal. Chem.*, 60 (1988) 451–454.
- 30 M. A. Franson, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 18th ed., 1992.
- 31 *Fed. Reg.*, 54 (1989) 40260.