Environmental Analytical Methods For Organics and Metals

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THE CHEMISTRY IS RIGHT!

INTRODUCTION

This course is designed for the segment of the environmental engineering community involved in site assessment activities. Although the techniques discussed apply in general to drinking water analysis and wastewater analysis, the emphasis is on methods for the analysis of groundwater, soil and solid waste. These methods are documented in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW846, USEPA/OSW.

For organics we will focus on EPA Methods 8260, 8270, and 8081/8082, but other techniques will also be reviewed. Methods for the measurement of petroleum hydrocarbons are covered in a separate course entitled **Petroleum Hydrocarbons and Petroleum Hydrocarbons Measurements.**

For metals we will focus on EPA 7000 series methods and Method 6010.

Our curriculum objectives are to:

1. Develop an understanding of the principles of each analysis and describe the measurement system.
2. Develop functional understanding of laboratory procedures.
3. Detail QA audits associated with each analysis and describe their meaning.
4. Provide method statistics for precision, accuracy and sensitivity.
5. Detail factors for methods selection.
6. Provide instruction for sampling, preservation and containers.

After completing the course the site professional should:

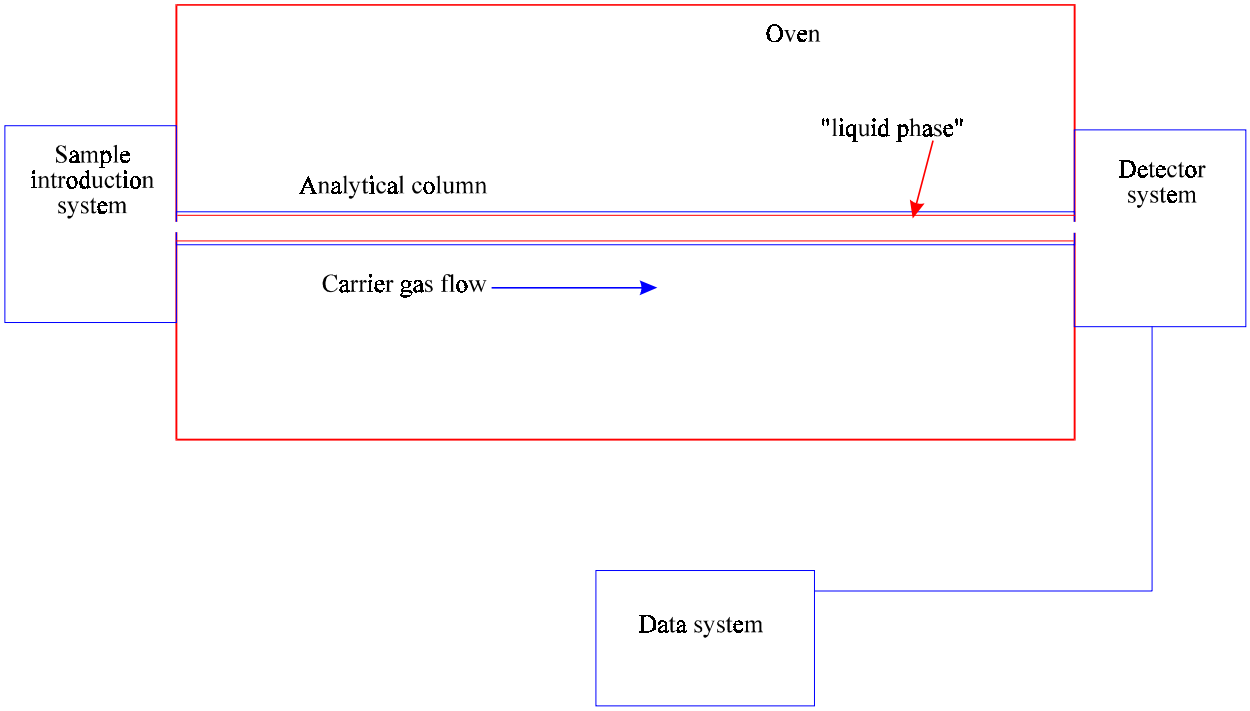
1. Have a working understanding of the analytical methods.
2. Know the scope and limits of the analyses.
3. Be able to specify analyses and deliverables.
4. Be able to interpret QC audit information in reports.
5. Be able to properly collect samples for specific analyses.

This course is approved for 8 technical credits by the Massachusetts Board of Registration of Hazardous Waste Site Cleanup Professionals.

Gas Chromatography

General Instrumentation

A gas chromatograph has four basic components: a sample introduction system, a column/oven assembly, a detector system, and a data system.



1. The sample introduction system is a device that presents the sample to the GC column. The simplest example is the injection port – a heated cylinder with a rubber septum for injecting sample with a syringe. The sample's components are volatilized in the injection port and swept onto the column by the carrier gas.

2. The carrier gas flows through the column. The components are absorbed on a material in the column called the *liquid phase*. The liquid phase is typically coated on the wall of a narrow, open-tubular column, which is 15 to 60 meters in length. This column is coiled inside a temperature-programmable oven.

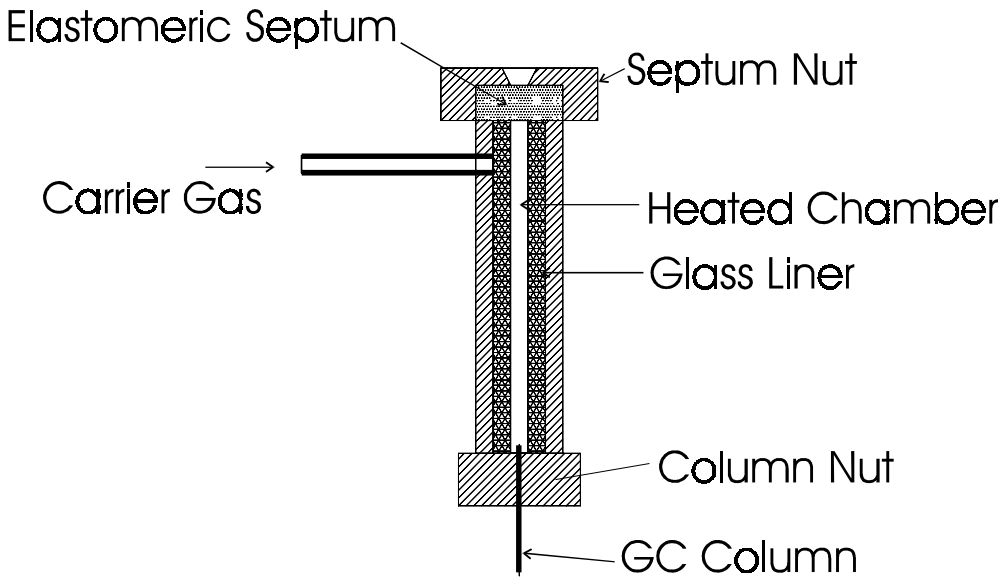
3. As time passes, the components migrate through the column at different rates and enter the detector – ideally as individual components. The detector senses

the presence of the component and sends a response to the data system in the form of a voltage. The voltage varies with component identity and concentration.

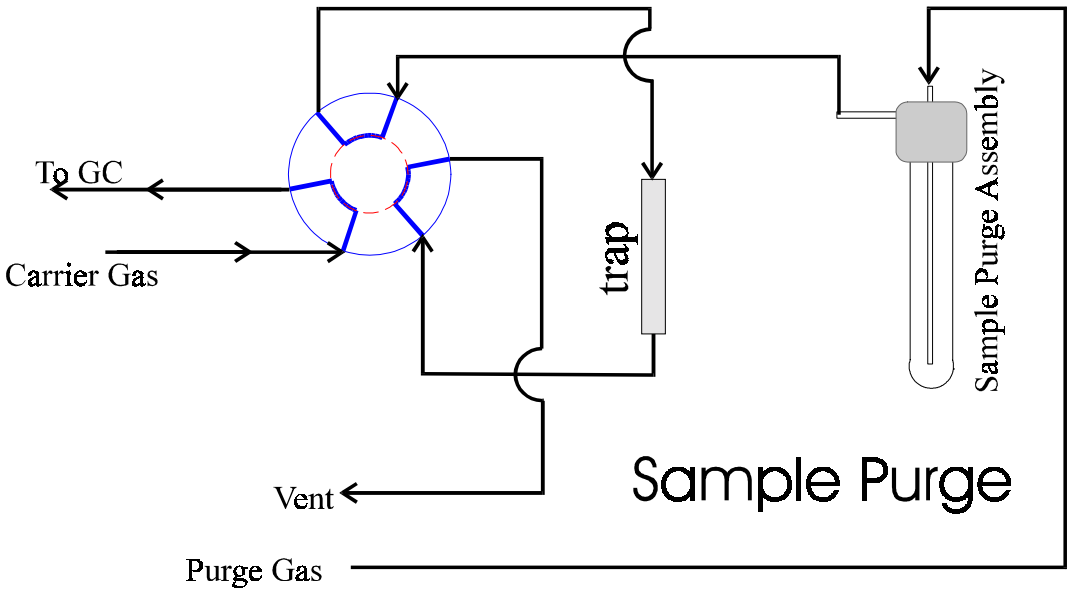
4. The data system records the detector output and usually provides data analysis software. Instrument control through the data system is common.

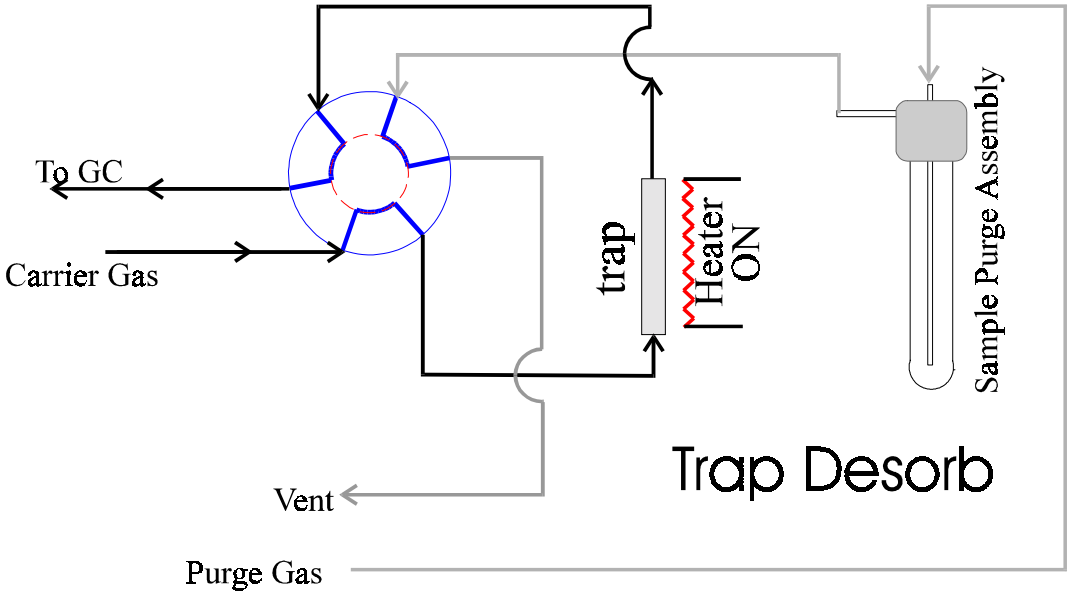
Sample Introduction Systems

The simplest sample introduction device is the injection port. The device is a heated chamber with an elastomeric septum for injecting a sample with a syringe. The sample is injected through the septum into a heated chamber where it is flash-volatilized. The chamber components are swept onto the GC column by the carrier gas. Typically, solvent solutions of analytes are injected where injected volume is between 1 µl and 10 µl.



Another common sample introduction device is the purge and trap sampler. This technique is used in the analysis of volatile components. The sample is sparged with helium in a purging chamber. The helium – laden with volatile components from the sample – is passed through an absorbent trap where the components are retained. After a fixed period of time – typically 11 to 15 min. – the helium flow through the trap is reversed and directed onto the GC column. The trap is simultaneously heated to desorb the sample components.


To GC
Carrier Gas
trap
Sample Purge Assembly
Vent
Sample Purge
Purge Gas


To GC
Carrier Gas
trap
Heater ON
Sample Purge Assembly
Vent
Trap Desorb
Purge Gas

Detector Systems

There are several detector types.

- Flame ionization detector (FID): Responds to compounds that produce ions when burned in a hydrogen-air flame. It will detect all organics, but some have poor response (for example, perchlorinated alkanes, carbon disulfide and formic acid).

- Photo-ionization detector (PID): Responds to compounds that produce ions when irradiated by a UV source. Responds well to aromatics and poorly to alkanes.

- Electrolytic conductivity detector (ELCD): Responds to compounds that undergo electrolysis and produce conductive ions. Halogenated compounds are well-detected.

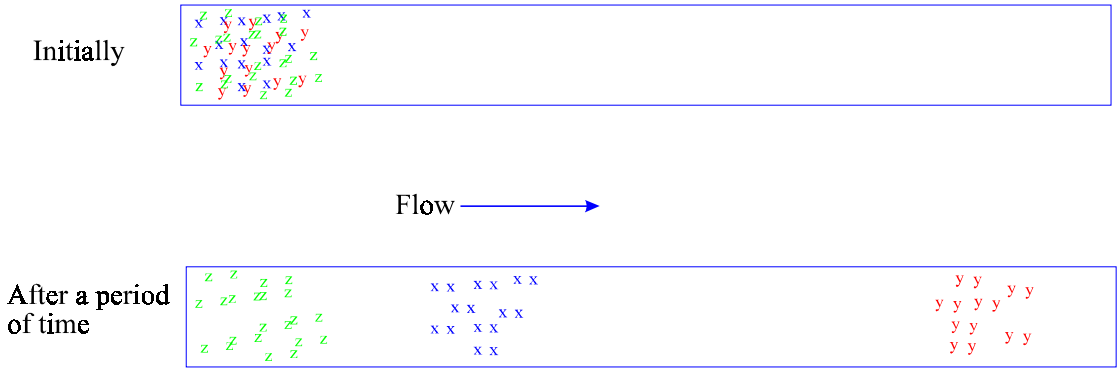
- Electron capture detector (ECD): Responds to compounds which "capture" β particles emitted by a ^{63}Ni source. The ECD is very sensitive to halogenated compounds. Sulfur and oxygen functional organics also respond.

- Nitrogen phosphorus detector (NPD): Responds to compounds that are ionized by a rubidium salt-based thermionic source. Nitrogen and phosphorus compounds are detected almost selectively.

- Thermal conductivity detector (hot wire): Senses differences in thermal conductivity between a reference gas and the analyte. This low-sensitivity detector is useful in fixed gases analysis (N_2, H_2, CO, CO_2, H_2S, etc.).

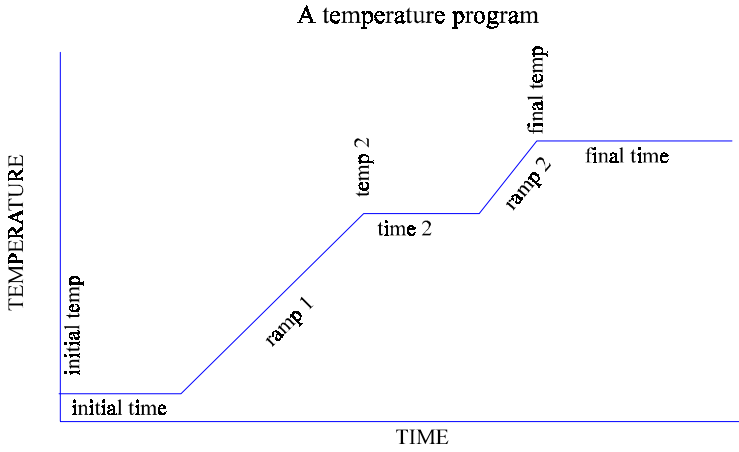
- Mass spectrometer: Provides a mass spectrum for each peak in the chromatographic profile. Discussed in detail later.

Component Separation

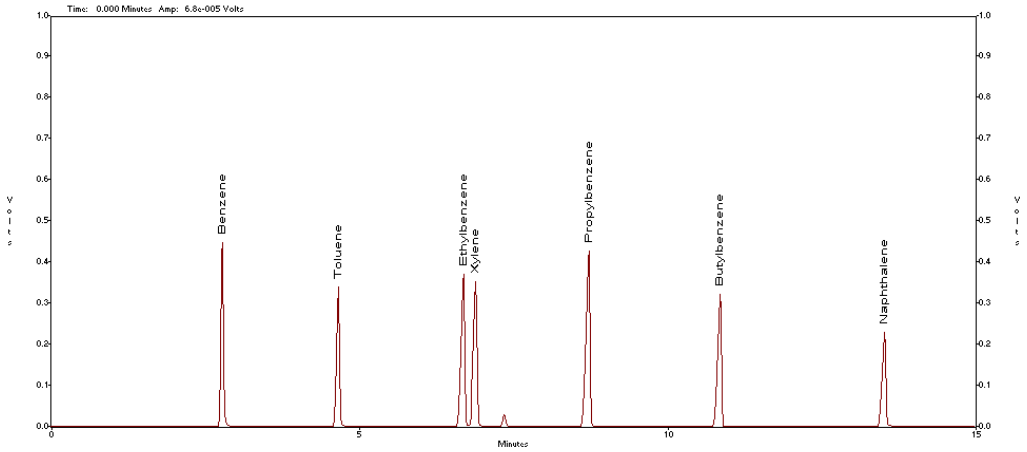


Immediately after sample introduction, all mixture components are concentrated at the column inlet. As time passes, components migrate at varied rates through the column. The degree to which a component is retained by the column depends upon its affinity for the liquid phase coated on the column compared with the component's affinity for the gas phase flowing through the column. The less volatile components – those with lower vapor pressures – move more slowly through the column.

The time required for a given component to move through the column to the detector is the component's *retention time*. The retention time for a component decreases with increasing temperature. The gas chromatograph's oven is usually programmed to rise in a specified temperature program to accomplish the separation of the analytes of interest.

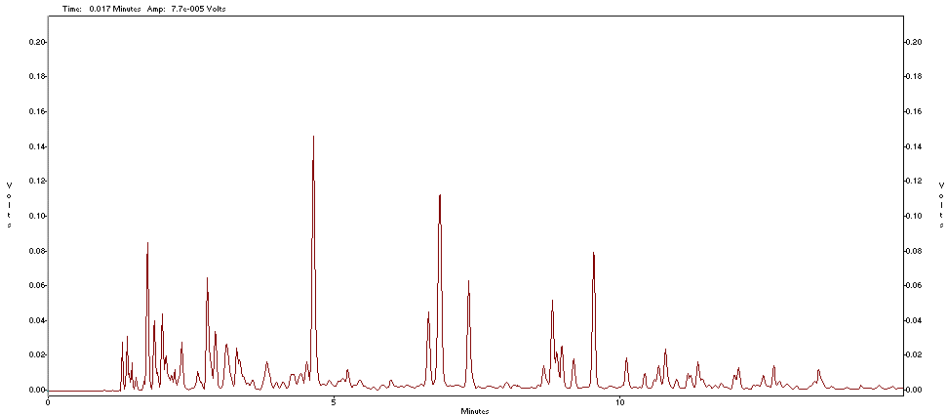


A typical chromatogram is presented below. The x-axis is a time scale. The y-axis is a voltage scale. The retention time for toluene in this example is 4.66 min.



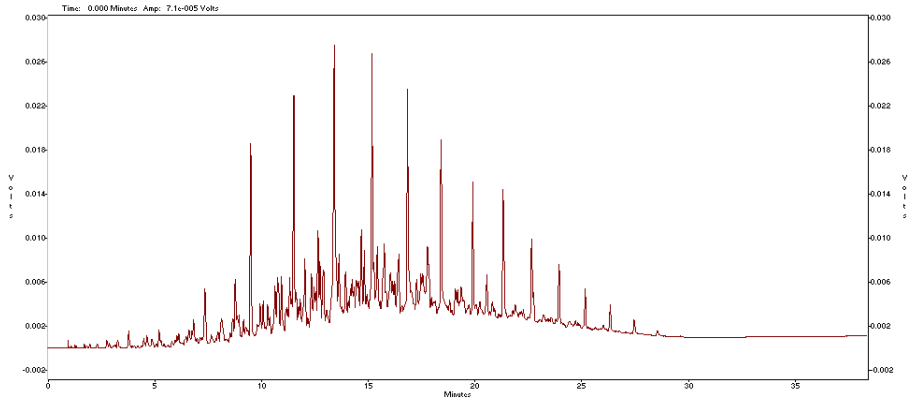
The area under any given peak is a function of the mass of the component passing through the detector. This property can be used to perform quantitative analysis. A sufficiently high concentration of a given component will saturate the detector and the mass/area function will become unreliable.

Below is a chromatogram for gasoline. Note that many of the component peaks in this profile are not completely separated from one another. These compounds are said to be partially resolved. When two peaks have the same retention time they are said to co-elute.



Conventional Detector Uncertainties

Real-world samples seldom have chromatographic component profiles where the peaks are all fully resolved. The baseline is rarely a straight horizontal line. The example below is a typical diesel fuel profile.



When integrating a peak to obtain an area for quantitative analysis, a decision must be made as to where the peak begins and ends. One must also decide where the baseline should be drawn.

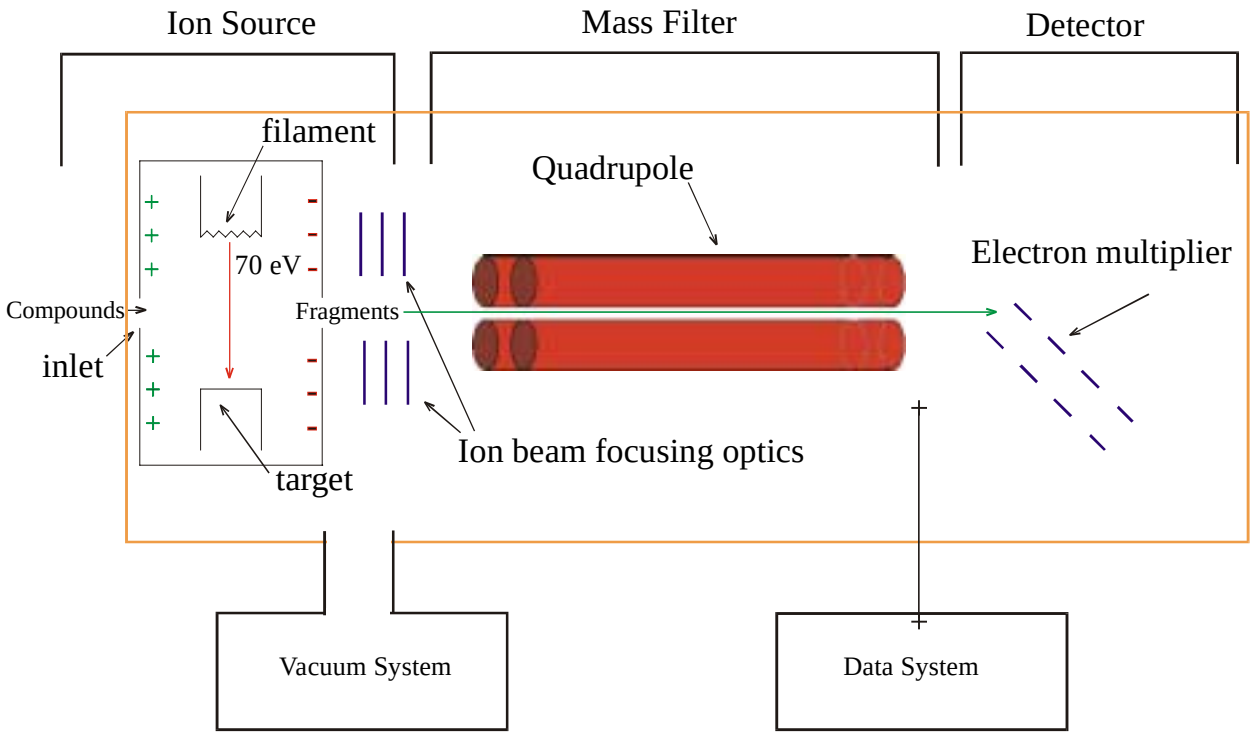
The profile above is riddled with peaks. Almost any retention time is likely to have a peak. Conventional detectors rely on retention time alone for qualitative analysis. Clearly, conventional detectors are not adequate for many environmental analytical problems.

Mass Spectrometry

Interfacing the gas chromatograph with a mass spectrometer solves the problems discussed above. The mass spectrometer is a separate instrument which can "fingerprint" a component for positive identification. Also, the mass spectrometer can be used as a compound-selective detector.

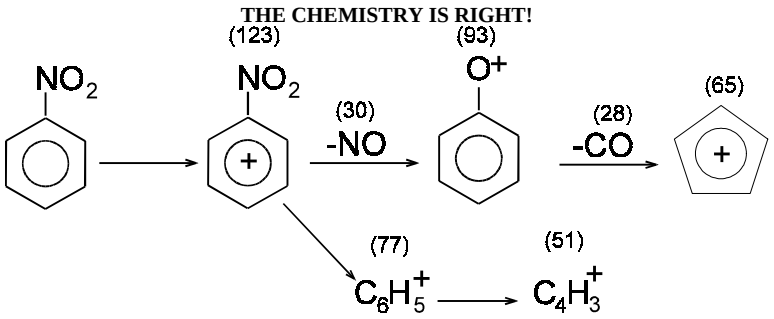
The mass spectrometer has five main components: the ion source, the mass filter, the detector, the vacuum system, and the data system.

The Mass Spectrometer

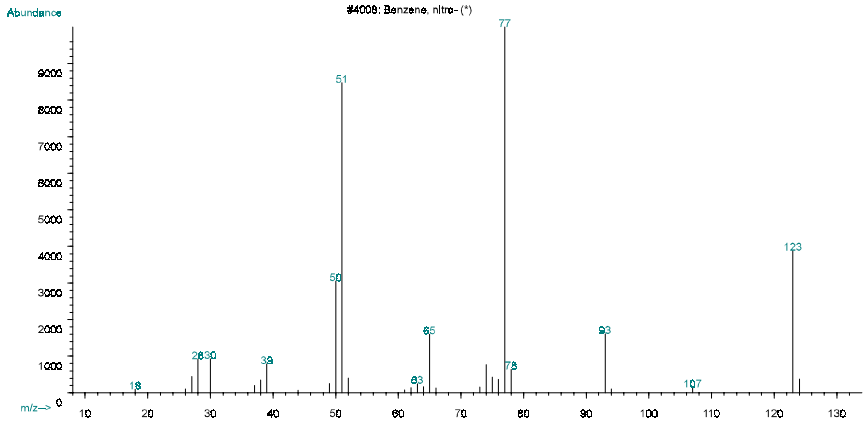


The Ion Source

As sample components enter the ion source the molecules are fragmented by a 70 eV electron beam. The fragments are electrostatically accelerated out of the ion source in a particle beam. As expected, the fragment mixture is complicated. For example, nitrobenzene undergoes the following fragmentations (there are many others):



The fragmentation process in the ion source generates a reproducible, characteristic mixture of fragments for a given compound. When the abundances of these fragments are plotted *vs.* their masses, a mass spectrum results:



The Mass Filter

The mass filter – depending upon the type – uses one of several particle deflection techniques to restrict the fragments emerging from the filter at any given time to fragments having a specific charge-to-mass ratio. Usually the operating characteristics of the filter are varied over time to produce a sequential *scanning* of selected fragment masses over a specified mass range. For example, a one-second scan covering masses between 35 amu and 500 amu is common.

The Detector

The detector senses the ion level emerging from the mass filter over time.

The Vacuum System

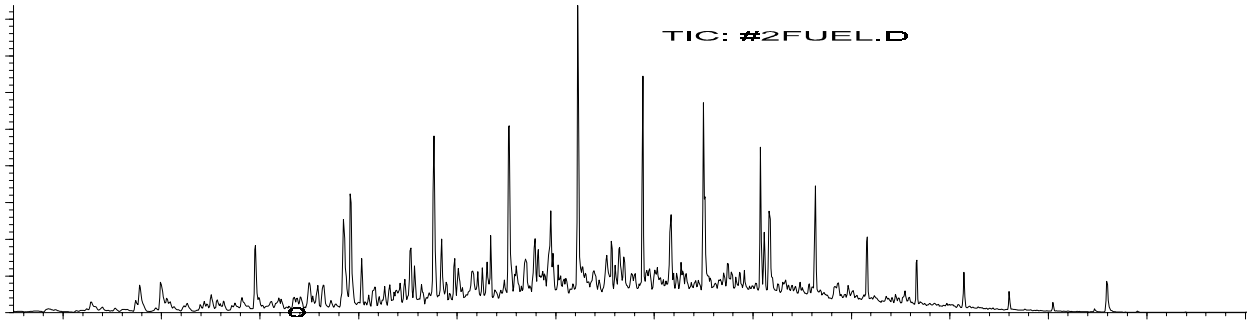
The entire mass spectrometer assembly is maintained under a high vacuum (10^{-6} mm Hg is typical). None of the system components will operate properly without this high vacuum.

The Data System

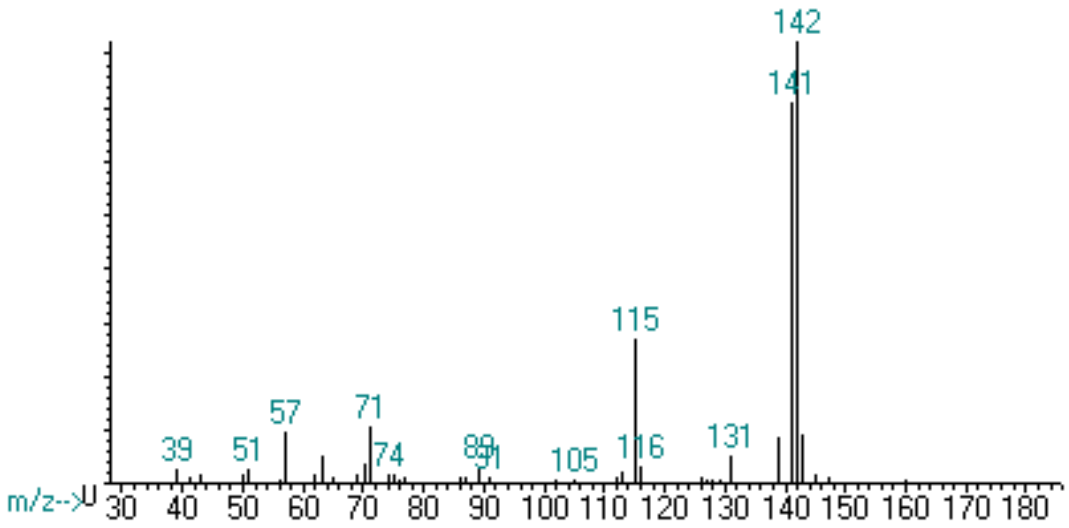
The data system controls the mass spectrometer instrumentation and collects, stores and processes instrument output.

Gas Chromatography/Mass Spectrometry

The mass spectrometer may be used as a detector on a gas chromatograph. Recall that the mass spectrometer performs a scan every second or so. If sequential scans are stored, a chromatogram can be obtained by summing the abundances of all the ions in each scan and plotting this total versus time. This type of chromatogram is called a Total Ion Chromatogram or TIC. The following is an example of a TIC for a fuel oil sample:

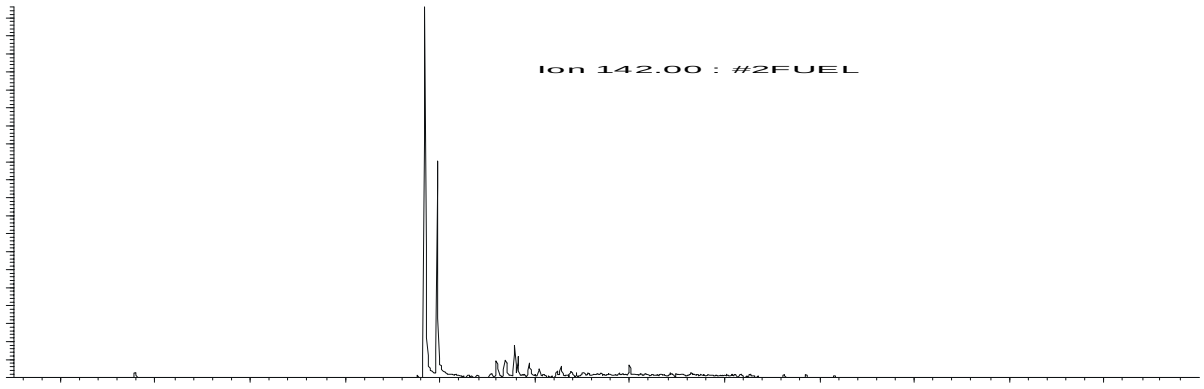


The analyst can prompt the data system to display the actual mass spectrum corresponding to any point in the chromatogram. For example, the spectrum corresponding to the point at 13.69 minutes is presented below:



The identity of any given peak in the chromatogram can be determined either by direct interpretation of the spectrum or by matching the spectrum with a spectral database. The spectrum above is the mass spectrum for methylnaphthalene.

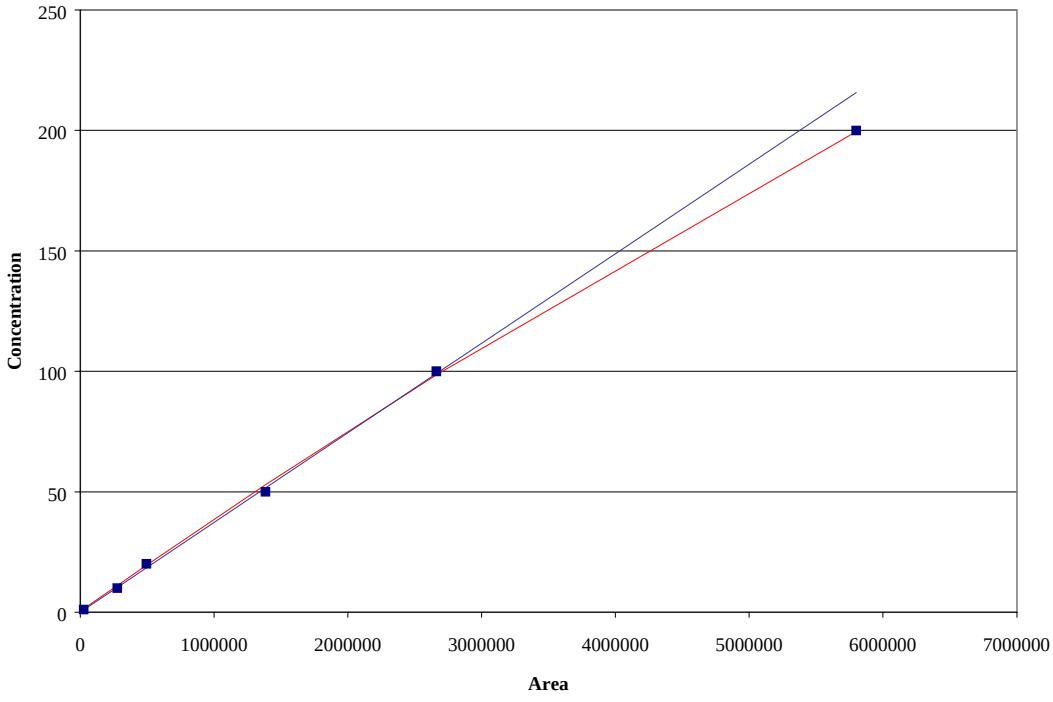
In addition to the TIC, chromatograms for specific ions can be obtained. These Extracted Ion Current Profiles, or EICPs, provide reasonably selective, baseline-resolved peaks for integration. Using these EICPs to identify compounds improves compound detection limits significantly. The following is an ECIP for ion 142, the base peak for methylnaphthalene. Note that both isomers are present in the profile.



Calibration

We can prepare a calibration graph for any given component by plotting peak areas from chromatograms of standards at various concentrations. The resulting graph may be used to quantify unknown samples. The points on the graph are actual data points. The blue line is an average response line for the data. The red line – the better fit in this case – is a quadratic fit. The calibration range in this case is 0 to 200 ug/l.

Concentration	Area	Response Factor
1	26185	26185
10	275254	27525
20	494143	24707
50	1383848	27677
100	2662098	26621
200	5800000	29000



This type of calibration is called an external standard calibration.

The terms "response factor, RF" and "average response factor, $\overline{RF}$" are defined as follows:

RF = area of a component/concentration of a component

The average response factor is the average of the response factors for all calibration points.

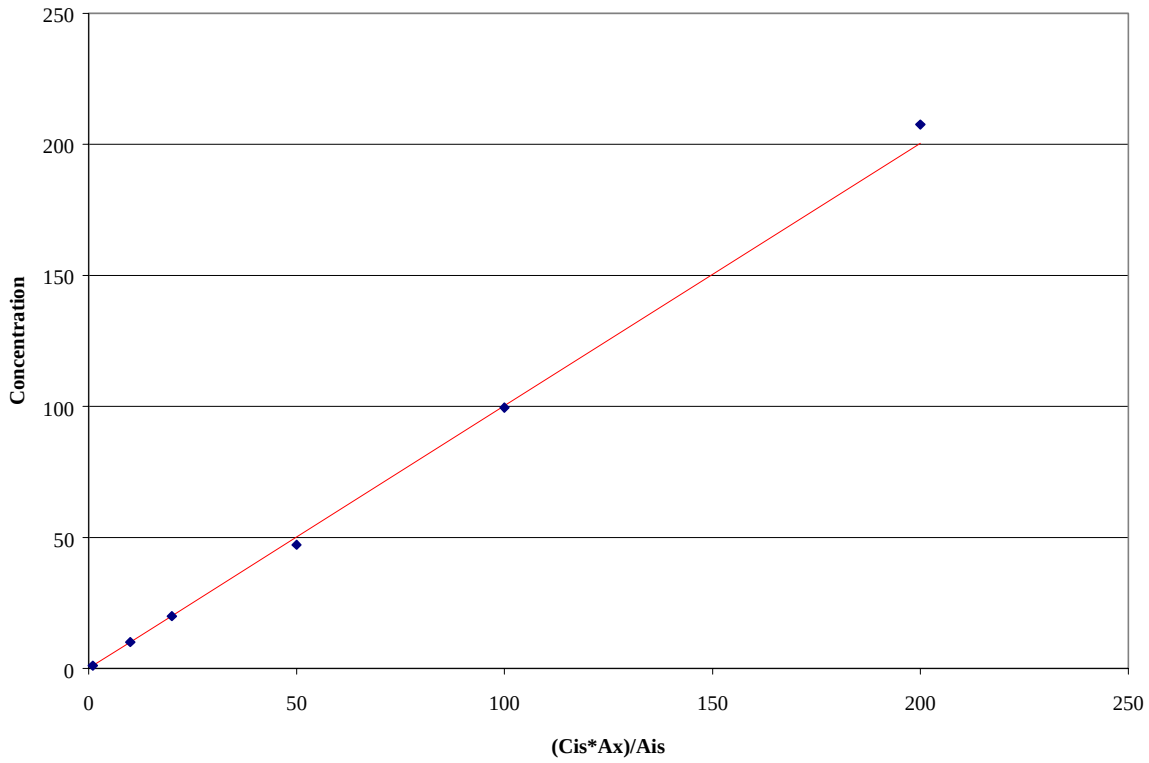
External standard calibrations drift over time, primarily because of changes in the detector's responsiveness. The useful lifetime of a calibration can be extended – and errors due to variations in the injected volume of standards and samples may be minimized – using the technique of internal standard calibration. In this technique an additional component – the internal standard – is added to all samples and standards. The concentration of this standard is a constant in all runs. In the calibration graph, the product of the component area and the internal standard concentration divided by the area of the internal standard is plotted against concentration. The effect is that all responses are normalized using the area of a fixed concentration of internal standard. In theory, as the detector's sensitivity changes for the analyte, it changes for the internal standard to the same degree and the ratio of the areas remains the same. It works! Internal standard calibrations have been known to remain valid for months.

For example, let's say the following standards have been prepared and analyzed:

Standard #	Concentration of Internal Standard, ug/ml	Concentration of Toluene, ug/ml	Area of Internal Standard Peak	Area of Toluene Peak
1	50	1	1263140	26185
2	50	10	1369624	275254
3	50	20	1239224	494143
4	50	50	1467653	1383848
5	50	100	1337526	2662098
6	50	200	1395545	5791499

The calibration graph for the internal standard normalized data is presented below. The red line represents the average response function. This is the same data used

to create the previous external standard example. Note that the quadratic fit is not needed in this case.



The term response factor is also used for internal standard calibrations, but it is defined as:

$$RF = (A_x \text{ X } C_{is})/(A_{is} \text{ X } C_x)$$

where:
A_x = Peak area of the analyte
A_{is} = Peak area of the internal standard
C_x = Concentration of the analyte
C_{is} = Concentration of the internal standard

EPA Methods Employing GC and GC/MS

History

The first EPA methods for organics analysis were wastewater methods. The Clean Water Act provided EPA with the regulatory authority to develop a system for preventing deterioration of the nation's waterways from pollution arising from wastewater discharges. The EPA developed a wastewater discharge permitting system (NPDES) which has a periodic monitoring requirement for permitees. In the late 1970s the EPA Environmental Monitoring and Support Laboratory in Cincinnati developed several techniques for various analyses. These methods – still in use today for wastewater testing – are GC and GC/MS techniques. They all have “600” series method numbers.

The primary techniques were EPA Method 624 for Volatile Organics, EPA Method 625 for Acid and Base/Neutral Extractable Organics, and EPA Method 608 for Organochlorine Pesticides and PCBs. Because EPA Methods 624 and 625 required a gas chromatograph/mass spectrometer – a very expensive instrument in the late 1970s – several alternative methods were developed that used less expensive conventional detectors for the analysis of specific categories of 624 and 625 analytes. The more commonly used were Method 601 for Volatile Halocarbons (uses an ELCD) and Method 602 for Volatile Aromatics (uses a PID).

Method 608 uses an electron capture detector (ECD) for the measurement of Organochlorine Pesticides and PCBs. This method was necessary to achieve the very low detection limit requirements needed to adequately monitor these compounds.

SW846

The EPA Office of Solid Waste used the 600 series test methods as a starting point in developing methods for groundwater, soil, solid waste, etc. The resulting methods were given “8000” series numbers and were documented in their methods manual entitled: *Test Methods for Evaluating Solid Waste* (commonly called SW846). As time passed, these methods were refined to better address analysis in the soil, groundwater, etc. matrix and to provide more substantial QA/QC procedures for the tests. The following table shows the general correlations between the wastewater and SW846 methods

Analytical Objective	Wastewater Method	SW846 Method, Original	SW846 Method, Revised
Volatile Organics	624	8240	8260
Acid/Base Neutral Extractables (Semivolatiles)	625	8250	8270
Organochlorine Pesticides and PCBs	608	8080	8081 and 8082

There are many other methods for Organics in SW846, most of which are conventional detector techniques for measuring analytes already covered by 8260 and 8270.

CLP Protocols

Laboratories providing services to the EPA do so under a government contract: the Contract Laboratory Program (CLP). Like all government contracts, EPA laboratory contracts have a statement-of-work. This section of the contract specifies what testing is to be done, how it is to be done, and how results are to be reported. The EPA commonly uses the analytical results to support its enforcement efforts, and the focus of the test protocols is the provision of evidence, but the methods themselves employ the same fundamental analytical strategy as the 8260, 8270, and 8080 methods.

Drinking Water Methods

Drinking water quality is monitored for compliance with the Primary Drinking Water Standard using a variety of organics analysis methods. These methods have "500" series numbers and include methods for low-level VOCs (524), certain semivolatiles (525) and a unique list of pesticides (505/508).

Target Analyte Lists

EPA's SW methods provide a list of compounds which **can (or may)** be analyzed by the technique. There is no method-required target analyte list. The compounds

to be measured and reported vary with application and should be determined by the end user of the data. The Contract Laboratory Program does have a required list of compounds, commonly referred to as the Target Compound List or TCL.

Lists of reported compounds for organics analyses vary considerably among laboratories. For general site investigation efforts, be sure your lab's list includes the TCL compounds. Also, consider library searching some fixed number (10-20 is typical) of non-target compounds as part of your analytical request.

Method Selection

EPA Methods 8260 (VOCs), 8270 (SVOCs) and 8082 (PCBs) are the primary tools for site investigation and site remediation work. Occasionally, conventional detector techniques for VOCs may be used for ongoing groundwater remediation process monitoring after (and only after) the site has been fully characterized using the 8260 technique.

If very low detection limits (e.g. 0.05 to 0.1 ppb for benzene) in groundwater are needed, consider the drinking water methods for VOCs and PNAs (524 and 525), but don't specify these methods if there is any sign of gross contamination.

Use CLP protocols when the analysis will provide evidence in the courtroom.

Volatile *vs*. Semivolatile Ranges

The terms volatile and semivolatile are arbitrary. Volatile organics are those which are analyzed using a purge and trap sample introduction technique. The range of compounds begins with gasses like vinyl chloride and extends to naphthalene. Semivolatile organics are analyzed by solvent extraction followed by direct injection. The semivolatile range begins with components having a vapor pressure similar to naphthalene and extends to compounds having very low vapor pressures like benzo (g,h,i) perylene.

EPA Method 8260

The current revision of Method 8260 is EPA Method 8260B. The method describes the protocol for the "determinative" steps in the analysis of VOCs.

Sample preparation/introduction methods – once covered in the previous versions of Method 8260 – are now described in other EPA methods.

Method 5030B

This method is the most current for the purge and trap introduction of volatiles from water samples. The technique involves sparging a 5-ml water sample (an earlier version of the method included a provision for the analysis of soils where a 5-gram soil sample was suspended in reagent water and sparged).

Water samples are collected in duplicate in 40-ml vials having Teflon-lined silicone rubber septa fitted into the cap. Care must be taken in sampling to avoid unnecessary agitation of the sample. When sealed, the vial must contain no air bubbles or headspace.

The method requires that the pH of the sample be adjusted to <2 at the time of sampling. However, usually the lab provides vials pre-preserved with a few drops of 1:1 HCl. Although unlikely in non-wastewater applications, residual chlorine must also be destroyed by adding 4 drops of 10% sodium thiosulfate solution to each sample.

Method 5035

This method is for the analysis of soils and gives three options for analysis:

- Low concentration soil method:

This procedure begins in the field when samples are taken. A separate sample is collected for solids analysis. The sample container is a pre-weighed vial with a magnetic stirring bar and sodium bisulfite preservative added. In the field, 5 grams of soil are added to the vial. Ideally, the sampler has a portable balance. In the lab, reagent water (and internal standards, etc.) are added without opening the vial. The sample is heated to 40°C and sparged while being stirred. The range for analyte concentration is 0.5 to 200 ug/kg.

- High-level method:

For this option, the soil is collected in a glass container with a Teflon-lined cap. In the lab, a portion of the soil is extracted with methanol. The methanol is then spiked into reagent water and analyzed by Method 5030. The range for analyte concentration is 25 ug/kg and up.

- High-level method with methanol preservation:

This procedure also begins in the field when samples are taken. A separate sample is collected for solids analysis. The sample container is a pre-weighed vial containing 10 ml methanol. In the field, 5 grams of soil are added to the vial. Again, the sampler should have a portable balance. The range for analyte concentration is 50 ug/kg and up.

Other Methods

Several other methods for introducing sample for Method 8260 analysis are available including: direct injection, dilution/direct injection, thermal desorption of air sampling tubes, and direct analysis of air in Tedlar bags.

The Determinative Steps – Method 8260

Initial Calibration Procedures

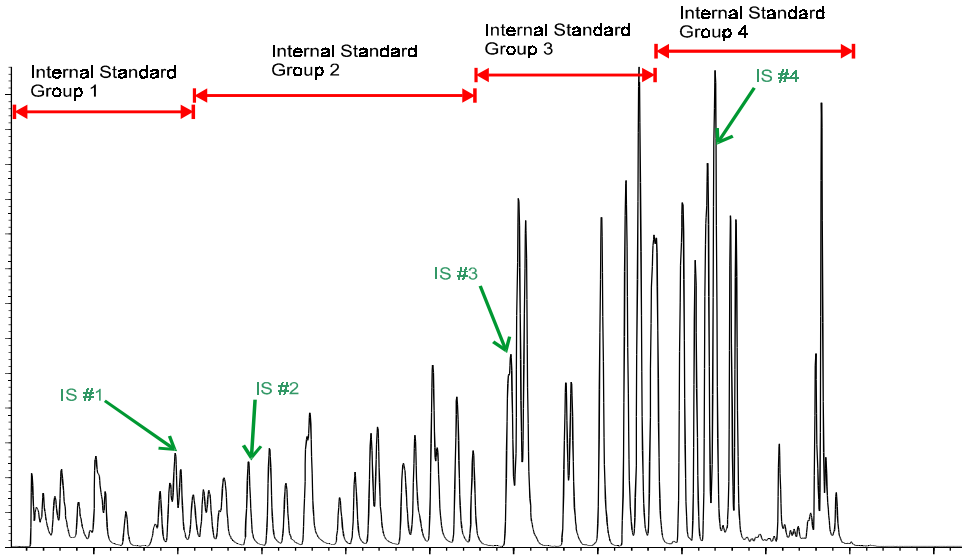
Prior to performing any analyses by this method the mass spectrometer is tuned so that it produces mass spectra that are consistent with a standard. Conformance with the standard is verified by obtaining a spectrum for bromofluorobenzene and comparing it to a specification.

BFB MASS - INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)

Mass	Intensity Required (relative abundance)
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than l0l% of mass 174
177	5 to 9% of mass 176

Failure to meet this specification – unless the failure is severe – has little to do with the reliability of test results. Generating mass spectra that are consistent with the standard is technically relevant only when library searching of non-target analytes is being performed.

EPA Method 8260 uses a five-point internal standard calibration. To obtain the calibration, a standard containing all of the compounds of interest is analyzed at five levels. Each run is spiked with an internal standard mixture. Compounds are grouped according to which internal standard they are associated with.



Laboratories are allowed to choose which compounds they use for internal standards. In the example above, the following internal standards are present:

Internal Standard #1:	Pentafluorobenzene
Internal Standard #2:	1,4-Difluorobenzene
Internal Standard #3:	Chlorobenzene-d5
Internal Standard #4:	1,4-Dichlorobenzene-d4

Response factors for each compound are calculated for each of the five calibration levels. The following table presents data for one internal standard group of a typical calibration. The areas are calculated from extracted ion current profiles for the compound's quantitation ion and not the total ion chromatogram. The method recommends a quantitation ion for each compound.

	Level, ug/l						
Compound	5.0	20	50	100	200	Avg	%RSD
1,4-Difluorobenzene	ISTD						
1,1-Dichloropropene	0.437	0.428	0.459	0.455	0.444	0.444	2.85
Carbon Tetrachloride	0.522	0.528	0.601	0.562	0.578	0.558	6.00
1,2-Dichloroethane-D4	0.326	0.314	0.328	0.331	0.317	0.323	2.33
Benzene	0.752	0.740	0.790	0.793	0.778	0.771	3.05
1,2-Dichloroethane	0.372	0.360	0.366	0.379	0.351	0.365	2.86
Trichloroethene	0.427	0.414	0.439	0.442	0.433	0.431	2.60
1,2-Dichloropropane	0.346	0.336	0.347	0.358	0.341	0.345	2.35
Bromodichloromethane	0.718	0.734	0.778	0.792	0.766	0.757	4.06
Dibromomethane	0.461	0.452	0.449	0.476	0.442	0.456	2.92
MIBK	0.394	0.387	0.358	0.400	0.356	0.379	5.48
cis-1,3-Dichloroprope	0.477	0.466	0.489	0.509	0.489	0.486	3.32
Toluene-D8	0.866	0.822	0.863	0.859	0.868	0.856	2.26
Toluene	0.847	0.845	0.894	0.895	0.879	0.872	2.82
Trans-1,3-Dichloropro	0.400	0.404	0.418	0.445	0.414	0.416	4.21
Ethyl Methacrylate	0.345	0.339	0.309	0.368	0.331	0.338	6.35
1,1,2-Trichloroethane	0.348	0.340	0.339	0.353	0.338	0.344	1.93
Ethylene Dibromide	0.613	0.606	0.594	0.629	0.575	0.603	3.39

Note: Response Factor (RF)=$(A_s \times C_{is})/(A_{is} \times C_s)$

A_s = Analyte Peak Area
C_{is} = Internal Standard Concentration
A_{is} = Internal Standard Peak Area
C_s = Analyte Concentration

Initial Calibration Acceptance Criteria

Before an initial calibration can be used, certain requirements must be met. Also, the method has additional recommended guidelines.

Response Factor Specifications

The method requires that the average response factors for the following compounds meet or exceed the following minimum values:

Chloromethane	0.1
1,1-Dichloroethane	0.1
Bromoform	0.1
Chlorobenzene	0.3
1,1,2,2 Tetrachloroethane	0.3

These five compounds are called the System Performance Check Compounds or SPCCs.

Average Response Factor % Relative Standard Deviation (RSD) Specifications

The method requires that the following compounds have an Average Response Factor % RSD of 30% or lower:

1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl chloride

These six compounds are called the Calibration Check Compounds or CCCs. The method further states that the Average Response Factor % RSD for these CCCs should be less than or equal to 15%. When the response factor % RSD for any target compound is above 15%, the method requires that an average response factor not be used to determine analyte concentrations (i.e., another calibration option such as curve fitting must be used).

Retention Time Specifications

The method indicates that the retention times for any analyte should not vary by more than 0.06 RRT units throughout the various levels of the calibration.

Sample Processing

After initial calibration, samples are tested in batches. Each batch has various quality audits included.

Tune Verification

Mass spectrometer tuning verification is performed at the beginning of the batch by injecting 50 ng of BFB. The specification for this audit was discussed previously. The remainder of the batch must occur within 12 hours of this audit. That is, the batch begins with the BFB tune and lasts up to 12 hours.

Calibration verification

A mixed standard with components at the calibration's midpoint concentration is analyzed.

SPCCs

Each SPCC compound in the calibration verification standard must meet its minimum response factor criterion. This is the same check that is applied during the initial calibration.

CCCs

If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20% difference or drift) for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

Internal Standards

The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required.

If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

Method Blank

The method blank consists of laboratory water or Ottawa sand. This run should not contain any target analyte above the reporting limit.

Laboratory Control Standard (LCS)

This audit is not strictly required by the method. For volatile organics, it is essentially a second calibration verification usually prepared from a second source stock.

Reporting Limit Standard

Again not required by the method, this audit consists of a standard with analyte concentrations at or near the reporting limit. All compounds should be detected in this run.

Surrogates

Each sample is spiked with surrogate compounds prior to analysis. These compounds – typically deuterium-labeled compounds which are highly unlikely to be found in environmental samples – are quantified and their recoveries calculated. If recoveries are poor, the problem may be a malfunctioning analytical system such as an intermittent leak. However, the problem may be caused by the sample matrix itself. For example, the surrogate compound may be solvated by a highly organic matrix – leading to poor purging efficiency.

When surrogates fail criteria, protocol requires that a malfunctioning analytical system be ruled out (through analysis of blanks, standards, flow measurements, etc.) and that the sample be re-analyzed to confirm surrogate failure.

Surrogate recoveries are reported with the sample results. When a surrogate fails to meet limits, a comment as to why the failure occurs should be made. In general, a poor surrogate recovery does not indicate poor workmanship – provided control in the analytical system has been demonstrated. Rather, it indicates a problem with the application of the method to the particular sample. This is commonly referred to as a *matrix effect*.

Surrogate failure in a method blank cannot be attributed to a matrix effect.

Internal standards

The method states:
"It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance."

A good practice is to apply the same internal standard criteria used for the continuing calibration to all analytical runs.

Matrix Spike (MS) and Matrix Spike Duplicate (MSD) analyses

This audit consists of spiking two additional portions of a sample with actual target analytes and measuring their recovery and percent difference. The audit provides accuracy and precision data for the sample matrix. As with surrogates, MS/MSD audits indicate reliability of the method's application to the matrix – provided system control is demonstrated.

Qualitative Analysis

Qualitative identity of a compound is based on two parameters: retention time and mass spectrum. Specifically, the relative retention time (RRT) of the sample component must agree with the standard component within ±0.06 RRT, and the relative intensities of the characteristic ions in the sample component's mass spectrum must agree within 30% of the relative intensities of these ions in the reference spectrum.

Quantitative Analysis

The area associated with the quantification ion for the analyte is used to calculate the concentration of the analyte in the sample by employing the initial calibration function. If the concentration of the analyte is higher than that of the highest calibration point, then the sample must be re-analyzed at a dilution. The dilution chosen should yield an area for that analyte in the top half of the calibration curve. When samples contain very high levels of components a potential for system contamination exists that must be ruled out through the analysis of a compliant blank.

Periodic and Ongoing Method Evaluations

The preceding discussion covered the analytical process as well as process quality control audits. However, these alone are not sufficient for generating data of known reliability. A laboratory's QA program must provide for establishing process limits for certain critical quality attributes, including sensitivity (detection limits), accuracy and precision.

Method Demonstrations

Each analyst is required to demonstrate ability to obtain results within the precision and accuracy guidelines given in the method. This demonstration consists of carrying a standard through all sample preparation and analysis steps in quadruplicate. The mean recovery and the relative standard deviation are determined for each analyte. These results are compared with method guidelines.

Detection Limits

The concept of detection limit is confusing for most data end-users. The term Detection Limit is defined in 40 CFR 136, Appendix B:

> "The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero."

40 CFR 136, Appendix B also specifies the procedure to be used in determining the detection limit. Again, a series of standards is carried through all preparation and analysis steps. This time the number of replicates is seven. The concentration of each analyte in the standard is set to be between 3 and 5 times the detection limit. Obviously, this is an iterative procedure if the approximate detection limit is not known in advance.

A standard deviation is obtained for the seven replicates. The detection limit is defined as 3.143 X STD DEV. (Note: the value 3.143 is the Student t value for 99% confidence and 6 degrees of freedom.)

Surrogate Recovery Limits, LCS Recovery Limits, and MS/MSD Recovery and Relative Percent Difference Limits

These limits are determined from historical data for each given matrix. The limits are initially established from a sample of results obtained while the process is

known to be in control. The actual limits are obtained using the Student t test for 99% confidence. For example, let's say we have seven LCS recovery results for benzene. The LCS recovery acceptance limits are:

Lower limit = mean recovery - 3.143 X STD DEV
Upper limit = mean recovery + 3.143 X STD DEV

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Typical 8260 MDLs

Compound	Water, ug/l	5035 soil medium level, ug/kg	5035 soil low level, ug/kg
	5 ml sample	1:1 Methanol, 100 ul spike	5 gram sample
Dichlorodifluoromethane	1.1	56	3.4
Chloromethane	1.3	64	3.8
Vinyl Chloride	2.2	110	6.6
Bromomethane	1.0	48	2.9
Chloroethane	1.1	57	3.4
Acetone	3.9	195	11.7
1,1-Dichloroethene	0.7	33	2.0
Carbon Disulfide	0.7	37	2.2
Methylene Chloride	0.7	37	2.2
tert-butyl Methyl Ether	0.3	16	0.9
trans-1,2 Dichloroethene	0.6	30	1.8
1,1-Dichloroethane	0.5	27	1.6
2-Butanone	2.0	98	5.9
2,2-Dichloropropane	1.0	49	2.9
cis-1,2-Dichloroethene	0.4	18	1.1
Chloroform	0.9	44	2.6
Bromochloromethane	1.0	50	3.0
1,1,1-Trichloroethane	0.3	17	1.0
1,1-Dichloropropene	0.7	36	2.1
Carbon Tetrachloride	0.7	33	2.0
Benzene	0.4	21	1.2
1,2-Dichloroethane	0.5	25	1.5
Trichloroethene	0.5	27	1.6
1,2-Dichloropropane	0.5	27	1.6
Bromodichloromethane	0.5	27	1.6
Dibromomethane	0.5	23	1.4
MIBK	0.6	29	1.7
cis-1,3-Dichloropropene	0.4	19	1.1
Toluene	0.4	22	1.3
Trans-1,3-Dichloropropene	0.5	25	1.5
1,1,2-Trichloroethane	0.5	24	1.4
Ethylene Dibromide	0.5	23	1.4
Tetrachloroethene	0.6	31	1.8
1,3-Dichloropropane	0.6	30	1.8
Chlorodibromomethane	0.5	26	1.5
Chlorobenzene	0.5	23	1.4
1,1,1,2-Tetrachloroethane	0.5	24	1.4
Ethylbenzene	0.5	23	1.4
m & p-Xylene	1.0	52	3.1
o-Xylene	0.5	24	1.4
Styrene	0.6	28	1.7
Bromoform	0.4	20	1.2
Isopropylbenzene	0.5	27	1.6
1,1,2,2-Tetrachloroethane	0.8	42	2.5
Bromobenzene	0.4	22	1.3
1,2,3-Trichloropropane	0.6	28	1.7
n-Propylbenzene	0.5	24	1.4
2-Chlorotoluene	0.4	22	1.3
1,3,5-Trimethylbenzene	0.6	29	1.7
4-Chlorotoluene	0.6	29	1.7
tert-Butylbenzene	0.6	28	1.7
1,2,4-Trimethylbenzene	0.5	26	1.6
sec-Butylbenzene	0.7	36	2.1
p-Isopropyltoluene	0.7	34	2.0
1,3-Dichlorobenzene	0.5	23	1.4
1,4-Dichlorobenzene	0.5	23	1.4
n-Butylbenzene	0.7	36	2.1
1,2-Dichlorobenzene	0.6	32	1.9
1,2-Dibromo-3-chloropropan	1.6	78	4.7
1,2,4-Trichlorobenzene	1.0	49	2.9
Naphthalene	2.1	103	6.2
1,2,3-Trichlorobenzene	2.1	103	6.2

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Typical 8260 Precision and Accuracy Data

	Average % Recovery	RSD Water	Average % Recovery	RSD Soil
Analyte	Water		Soil	
Chloromethane	91.7	2.4	110.6	4.1
Vinyl Chloride	96.0	4.0	115.6	3.3
Bromomethane	88.5	1.7	89.4	10.3
Trichlorofluoromethane	89.7	2.4	107.0	3.9
Chloroethane	89.2	2.3	108.8	2.2
Acetone	91.1	4.8	90.7	8.0
1,1-Dichloroethene	91.6	2.6	99.5	5.8
Methylene Chloride	79.2	6.1	101.2	1.5
tert-butyl Methyl Ether	96.8	3.1	100.8	1.5
trans-1,2 Dichloroethene	93.8	2.4	99.8	3.0
1,1-Dichloroethane	94.7	2.0	99.5	2.2
2-Butanone	97.3	3.5	105.3	5.0
2,2-Dichloropropane	99.3	1.7	89.6	4.7
cis-1,2-Dichloroethene	95.6	1.9	98.9	2.1
Chloroform	94.6	2.1	96.7	2.3
Bromochloromethane	94.3	2.5	98.3	1.1
1,1,1-Trichloroethane	94.3	2.0	96.0	4.3
1,1-Dichloropropene	93.5	2.2	96.4	5.0
Carbon Tetrachloride	95.6	2.1	97.8	6.5
Benzene	95.1	2.0	97.9	2.3
1,2-Dichloroethane	96.4	2.0	93.7	1.9
Trichloroethene	93.1	2.1	94.4	3.0
1,2-Dichloropropane	96.5	1.8	98.1	1.8
Bromodichloromethane	97.5	1.9	96.0	1.6
Dibromomethane	97.8	2.5	99.7	1.5
MIBK	101.5	3.5	107.4	2.6
cis-1,3-Dichloropropene	99.3	2.2	92.5	2.0
Toluene	95.5	1.8	97.4	2.2
Trans-1,3-Dichloropropene	104.8	2.3	88.6	3.1
1,1,2-Trichloroethane	97.5	2.7	100.1	1.3
Ethylene Dibromide	100.5	2.6	99.8	1.2
2-Hexanone	100.1	3.4	109.5	2.7
Tetrachloroethene	92.8	1.7	93.6	4.7
1,3-Dichloropropane	97.9	2.2	98.5	1.2
Chlorodibromomethane	99.3	2.1	101.4	1.6
Chlorobenzene	95.0	1.8	97.4	1.7
1,1,1,2-Tetrachloroethane	97.2	1.5	99.1	2.0
Ethylbenzene	94.2	1.7	94.1	2.8
m & p-Xylene	94.9	3.2	93.3	2.9
o-Xylene	95.1	1.5	93.1	1.9
Styrene	95.9	1.5	95.3	1.2
Bromoform	100.8	2.4	106.6	2.9
Isopropylbenzene	93.7	1.4	89.3	3.4
1,1,2,2-Tetrachloroethane	100.4	3.2	112.7	1.0
Bromobenzene	94.9	1.7	95.9	1.5
1,2,3-Trichloropropane	97.0	2.8	102.4	1.3
n-Propylbenzene	92.2	1.1	86.9	3.6
2-Chlorotoluene	93.8	1.3	90.1	2.6
1,3,5-Trimethylbenzene	92.2	0.8	87.1	2.9
4-Chlorotoluene	93.6	1.2	90.3	2.5
tert-Butylbenzene	94.2	1.0	85.0	3.2
1,2,4-Trimethylbenzene	92.4	0.8	88.4	2.5
sec-Butylbenzene	93.4	0.9	79.2	3.8
p-Isopropyltoluene	92.2	0.5	80.0	3.5
1,3-Dichlorobenzene	92.9	1.1	92.1	2.0
1,4-Dichlorobenzene	92.7	1.3	92.5	2.1
n-Butylbenzene	91.0	0.6	73.9	3.4
1,2-Dichlorobenzene	94.0	1.3	93.8	1.4
1,2-Dibromo-3-chloropropan	103.6	2.6	104.3	3.4
1,2,4-Trichlorobenzene	87.8	0.4	100.4	5.6

Requesting Additional Data Elements

Laboratory reports typically present results for sample and QC audits such as surrogate recoveries and MS/MSD analyses. Procedural audits such as initial calibration criteria checks, ongoing calibration checks, internal standard retention time and response audits, etc. are not generally included. You will need to specify these deliverables if you want to review this data. Whenever possible, you should request this data when the project begins and not after samples have been analyzed and results reported. Also, be prepared for extra charges and delays.

What should you request? What form will the data be in and how should it be reviewed? There are several answers to these questions. The following is one effective and simple set of data elements to request.

Item #1: Initial calibration summary.
Compare the results on this page to the initial calibration criteria for CCCs and SPCCs.

Item #2: Continuing calibration evaluation.
Compare the results on this page to the initial calibration criteria for CCCs and SPCCs.

Item #3: Batch QC Check Report
This report details samples in the batch, internal standard areas, surrogate recoveries, tune compliance, and batch length compliance.

Item #4: Quant output and chromatograms for the standards, samples, blanks, etc.

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BFB Tune Report

Data File : C:\HPCHEM\1\DATA\S28\S2800.D Vial: 1
Acq On : 28 Jan 99 10:07 am Operator:
Sample : 50ng bfb tune vw980420a2 Inst : GC/MS Ins
Misc : 2ul inj jhb Multiplr: 1.00
MS Integration Params: rteint.p

Method : C:\HPCHEM\1\METHODS\BTEX8260.M (RTE Integrator)
Title : 8260A Water/Medium Level Analysis 11/08/96

Spectrum Information: Scan 157

Target Mass	Rel. to Mass	Lower Limit%	Upper Limit%	Rel. Abn%	Raw Abn	Result Pass/Fail
50	95	8	40	14.3	37008	PASS
75	95	30	66	41.8	108252	PASS
95	95	100	100	100.0	259136	PASS
96	95	5	9	6.5	16785	PASS
173	174	0.00	2	0.0	0	PASS
174	95	50	120	70.4	182400	PASS
175	174	4	9	7.2	13189	PASS
176	174	93	101	98.8	180288	PASS
177	176	5	9	6.6	11919	PASS

Initial Calibration Summary

Method : C:\HPCHEM\1\METHODS\BTEX8260.M (RTE Integrator)
Title : 8260A Water/Medium Level Analysis 11/08/96
Last Update : Mon Jan 25 11:49:29 1999
Response via : Initial Calibration

Calibration Files
10 =S2503.D 20 =S2502.D 50 =S2501.D
100 =S2504.D 200 =S2505.D

		Compound	10	20	50	100	200	Avg	%RSD
1)	I	Pentafluorobenzene	----------ISTD----------						
2)	CPM	Chloromethane	0.135	0.132	0.129	0.107	0.103	0.121	12.48
3)	CPM	Vinyl Chloride	0.156	0.150	0.144	0.115	0.105	0.134	16.85
4)	CMP	1,1-Dichloroethene	0.272	0.304	0.328	0.280	0.276	0.292	8.15
5)	CPM	1,1-Dichloroethane	0.410	0.443	0.466	0.399	0.391	0.422	7.56
6)	CPM	Chloroform	0.448	0.506	0.539	0.465	0.464	0.484	7.70
7)	I	1,4-Difluorobenzene	----------ISTD----------						
8)	S	1,2-Dichloroethane-D4	0.258	0.271	0.300	0.250	0.243	0.264	8.43
9)	CMP	Benzene	0.690	0.772	0.799	0.717	0.722	0.740	6.02
10)	M	1,2-Dichloropropane	0.273	0.304	0.321	0.289	0.291	0.296	6.10
11)	S	Toluene-D8	0.630	0.667	0.794	0.629	0.628	0.669	10.69
12)	MCP	Toluene	0.755	0.837	0.881	0.795	0.797	0.813	5.87
13)	I	Chlorobenzene-D5	----------ISTD----------						
14)	MCP	Chlorobenzene	0.791	0.878	0.926	0.828	0.830	0.851	6.16
15)	CPM	Ethylbenzene	1.033	1.161	1.204	1.104	1.098	1.120	5.83
16)	CPM	m & p-Xylene	0.862	0.958	1.001	0.896	0.886	0.921	6.24
17)	CPM	o-Xylene	0.871	0.974	1.032	0.924	0.924	0.945	6.41
18)	CPM	Bromoform	0.429	0.491	0.555	0.495	0.512	0.497	9.19
19)	SCP	Bromofluorobenzene	0.734	0.791	0.996	0.757	0.733	0.802	13.83
20)	I	1,4-Dichlorobenzene-D	----------ISTD----------						
21)	CPM	1,1,2,2-Tetrachloroet	0.941	0.998	1.046	0.890	0.903	0.956	6.85
22)	M	Naphthalene	0.724	0.758	0.793	0.629	0.641	0.709	10.14

(#) = Out of Range

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Continuing Calibration Summary

Data File : C:\HPCHEM\1\DATA\S28\S2801.D Vial: 1
Acq On : 28 Jan 99 10:32 am Operator:
Sample : vstd050 50ppb std vw99(0120b,c,0104a) Inst : GC/MS Ins
Misc : 5.0mls jhb Multiplr: 1.00
MS Integration Params: rteint.p

Method : C:\HPCHEM\1\METHODS\BTEX8260.M (RTE Integrator)
Title : 8260A Water/Medium Level Analysis 11/08/96
Last Update : Mon Jan 25 11:49:29 1999
Response via : Multiple Level Calibration

Min. RRF : 0.050 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 100% Max. Rel. Area : 200%

		Compound	AvgRF	CCRF	%Dev	Area%	Dev(min)
1	I	Pentafluorobenzene	1.000	1.000	0.0	97	-0.02
2	CPM	Chloromethane	0.121	0.128	-5.8	96	0.00
3	CPM	Vinyl Chloride	0.134	0.146	-9.0	98	-0.01
4	CMP	1,1-Dichloroethene	0.292	0.334	-14.4	98	-0.01
5	CPM	1,1-Dichloroethane	0.422	0.495	-17.3	103	-0.02
6	CPM	Chloroform	0.484	0.558	-15.3	100	-0.02
7	I	1,4-Difluorobenzene	1.000	1.000	0.0	102	-0.01
8	S	1,2-Dichloroethane-D4	0.264	0.307	-16.3	105	-0.02
9	CMP	Benzene	0.740	0.800	-8.1	102	-0.01
10	M	1,2-Dichloropropane	0.296	0.334	-12.8	106	-0.02
11	S	Toluene-D8	0.669	0.793	-18.5	102	0.00
12	MCP	Toluene	0.813	0.872	-7.3	101	-0.02
13	I	Chlorobenzene-D5	1.000	1.000	0.0	102	-0.02
14	MCP	Chlorobenzene	0.851	0.897	-5.4	99	-0.02
15	CPM	Ethylbenzene	1.120	1.190	-6.2	101	-0.02
16	CPM	m & p-Xylene	0.921	0.972	-5.5	99	-0.02
17	CPM	o-Xylene	0.945	1.002	-6.0	99	-0.02
18	CPM	Bromoform	0.497	0.497	0.0	91	-0.01
19	SCP	Bromofluorobenzene	0.802	0.962	-20.0	98	-0.02
20	I	1,4-Dichlorobenzene-D4	1.000	1.000	0.0	93	-0.01
21	CPM	1,1,2,2-Tetrachloroethane	0.956	1.164	-21.8	103	-0.02
22	M	Naphthalene	0.709	0.560	21.0	65	-0.01

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QA-QC Check Report for Batch

Tune File : C:\HPCHEM\1\DATA\S28\S2800.D
Tune Time : 28 Jan 99 10:07 am

Daily Calibration File : C:\HPCHEM\1\DATA\S20\S2001.D

					2508990	2689290	2139730	1407300
File	Sample	Surrogate Recovery %			Internal Standard Responses			
S2802.D	vblk01 i	98	101	99	2361915	2614097	2166539	1288256
S2803.D	vblk02 i	98	101	101	2298074	2544030	2096417	1248229
S2804.D	vlcs01 v	103	100	97	2264523	2516200	2049031	1277689
S2805.D	J0127-05	96	99	98	2318637	2575881	2146091	1293454
S2806.D	J0127-05	99	101	100	2279418	2527519	2096427	1254288

t - fails 12hr time check * - fails criteria

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Quantitation Report

Data File : C:\HPCHEM\1\DATA\S28\S2804.D Vial: 4
Acq On : 28 Jan 99 12:01 pm Operator:
Sample : vlcs01 vw981117c Inst : GC/MS Ins
Misc : 5.0mls jhb Multiplr: 1.00
MS Integration Params: rteint.p
Quant Time: Feb 1 15:08 1999 Quant Results File: BTEX8260.RES

Quant Method : C:\HPCHEM\1\METHODS\BTEX8260.M (RTE Integrator)
Title : 8260A Water/Medium Level Analysis 11/08/96
Last Update : Mon Jan 25 11:49:29 1999
Response via : Initial Calibration
DataAcq Meth : 8260-31

Internal Standards	R.T.	QIon	Response	Conc	Units	Dev(Min)
1) Pentafluorobenzene	4.58	168	2264523	50.00	ug/L	0.02
7) 1,4-Difluorobenzene	6.05	114	2516200	50.00	ug/L	0.02
13) Chlorobenzene-D5	11.75	117	2049031	50.00	ug/L	0.00
20) 1,4-Dichlorobenzene-D4	16.93	152	1277689	50.00	ug/L	0.00
System Monitoring Compounds						
8) 1,2-Dichloroethane-D4	5.44	65	778566	58.53	ug/L	0.02
Spiked Amount 56.800	Range 76 - 114		Recovery = 103.05%			
11) Toluene-D8	8.67	98	2000279	59.37	ug/L	0.02
Spiked Amount 59.400	Range 88 - 110		Recovery = 99.95%			
19) Bromofluorobenzene	14.50	95	1987035	60.44	ug/L	0.00
Spiked Amount 62.100	Range 86 - 115		Recovery = 97.33%			
Target Compounds						Qvalue
4) 1,1-Dichloroethene	2.79	61	773519	58.50	ug/L	96
5) 1,1-Dichloroethane	3.66	63	1129006	59.11	ug/L	97
6) Chloroform	4.49	83	1261550	57.51	ug/L	100
9) Benzene	5.53	78	1987142	53.35	ug/L	99
10) 1,2-Dichloropropane	6.83	63	838975	56.38	ug/L	99
12) Toluene	8.82	91	2186200	53.42	ug/L	100
14) Chlorobenzene	11.84	112	1847235	52.99	ug/L	99
15) Ethylbenzene	12.01	91	2370047	51.65	ug/L	100
16) m & p-Xylene	12.18	91	4005666	106.17	ug/L	99
17) o-Xylene	13.10	91	2045819	52.83	ug/L	100
18) Bromoform	13.88	173	1044345	51.33	ug/L	100
21) 1,1,2,2-Tetrachloroethane	14.51	83	1470860	60.23	ug/L	99
22) Naphthalene	19.90	128	710227	39.21	ug/L	100

(#) = qualifier out of range (m) = manual integration
S2804.D BTEX8260.M Mon Feb 01 15:22:48 1999

Semivolatile Organics by EPA 8270

The current revision of Method 8270 is EPA Method 8260C. The method describes the protocol for the "determinative" steps in the analysis of SVOCs. Sample preparation is discussed in several additional methods. Users of analytical services rarely concern themselves with this fundamentally important preparative method. The more commonly used methods are discussed below.

Water Extraction Methods

Semivolatile target analytes consist of several different compound classes, e.g. phthalates, PNAs, nitroaromatics, phenols, etc. The optimum extraction pH for these individual classes varies. Methods for water extraction require two extractions, one under acidic conditions and one under basic conditions.

Method 3510C: Separatory Funnel Liquid-Liquid Extraction

A measured volume of sample is solvent extracted using a separatory funnel. The extract is dried and concentrated using a KD evaporator. Separatory funnel extraction utilizes relatively inexpensive glassware and is fairly rapid (three 2-minute extractions followed by filtration) but is labor intensive, uses fairly large volumes of solvent and is subject to emulsion problems.

Method 3520C: Continuous Liquid-Liquid Extraction

A measured volume of sample is extracted with solvent in a continuous liquid-liquid extractor. The extract is dried and concentrated using a KD evaporator. Continuous extractors are excellent for samples with particulates (of up to 1% solids) that cause emulsions, provide more efficient extraction of analytes that are difficult to extract and, once loaded, require no hands-on manipulation. However, they require more expensive glassware, use fairly large volumes of solvent and involve a rather lengthy extraction time (6 to 24 hours).

Soil/Waste Preparation Methods

Soil extraction methods ignore the pH variable and specify extraction of the sample without pH adjustment. This oversight has significant consequences for analyte recoveries, particularly for phenols in basic matrices.

Method 3540C: Soxhlet Extraction

A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble and extracted in a Soxhlet extractor. The extract is dried and concentrated using a KD evaporator. Soxhlet extraction uses relatively inexpensive glassware, and once loaded requires no hands-on manipulation, provides efficient extraction, but is rather lengthy (16 to 24 hours) and uses fairly large volumes of solvent. It is considered a rugged extraction method because there are very few variables that can adversely affect extraction efficiency.

Method 3541: Automated Soxhlet Extraction

A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble and extracted in an automated Soxhlet extractor. This device allows the extraction thimble to be lowered into the boiling liquid for the first hour and then extracted in the normal thimble position for one additional hour. The automated Soxhlet allows equivalent extraction efficiency in 2 hours but requires a rather expensive device.

Method 3550B: Ultrasonic Extraction

A known weight of sample is mixed with anhydrous sodium sulfate and solvent extracted using ultrasonic extraction. The extract is dried and concentrated using a KD evaporator. Ultrasonic extraction is fairly rapid (three 3-minute extractions followed by filtration) but uses relatively large volumes of solvent, requires a somewhat expensive device, and requires following the details of the method very closely to achieve acceptable extraction efficiency (proper tuning of the ultrasonic device is critical). Even with proper method execution, this technique is much less efficient than the other extraction techniques described above. This is most evident with very non-polar organic compounds that are normally strongly adsorbed to the soil matrix. Also, the method works poorly with clays and other occluded matrices. In addition, there are concerns that the ultrasonic energy may lead to

breakdown of some compounds. Unfortunately for the data user, this is the most common procedure used by labs.

Method 3580A: Waste Dilution

This is hardly a method as it involves simple dilution of sample into solvent. It is designed for wastes that are completely soluble in the dilution solvent.

Extract Cleanup:

Concentrated extracts can frequently be analyzed without cleanup because the 8270 technique employs a mass spectrometer, which has compound selective capability. This capability enables quantitation of target analytes in the presence of co-eluting interferences. This is fortunate because the target analyte list is a diverse list of compounds with highly varied properties and most cleanup methods would reduce recoveries of at least some compounds of interest.

Occasionally samples are contaminated with significant levels of high molecular weight organics such as asphalt fractions from petroleum or fatty acids. These materials tend to foul injection ports and columns, ultimately degrading their performance. These interferences can be removed without impacting recoveries of 8270 target analytes by using a technique that separates extract components on the basis of their molecular size. This technique is called gel permeation chromatography.

The Determinative Steps – Method 8270:

Initial Calibration Procedures

Prior to performing any analyses by this method the mass spectrometer is tuned so that it produces mass spectra that are consistent with a standard. Conformance with the standard is verified by obtaining a spectrum for decafluoro-triphenylphosphine (DFTPP) and comparing it to a specification.

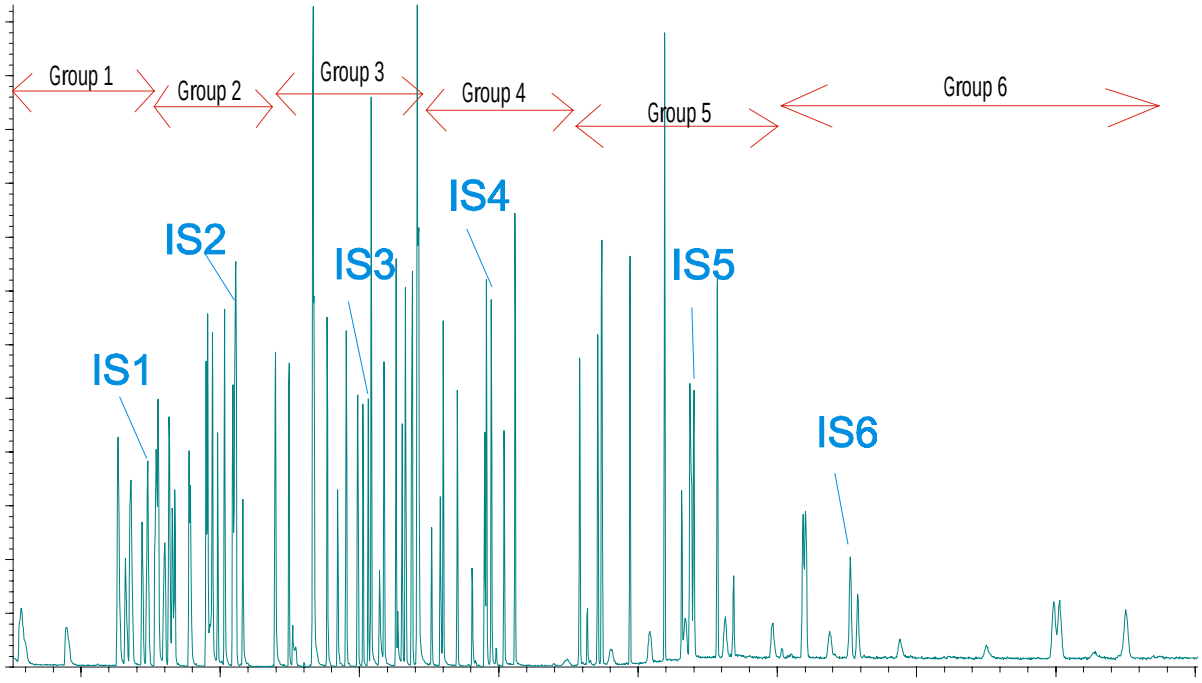
DFTPP Ion Abundance Criteria

ION	Criterion
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

As with VOCs, failure to meet this specification – unless the failure is severe – has little to do with the reliability of test results. Generating mass spectra that are consistent with the standard is technically relevant only when library searching of non-target analytes is being performed.

The DFTPP is analyzed by injecting a standard that contains this compound. The method recommends that this standard also contain DDT, benzidine, and pentachlorophenol. These compounds are used to assess injection port and column inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible.

EPA Method 8270 uses a five-point internal standard calibration. To obtain the calibration, a standard containing all of the compounds of interest is analyzed at five levels. Each run is spiked with an internal standard mixture. Compounds are grouped according to which internal standard they are associated with.



Laboratories are allowed to choose which compounds they use for internal standards. In the example above, the following internal standards are present:

Internal Standard #1:	1,4-Dichlorobenzene-d4
Internal Standard #2:	Naphthalene-d8
Internal Standard #3:	Acenaphthene-d10
Internal Standard #4:	Phenanthrene-d10
Internal Standard #5:	Chrysene-d12
Internal Standard #6:	Perylene-d12

Response factors for each compound are calculated for each of the five calibration levels. The following table presents data for one internal standard group of a typical calibration. The areas are calculated from extracted ion current profiles for the compound's quantitation ion and not the total ion chromatogram. The method recommends a quantitation ion for each compound.

Compound	Level, ug/ml 10	25	40	60	80	Avg	%RSD
Perylene-d12	----------ISTD----------						
Di-n-octyl phthalate	3.170	4.117	3.231	3.466	3.544	3.506	10.72
Benzo(b)fluoranthene	1.540	1.812	1.476	1.687	1.683	1.640	8.11
Benzo(k)fluoranthene	1.414	1.704	1.476	1.388	1.400	1.476	8.93
Benzo(a)pyrene	1.158	1.374	1.185	1.212	1.207	1.227	6.90
Indeno(1,2,3-cd)pyrene	0.885	1.232	0.995	0.989	1.014	1.023	12.43
Dibenz(a,h)anthracene	0.820	1.026	0.842	0.833	0.849	0.874	9.81
Benzo(g,h,i)perylene	0.789	0.947	0.751	0.749	0.768	0.801	10.40

Note: Response Factor (RF)=$(A_s \times C_{is})/(A_{is} \times C_s)$

A_s = Analyte Peak Area
C_{is} = Internal Standard Concentration
A_{is} = Internal Standard Peak Area
C_s = Analyte Concentration

Initial Calibration Acceptance Criteria

Before an initial calibration can be used, certain requirements must be met. Also, the method has additional recommended guidelines.

Response Factor Specifications

The method requires that the average response factors for the following compounds meet or exceed the following minimum values:

Compound	Minimum RF
N-nitroso-di-n-propylamine	0.05
2,4-dinitrophenol	0.05
hexachlorocyclopentadiene	0.05
4-nitrophenol.	0.05

These five compounds are called the System Performance Check Compounds or SPCCs.

Average Response Factor % RSD Specifications

The method requires that the following compounds have an Average Response Factor % RSD of 30% or lower:

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

These compounds are called the Calibration Check Compounds or CCCs. The method further states that the Average Response Factor % RSD for these CCCs should be less than or equal to 15%. When the response factor % RSD for any target compound is above 15%, the method requires that an average response factor not be used to determine analyte concentrations (i.e., another calibration option such as curve fitting must be used).

Retention Time Specifications

The method indicates that the retention times for any analyte should not vary by more than 0.06 RRT units throughout the various levels of the calibration.

Sample Processing

After initial calibration, samples are tested in batches. Each batch has various quality audits included.

Tune Verification

Mass spectrometer tuning verification is performed at the beginning of the batch by injecting 50 ng of DFTPP. The specification for this audit was discussed previously. The remainder of the batch must occur within 12 hours of this audit.

Calibration Verification

A mixed standard with components at the calibration's midpoint concentration is analyzed.

SPCCs

Each SPCC compound in the calibration verification standard must meet its minimum response factor criterion. This is the same check that is applied during the initial calibration.

CCCs

If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20% difference or drift) for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

Internal standards

The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required.

If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

Method Blank

The method blank consists of laboratory water or Ottawa sand carried through the sample preparation. This run should not contain any target analyte above the reporting limit.

Laboratory Control Standard (LCS)

This audit is not strictly required by the method. For semivolatile organics, it is a second source standard that has been carried through all preparative steps.

Reporting Limit Standard

Again not required by the method, this audit consists of a standard with analyte concentrations at or near the reporting limit. All compounds should be detected in this run.

Surrogates

Each sample is spiked with surrogate compounds prior to extraction. These compounds – typically deuterium-labeled compounds, which are highly unlikely to be found in environmental samples – are quantified and their recoveries calculated. If recoveries are poor, the problem may be a malfunctioning analytical system such as an intermittent leak. However, the problem may be caused by the sample matrix itself. For example, nitrobenzene-d5 may be converted to analine-d5 by a reducing organic matrix.

When surrogates fail criteria, protocol requires that a malfunctioning analytical system be ruled out (through analysis of blanks, standards, flow measurements, etc.) and that the sample be re-analyzed to confirm surrogate failure.

Surrogate recoveries are reported with the sample results. When a surrogate fails to meet limits, a comment as to why the failure occurs should be made. In general, a poor surrogate recovery does not indicate poor workmanship – provided control in the analytical system has been demonstrated. Rather it indicates a problem with the application of the method to the particular sample. This is commonly referred to as a “matrix effect.”

Internal Standards

The method states:
"It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance."

A good practice is to apply the same internal standard criteria used for the continuing calibration to all analytical runs.

Matrix Spike (MS) And Matrix Spike Duplicate (MSD) Analyses

This audit consists of spiking two additional portions of a sample with actual target analytes and measuring their recovery and percent difference. The audit provides accuracy and precision data for the sample matrix. As with surrogates, MS/MSD audits indicate reliability of the method's application to the matrix – provided system control is demonstrated.

Qualitative Analysis

Qualitative identity of a compound is based on two parameters: retention time and mass spectrum. Specifically, the relative retention time (RRT) of the sample component must agree with the standard component within ±0.06 RRT, and the relative intensities of the characteristic ions in the sample component's mass spectrum must agree within 30% of the relative intensities of these ions in the reference spectrum.

Quantitative Analysis

The area associated with the quantification ion for the analyte is used to calculate the concentration of the analyte in the sample by employing the initial calibration function. If the concentration of the analyte is higher than that of the highest calibration point, then the sample must be re-analyzed at a dilution. The dilution chosen should yield an area for that analyte in the top half of the calibration curve.

Periodic and Ongoing Method Evaluations

The evaluation of detection limits, surrogate recovery limits, LCS recovery limits and MS/MSD recovery and relative percent difference limits must be performed. Method demonstrations also are required. The procedure used is the same as that for VOCs except that all sample preparation steps are included in the process.

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Typical Method 8270 MDLs

	water, ug/l	soil, ug/kg
		MDL
n-Nitrosodimethylamine	2.9	498
Pyridine	1.1	45
2-Picoline	1.2	50
Methyl methanesulfonate	0.8	47
Ethyl methanesulfonate	0.9	34
Phenol	2.0	94
Aniline	1.1	86
bis(2-Chloroethyl)ether	1.3	53
2-Chlorophenol	2.4	65
1,3-Dichlorobenzene	1.5	38
1,4-Dichlorobenzene	1.3	40
Benzyl alcohol	1.6	31
1,2-Dichlorobenzene	1.3	39
2-Methylphenol	2.5	161
bis(2-chloroisopropyl)ethe	1.6	238
Indene	1.2	49
4-Methylphenol	4.1	134
n-Nitroso-di-n-propylamine	0.7	39
Hexachloroethane	1.6	39
Acetophenone	1.1	39
Nitrobenzene	1.0	42
n-Nitrosopiperidine	0.7	36
Isophorone	1.2	27
2-Nitrophenol	2.4	76
bis(2-Chloroethoxy)methane	1.8	21
2,4-Dichlorophenol	1.1	75
1,2,4-Trichlorobenzene	2.5	37
Dimethylphenethylamine	1.3	71
Naphthalene	1.1	40
4-Chloroaniline	1.0	71
2,6-Dichlorophenol	2.3	91
Hexachlorobutadiene	1.7	39
Quinoline	1.5	22
n-Nitrosodibutylamine	0.7	26
4-Chloro-3-methylphenol	4.0	73
2-Methylnaphthalene	1.1	34
1-Methylnaphthalene	1.1	31
Hexachlorocyclopentadiene	0.2	62
1,2,4,5-Tetrachlorobenzene	1.4	44
2,4,6-Trichlorophenol	3.3	666
2,4,5-Trichlorophenol	2.6	628
Biphenyl	1.3	37
2-Chloronaphthalene	1.4	35
1-Chloronaphthalene	1.4	36
2-Nitroaniline	1.0	52
Dimethyl phthalate	1.4	41
Acenaphthylene	1.1	65
2,6-Dinitrotoluene	1.1	44
3-Nitroaniline	0.9	74

Typical Method 8270 MDLs (continued)

Acenaphthene	1.2	31
2,4-Dinitrophenol	50.0	194
4-Nitrophenol	0.5	113
Pentachlorobenzene	1.3	56
Dibenzofuran	1.2	36
2,3,4,6-Tetrachlorophenol	2.7	93
2,4-Dinitrotoluene	1.2	37
Diethyl phthalate	1.1	54
Fluorene	1.1	37
4-Chlorophenyl phenyl ethe	1.2	46
4-Nitroaniline	1.2	94
4,6-Dinitro-2-methylphenol	2.0	176
4-Aminobiphenyl	1.2	44
Diphenylamine	1.4	466
n-Nitrosodiphenylamine	1.2	46
1,2-Diphenylhydrazine	1.3	51
Phenacetin	1.2	57
4-Bromophenyl phenyl ether	1.3	50
Hexachlorobenzene	1.2	49
Pronamide	1.1	35
Pentachlorophenol	50.0	135
Pentachloronitrobenzene	1.2	34
Phenanthrene	1.3	37
Anthracene	1.2	36
Carbazole	1.4	33
Di-n-butylphthalate	1.2	613
Fluoranthene	1.2	53
Benzidine	50.0	302
Pyrene	1.5	41
p-Dimethylaminoazobenzene	1.1	66
Butyl benzyl phthalate	1.5	37
Benzo(a)anthracene	1.2	34
Chrysene	1.2	46
bis(2-Ethylhexyl)phthalate	2.1	300
Di-n-octyl phthalate	2.6	792
7,12-Dimethylbenz(a)anthra	1.2	46
Benzo(b)fluoranthene	1.8	58
Benzo(k)fluoranthene	1.2	68
Benzo(a)pyrene	1.3	201
Dibenz(a,j)acridine	1.5	44
Indeno(1,2,3-cd)pyrene	1.7	183
Dibenz(a,h)anthracene	1.3	205
Benzo(g,h,i)perylene	2.6	208

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EPA 8270 Guidelines for Precision and Accuracy for Water

Analyte	Test Conc. ug/l	Limit for Std Dev	Range for AVE	% Recovery Range
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Anthracene	100	32	43.4-118.0	27-133
Benz(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39	31.7-148.0	17-163
Benzo(g,h,i)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
Bis(2-chloroethyl) ether	100	55	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl) ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl) phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23	64.9-114.4	53-127
2-Chloronaphthalene	100	13	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
Dibenzo(a,h)anthracene	100	70	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Diethyl phthalate	100	26.5	D-100.0	D-114

EPA 8270 Guidelines for Precision and Accuracy for Water (continued)

Analyte	Test Conc. ug/l	Limit for Std Dev	Range for AVE	% Recovery Range
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octyl phthalate	100	31.4	18.6-131.8	4-146
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

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SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY AUTOMATED SOXHLET (METHOD 3541)
(from SW846)

Analyte	Mean Recovery, %	RSD, %
Phenol	47.8	5.6
Bis(2-chloroethyl)ether	25.4	13
2-Chlorophenol	42.7	4.3
2-Methylphenol	17.6	6.6
Bis(2-chloroisopropyl)ether	15	15
4-Methylphenol	23.4	6.7
N-Nitroso-di-n-propylamine	41.4	6.2
Nitrobenzene	28.2	7.7
Isophorone	56.1	4.2
2-Nitrophenol	36	6.5
2,4-Dimethylphenol	50.1	5.7
Bis(2-chloroethoxy)methane	44.1	3
2,4-Dichlorophenol	55.6	4.6
1,2,4-Trichlorobenzene	18.1	31
Naphthalene	26.2	15
4-Chloroaniline	55.7	12
4-Chloro-3-methylphenol	65.1	5.1
2-Methylnaphthalene	47	8.6
Hexachlorocyclopentadiene	19.3	19
2,4,6-Trichlorophenol	70.2	6.3
2,4,5-Trichlorophenol	26.8	2.9
2-Chloronaphthalene	61.2	6
2-Nitroaniline	73.8	6
Dimethyl phthalate	74.6	5.2
Acenaphthylene	71.6	5.7
3-Nitroaniline	77.6	5.3
Acenaphthene	79.2	4
2,4-Dinitrophenol	91.9	8.9

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SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY AUTOMATED SOXHLET (METHOD 3541)
(from SW846)
continued

Analyte	Mean Recovery, %	RSD, %
4-Nitrophenol	62.9	16
Dibenzofuran	82.1	5.9
2,4-Dinitrotoluene	84.2	5.4
2,6-Dinitrotoluene	68.3	5.8
Diethyl phthalate	74.9	5.4
4-Chlorophenyl-phenyl ether	67.2	3.2
Fluorene	82.1	3.4
4-Nitroaniline	79	7.9
4,6-Dinitro-2-methylphenol	63.4	6.8
N-Nitrosodiphenylamine	77	3.4
4-Bromophenyl-phenyl ether	62.4	3
Hexachlorobenzene	72.6	3.7
Pentachlorophenol	62.7	6.1
Phenanthrene	83.9	5.4
Anthracene	96.3	3.9
Di-n-butyl phthalate	78.3	40
Fluoranthene	87.7	6.9
Pyrene	102	0.8
3,3'-Dichlorobenzidine	25.2	11
Benzo(a)anthracene	73.4	3.8
Bis(2-ethylhexyl) phthalate	77.2	4.8
Chrysene	76.2	4.4
Di-n-octyl phthalate	83.1	4.8
Benzo(b)fluoranthene	82.7	5
Benzo(k)fluoranthene	71.7	4.1
Benzo(a)pyrene	71.7	4.1
Indeno(1,2,3-cd)pyrene	72.2	4.3
Dibenzo(a,h)anthracene	66.7	6.3
Benzo(g,h,i)perylene	63.9	8

Requesting Additional Data Elements

The following is one effective and simple set of data elements to request.

Item #1: Initial calibration summary.
Compare the results on this page to the initial calibration criteria for CCCs and SPCCs.

Item #2: Continuing calibration evaluation.
Compare the results on this page to the initial calibration criteria for CCCs and SPCCs.

Item #3: Batch QC Check Report
This report details samples in the batch, internal standard areas, surrogate recoveries, tune compliance, and batch length compliance.

Item #4: Quant output and chromatograms for the standards, samples, blanks, etc.

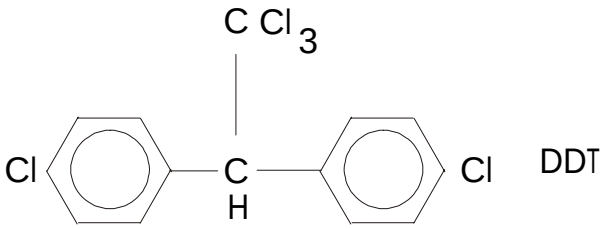
Item #5: Extraction Logs

Pesticides and PCBs

General background

Pesticides

In the 1950s, Rachael Carson wrote a book entitled *Silent Spring*. This book discussed the environmental harms of certain pesticides in common use at the time. These pesticides were in the general family of organochlorine pesticides of which the book's principal protagonist DDT is a member.



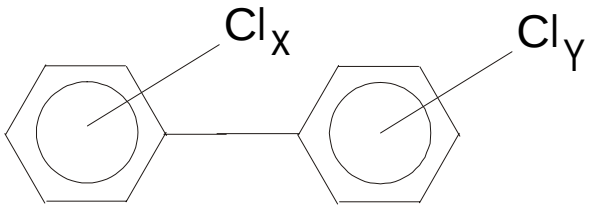
The concerns raised by the book were adopted by environmental activists who lobbied for the creation of the EPA and for legislation controlling the use, distribution in commerce, and environmental release of these chemicals. The EPA established permits, developed analytical methods and set policy targeting these compounds. In the 1970s, use of the majority of these compounds was discontinued as a result of the EPA's efforts. The pesticides in use today are of different chemical families – such as organophosporus pesticides, carbamates, and triazines – but the focus on organochlorine pesticides has not evolved. Wastewater permits, hazardous waste regulations and site assessment guidelines still exclusively specify the analysis of this class of pesticides. Be aware that when you request a pesticides analysis by method 8080, 8081, or 608, you are having your samples tested for the presence of an essentially banned list of target analytes. There are thousands of pesticides and pesticide metabolites.

The organochlorine pesticides typically included in target analyte lists are: Aldrin, α-BHC, β-BHC, δ-BHC, γ-BHC, α-Chlordane, γ-Chlordane, Chlordane, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, Dieldrin, Endosulfan I, Endosulfan II, Endosulfan sulfate, Endrin, Endrin aldehyde, Endrin Ketone, Heptachlor, Heptachlor epoxide, Methoxychlor, and Toxaphene. All except chlordane and toxaphene are individual chemical species. Chlordane and toxaphene are distributed mixtures of homologous chlorinated compounds.

PCBs

PCBs are mixtures of chlorine-substituted biphenyls which have the following general structure. There are 209 individual compounds or congeners with this structure.

A PCB congener



x and or y = 0,1,2,3,4,5

The mixtures were made by first batch-chlorinating biphenyl, distilling, and collecting fractions boiling within predetermined temperature windows. The fractions were sold with the product name Aroclor. The different fractions had different viscosities, different volatilities, different degrees of chlorination and different applications. They were designated with product numbers. For example, Aroclor 1232 was a light end fraction, low viscosity oil used in capacitors. Aroclor 1242 was a middle end fraction, medium viscosity oil used in transformers. Aroclor 1268 was a heavy end, high viscosity oil used in forges.

These materials were manufactured and sold in the 1960s and 1970s. They are very stable materials and they persist in the environment. The EPA banned their distribution in commerce in the late 1970s but the ban did not require that they be removed from existing equipment. Some equipment in use today is still charged with these oils. The ban was a TSCA action. The language of the regulations defined a *PCB contaminated oil* as one having a total PCB level above 50 ppm and a *PCB oil* as one having a concentration above 500 ppm. These are not limits to be used for hazard characterization, nor are they limits to be used for risk assessment. They are simply threshold values for equipment owners to use in TSCA compliance decision making. However, landfill owner/operators, engineers, and regulators often use the 50 ppm value as a guideline limit.

Electron Capture Gas Chromatography

Both organochlorine pesticides and PCBs have strong electron capture detector responses due to the presence of chlorine in their molecules. This response allows their detection and quantitation at levels 1000 times better than is possible using GC/MS. Toxicological considerations require this high sensitivity for these materials.

The electron capture detector is a conventional detector and as such does not enable unambiguous compound identification because retention time is the only basis for qualitative analysis. Therefore the protocols for analysis require analysis of sample extracts using two different types of GC columns. Only when a positive hit for a given analyte occurs on both columns is the compound considered present. GC/MS can also be used for confirmation, but it only works when levels are quite high.

Other compounds with electron capture response co-elute with pesticides and PCBs, and the ability to detect target analytes is frequently impaired by the presence of these interferents. Several extract cleanup steps are provided for eliminating the interferences.

PCBs and mixed component pesticides such as chlordane and toxaphene produce an electron capture chromatographic pattern rather than a single discrete peak. Qualitative identification requires recognition of the pattern in the sample extract. To obtain quantitative results, several peaks within the pattern are chosen to represent the mixture and are quantified individually and averaged for a final result.

EPA Methods 8080, 8081 and 8082

In earlier revisions of SW846, both pesticides and PCBs were covered by a single method – Method 8080. The most recent revision has the analyses split out into 8081 for pesticides and 8082 for PCBs. Sample preparation is discussed in several additional methods. Again, users of analytical services rarely concern themselves with this fundamentally important preparative method. The extraction methods are the same as those for EPA Method 8270, except that when dichloromethane is used as the extraction solvent, it must be later exchanged with hexane to avoid detector problems.

Extract Cleanup:

Concentrated extracts usually require some type of cleanup. The cleanup used depends on the types of interferents present.

Acid Cleanup

This cleanup can only be used for PCB analyses. The extract is mixed with concentrated sulfuric acid, mixed and allowed to settle. The extract is removed and subjected to additional cleanup if required. A similar permanganate cleanup is sometimes included with this procedure.

Florisil Cleanup

Florisil is a trade name for activated magnesium silicate. Extracts are cleaned by passing them through columns packed with this absorbent using standard liquid chromatography techniques.

GPC Cleanup

Samples contaminated with significant levels of high molecular weight organics may be cleaned by subjecting the extract to gel permeation chromatography. This method can also be used to remove elemental sulfur. The technique separates components based on their molecular size.

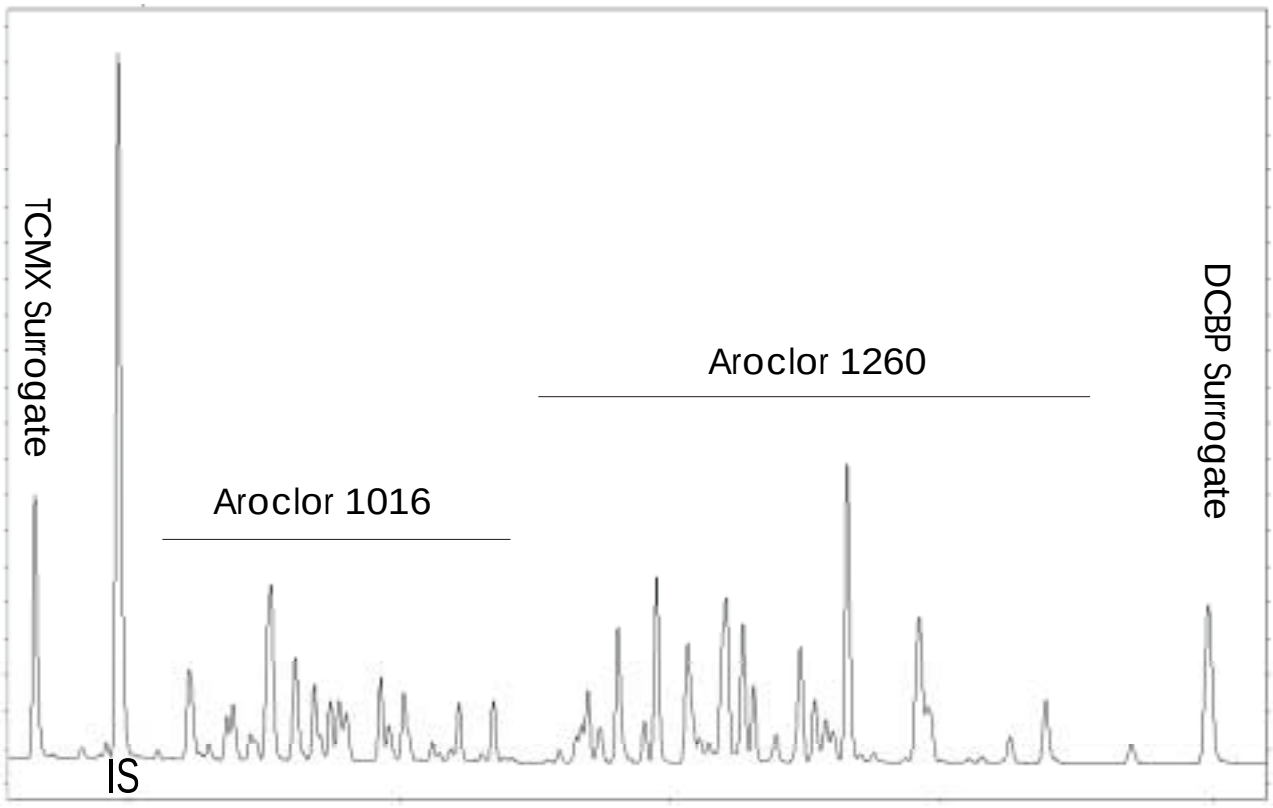
The Determinative Steps, Method 8081/8082

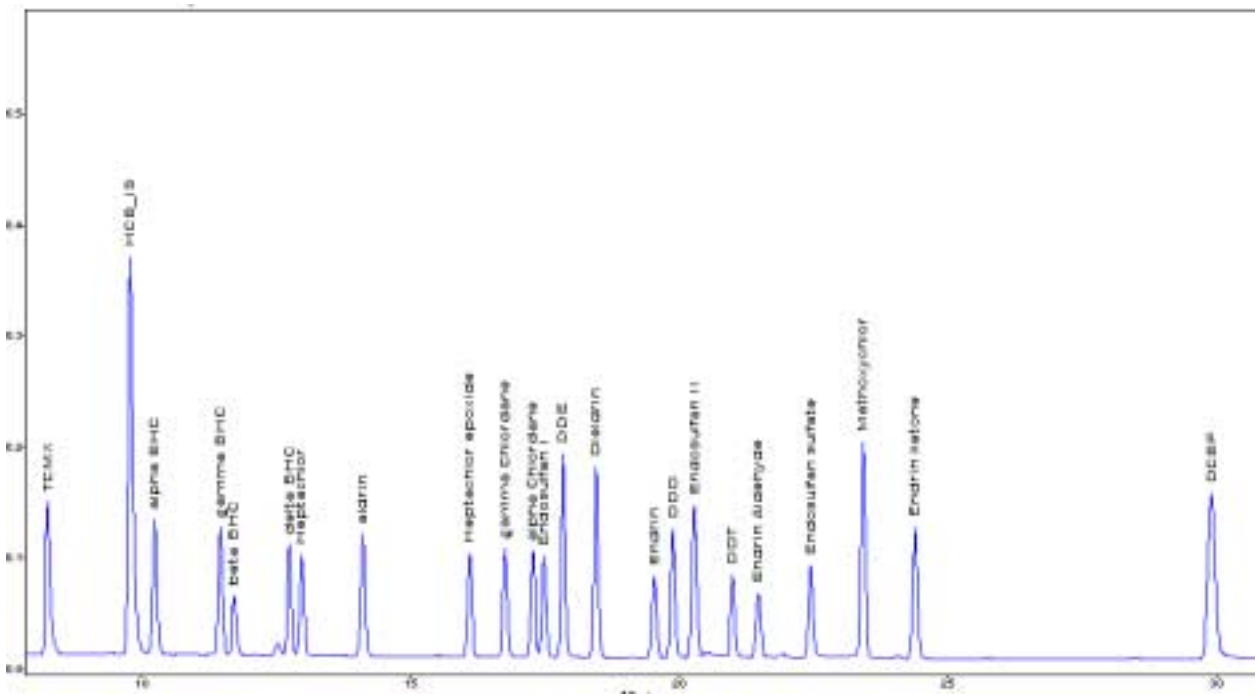
Analyses are performed on two different analytical columns. Usually this is accomplished by connecting both columns to a "Y" union, which also connects to a common injection port. Each column goes to a separate detector and separate chromatographic data channels monitor analysis independently. All calibration and sample analysis processing is performed twice, one for each data channel.

Initial Calibration Procedures

A five-point standard calibration (either internal standard or external standard calibration logic is acceptable) is used. For pesticides, a standard containing all of the discrete compounds is analyzed at five levels. Chlordane and toxaphene are analyzed at one level for pattern recognition and measurement.

For PCBs, a mixture of Aroclor 1016 and 1260 is prepared and designated "Aroclor 1060." Each Aroclor in this mix is analyzed at five levels for the calibration. A one-point standard for the other Aroclors is analyzed for pattern recognition and measurement. Some sample chromatograms are presented below.


TCMX Surrogate
IS
Aroclor 1016
Aroclor 1260
DCBP Surrogate


TCMX
HCBLIS
alpha BHC
gamma BHC
beta BHC
delta BHC
Heptachlor
aldrin
Heptachlor epoxide
gamma chlordane
alpha Chlordane
Endosulfan I
DDE
dieldrin
endrin
DDD
Endosulfan II
DDT
Endrin aldehyde
Endosulfan sulfate
Methoxychlor
Endrin ketone
DCBP

Initial Calibration Acceptance Criteria

If the RSD for each analyte is less than 20%, then the response of the instrument is considered linear and the mean calibration factor can be used to quantify sample results. If the RSD is greater than 20%, then linearity through the origin cannot be assumed. The analyst must use a calibration curve or a non-linear calibration model (e.g., a polynomial equation) for quantitation.

Retention Time Specifications

Qualitative identification of a target analyte's presence in a sample is based on whether a component peak has the same retention time as that analyte's retention time in the standard. How close to the same retention time constitutes a match? SW846 recommends a technique for establishing retention time windows:

- Make three injections of all single component standard mixtures and multi-component analytes (such as PCBs) over the course of a 72-hour period. Serial injections or injections over a period of less than 72 hours may result in retention time windows that are too tight.

- Record the retention time for each single component analyte and surrogate to three decimal places. Calculate the mean and standard deviation of the three absolute retention times for each single component analyte.

- The width of the retention time window for each analyte is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period.

Note: The center of the retention time window is established by using the calibration verification's retention times.

Sample Processing

After initial calibration, samples are tested in batches. Each batch has various quality audits included.

Calibration Verification

A mixed standard with components at the calibration's midpoint concentration is analyzed. The calibration check must agree with the initial calibration to within 15%. If this condition is met and an average response factor calibration is being used, then either the initial calibration RF or a new RF calculated from the continuing calibration may be used. When curve fitting is being used, the initial calibration polynomial is used.

The calibration verification is repeated at least every 12 hours and must be repeated at the end of the batch to demonstrate that the system has remained in control for all analytical runs. Only data sandwiched between compliant calibration checks is usable.

Method Blank

The method blank consists of laboratory water or Ottawa sand carried through the entire sample preparation. This run should not contain any target analyte above the reporting limit.

Laboratory Control Standard (LCS)

This audit is not strictly required by the method. It is a standard which has been subjected to all preparative steps.

Surrogates

Each sample is spiked with surrogate compounds (tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCBP)) prior to extraction. These compounds are quantified and their recoveries calculated. If recoveries are poor, the problem may be a malfunctioning analytical system such as an intermittent leak. However, the problem may be caused by the sample matrix itself. Unlike GC/MS techniques which enable quantitation of analytes in the presence of high background or co-eluting peaks in the chromatogram, this conventional detector technique may show poor surrogate recoveries caused by the inability to recognize and properly integrate the appropriate peaks. This effect does not necessarily have any relevance to results reliability.

When surrogates fail criteria, protocol requires that a malfunctioning analytical system be ruled out (through analysis of blanks, standards, flow measurements, etc.) and that the sample be re-analyzed to confirm surrogate failure.

Surrogate recoveries are reported with the sample results. When a surrogate fails to meet limits, a comment as to why the failure occurs should be made. In general, a poor surrogate recovery does not indicate poor workmanship – provided control in the analytical system has been demonstrated. Rather, it indicates a problem with the application of the method to the particular sample. This is commonly referred to as a "matrix effect."

Qualitative Analysis

For discrete component pesticides, qualitative identity of a compound is based on a component's having the same retention time as a target analyte on both columns. For multi-component pesticides and PCBs, presence of the analyte is based on pattern recognition.

Quantitative Analysis

For discrete component pesticides, the area under the chromatographic peak for the analyte is used to calculate the concentration of the analyte in the sample by employing the initial calibration function.

For mixed component pesticides and PCBs, at least three peaks are chosen to represent the mix, and the areas for these peaks are compared with a calibration for those same peaks.
Finally, the results for the peaks are averaged. If the concentration of the analyte is higher than that of the highest calibration point, then the sample must be re-analyzed at a dilution. The dilution chosen should yield an area for that analyte in the top half of the calibration curve.
Remember that when pesticides/PCBs are detected in a sample, it means that they were detected on both columns. Which set of results is used to calculate the final result? The method recommends that the result used be the higher of the two.

When results are confirmed using a second GC column of dissimilar stationary phase, the analyst should check the agreement between the quantitative results on both columns once the identification has been confirmed. Unless otherwise specified in an approved project plan, the

higher result should be reported, as this is a conservative approach relative to protection of the environment.

This element is an unfortunate issue of policy with no technical basis. In fact, it is in direct conflict with sound reasoning. When a component co-elutes with an analyte on one column it usually does not on the second column – yielding a lower area. The lower number is correct. CLP protocols recognize this fact and hopefully future revisions of the 8081/8082 methods will reflect further reasoning on this issue.

Method Detection Limits

Reporting limits for pesticides and PCBs are usually based on a numerical value derived from the lowest calibration point rather than a value based on statistical analysis. However, the laboratory still performs the usual MDL studies. Common reporting limits for PCBs are as follows:

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Typical Reporting Limits for Pesticides and PCBs

Analyte	Water	Soil
	Limit, ug/l	Limit, ug/kg
α BHC	0.05	5
γ BHC (Lindane)	0.05	5
β BHC	0.05	5
Heptaclor	0.05	5
δ BHC	0.05	5
Aldrin	0.05	5
Heptaclor Epoxide	0.05	5
α Chlordane	0.05	5
γ Chlordane	0.05	5
Endosulfan I	0.05	5
4,4’ DDE	0.1	10
Dieldrin	0.1	10
Endrin	0.1	10
4,4’ DDD	0.1	10
Endosulfan II	0.1	10
4,4’ DDT	0.1	10
Endrin Aldehyde	0.1	10
Endosulfan Sulfate	0.1	10
Methoxyclor	0.5	50
Endrin Ketone	0.1	10
Toxaphene	50	5000
Chlordane	1.0	100
PCBs		
1016	1	100
1221	2	200
1232	1	100
1242	1	100
1248	1	100
1254	1	100
1260	1	100

Precision and Accuracy

Method 8081 fails to provide guidelines for precision and accuracy for pesticides in water or soils – except for some data relevant to a solid phase extraction technique. Our laboratory precision and accuracy data for water is tabulated below. These studies are performed on laboratory water and Ottawa sand. Real-world matrices will not give such exemplary results.

Pesticide	Soil Average Recovery %	RSD %	Water Average Recovery %	RSD %
TCMX	92.1	5.1	88.4	5.5
alpha BHC	92.4	7.5	99.9	2.2
gamma BHC	89.1	7.9	100.4	2.2
beta BHC	83.2	5.8	100.3	3.5
delta BHC	86.3	8.9	101.2	3.3
Heptachlor	101.5	6.1	100.8	1.7
aldrin	96.6	7.7	102.8	4.4
Heptachlor epoxide	95.4	6.6	103.1	2.3
gamma chlordane	97.8	7.7	102.4	2.5
alpha chlordane	96.4	7.9	104.1	2.5
DDE	97.3	7.3	102.3	3.0
Endosulfan I	94.6	8.6	99.7	3.4
Dieldrin	98.0	7.2	103.7	2.7
Endrin	104.7	8.2	105.6	3.7
DDD	98.8	9.0	103.4	3.1
Endosulfan II	89.7	8.2	104.7	2.0
DDT	101.8	8.7	105.0	2.4
Endrin aldehyde	94.4	6.6	102.5	3.8
Methoxychlor	100.2	7.9	99.2	3.2
Endosulfan sulfate	101.7	8.7	104.1	1.5
Endrin Ketone	99.8	7.8	106.0	2.4
DCBP	90.9	8.0	93.5	3.2

Method 8082 PCB precision and accuracy guidelines are reproduced on the following page.

MULTIPLE LABORATORY PRECISION AND ACCURACY DATA
FOR THE EXTRACTION OF PCBs FROM SPIKED SOIL
BY METHOD 3541 (AUTOMATED SOXHLET)

		Percent Recovery						
		Aroclor 1254			Aroclor 1260			
		Spike Conc. (µg/kg)			Spike Conc. (µg/kg)			
		5	50	500	5	50	500	All Levels
Laboratory 1	N	3	3		3	3		12
	Mean	101.2	74.0		83.9	78.5		84.4
	S. D.	34.9	41.8		7.4	7.4		26.0
Laboratory 2	N		6	6		6	6	24
	Mean		56.5	66.9		70.1	74.5	67.0
	S. D.		7.0	15.4		14.5	10.3	13.3
Laboratory 3	N	3	3		3	3		12
	Mean	72.8	63.3		70.6	57.2		66.0
	S. D.	10.8	8.3		2.5	5.6		9.1
Laboratory 4	N	6	6		6	6		24
	Mean	112.6	144.3		100.3	84.8		110.5
	S. D.	18.2	30.4		13.3	3.8		28.5
Laboratory 5	N		3	3		3	3	12
	Mean		97.1	80.1		79.5	77.0	83.5
	S. D.		8.7	5.1		3.1	9.4	10.3
Laboratory 6	N	2	3		3	4		12
	Mean	140.9	127.7		138.7	105.9		125.4
	S. D.	4.3	15.5		15.5	7.9		18.4
Laboratory 7	N	3	3		3	3		12
	Mean	100.1	123.4		82.1	94.1		99.9
	S. D.	17.9	14.6		7.9	5.2		19.0
Laboratory 8	N	3	3		3	3		12
	Mean	65.0	38.3		92.8	51.9		62.0
	S. D.	16.0	21.9		36.5	12.8		29.1
All Laboratories	N	20	30	9	21	31	9	120
	Mean	98.8	92.5	71.3	95.5	78.6	75.3	87.6
	S. D.	28.7	42.9	14.1	25.3	18.0	9.5	29.7

Requesting Additional Data Elements

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Item #2: Continuing calibration evaluations.

Item #3: Batch QC Check Report
This report details samples in the batch, internal standard areas, surrogate recoveries, and batch length compliance.

Item #4: Quant output and chromatograms for the standards, samples, blanks, etc.

Item #5: Extraction Logs

Other Conventional Detector GC Methods

In addition to the 8081/8082 pesticides/PCB methods, SW846 has several other conventional detector GC methods.

Method 8011: 1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography. This ECD method is needed to achieve very low detection limits (0.01 ppb) for these analytes. EPA Method 8260 is usually used to determine these compounds.

Method 8015B: Nonhalogenated Organics Using GC/FID. The target analyte list for this method is typically analyzed by EPA 8260. This method offers no advantage over the 8260 method, and is vexed with the usual false positives and interference problems typical of conventional detector methods. This method is sometimes referenced – inappropriately – as the standard method for the analysis of gasoline range organics.

Method 8021B: Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors: Again, EPA 8260 is the method of choice for this parameter list. Detection limits are somewhat lower for some compounds using this method, but the qualitative uncertainties overwhelm any detection limit advantages.

Method 8041: Phenols, **Method 8061A:** Phthalate Esters, **Method 8070A:** Nitrosamines, **Method 8091:** Nitroaromatics and Cyclic Ketones, **Method 8100:** Polynuclear Aromatic Hydrocarbons, **Method 8111:** Haloethers, **Method 8121:** Chlorinated Hydrocarbons, **Method 8131:** Aniline and Selected Derivatives **and Method 8141A:** Organophosphorus Compounds. These are conventional detector methods for analytes that are more reliably analyzed by EPA 8270. Again, some arguments may be made that certain analytes have better responses using conventional detectors. However, minor detection limit advantages apply only to clean, interference-free samples and the risk of false positives is always present with conventional detectors. The methods all recommend confirmation using 8270 when ever analytes are detected using these methods.

Method 8151A: Chlorinated Herbicides by GC Using Methylation or

Pentafluorobenzylation Derivatization. As with the pesticide and PCB methods, this conventional detector technique is a necessity for obtaining reliable results for herbicides. GC/MS is not sensitive enough for obtaining the required detection levels. Also, the method has a necessary, built-in sample preparation. Chlorinated phenoxy acid herbicides must be extracted from an acidified matrix. Once extracted, they are reactive, polar compounds, which produce broad, tailing chromatographic peaks. Proper analysis requires that these compounds be derivatized (converted from organic acids to organic methyl esters) prior to analysis.

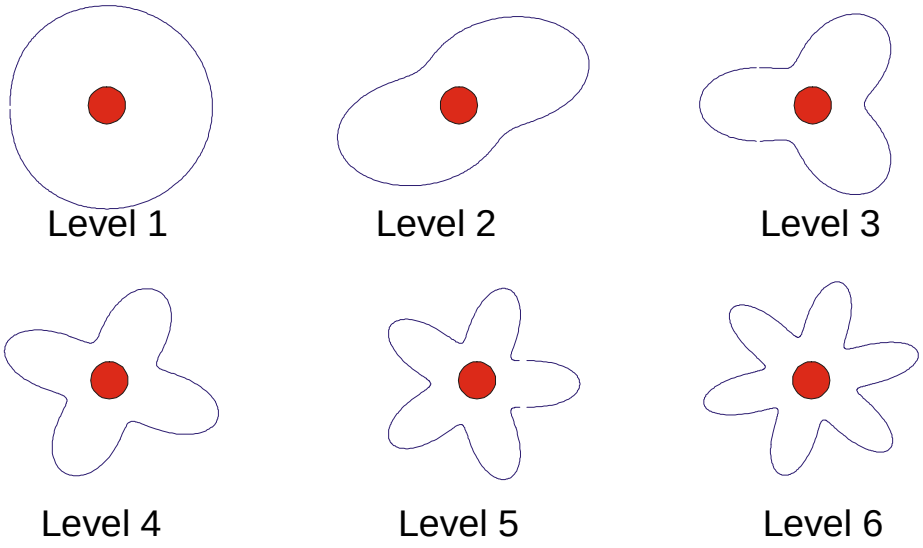
The method also provides for the analysis of methyl esters – as well as other esters – of these compounds in the samples themselves. The option to measure these esters takes the form of an additional hydrolysis step. Whether the hydrolysis step is included or not, the preparation steps in this method are several. As with any quantitative analysis, every sample-handling step diminishes recovery.

METALS

Electronic Structure

There are several models for understanding atomic structure and spectroscopy. The model presented here is sufficient for an intuitive understanding of the measurement process without bogging down in mathematical rigors.

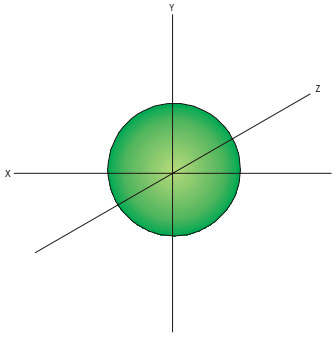
Our model begins with the atom being represented by a nucleus surrounded by electrons. These electrons behave like standing waves in that only completed wave cycles are stable (permitted).



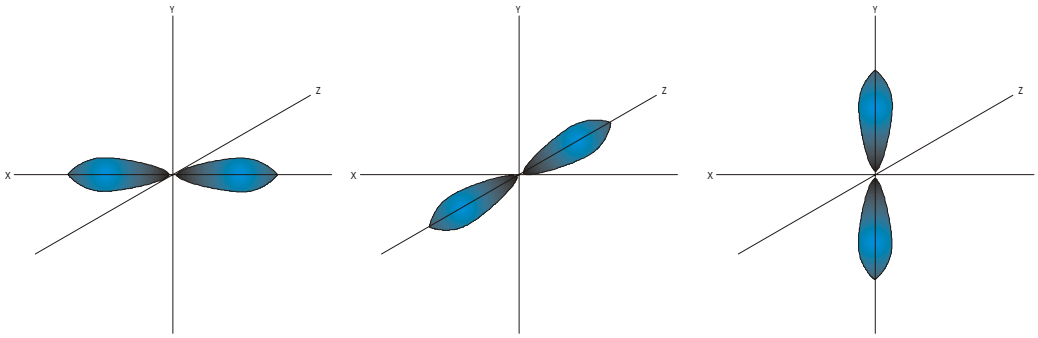
The energy of the electron is a function of its wavelength, so only discrete energy levels are allowed.

In reality, these waves exist in three dimensions and more than one configuration exists for the various energy levels. These configurations are called atomic orbitals.

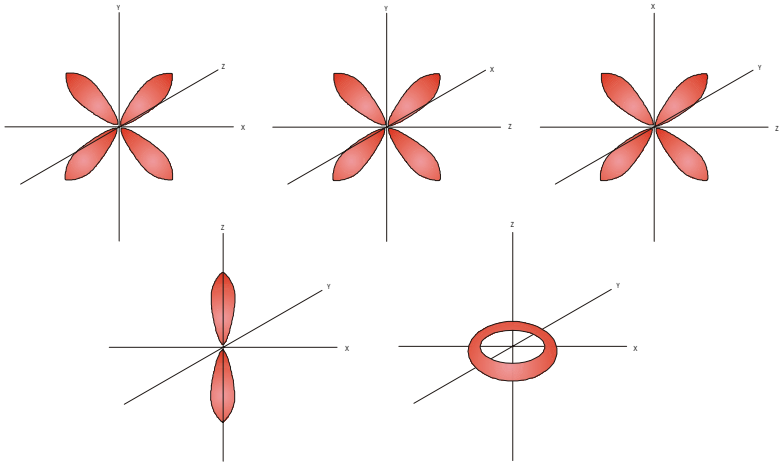
Level 1 has one orbital called an *s* orbital:



Energy level 2 has three orbitals called *p* orbitals:

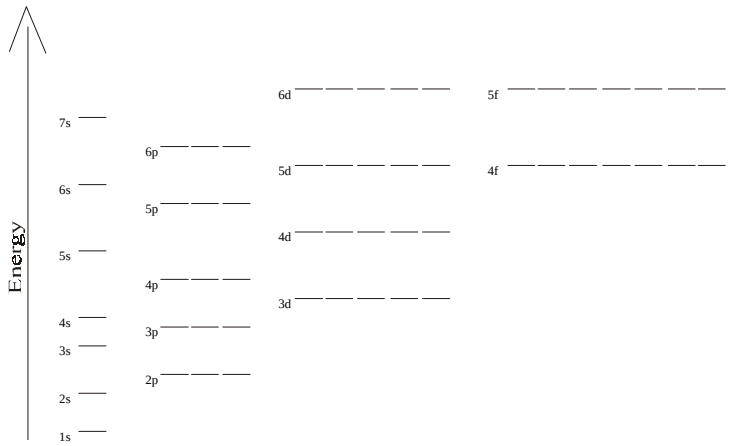


Level 3 has five *d* orbitals:

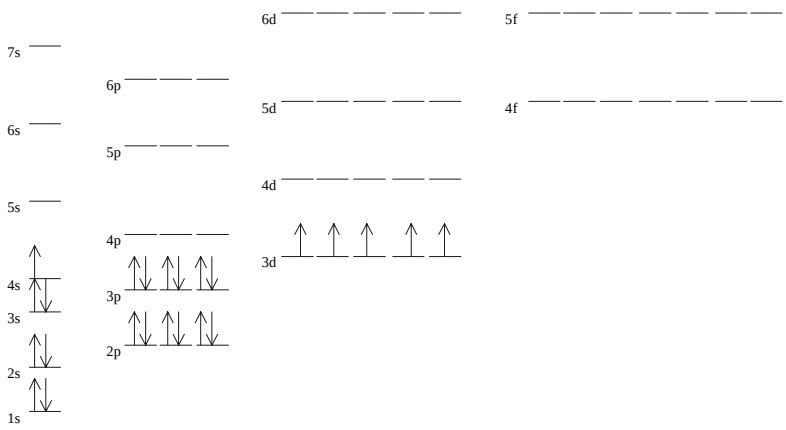


(consider a visit to http://wulff.mit.edu/orbs/)
Two electrons can occupy each orbital, but only if their magnetic polarities are opposite. These orbitals are arranged in shells with increasing distance from the

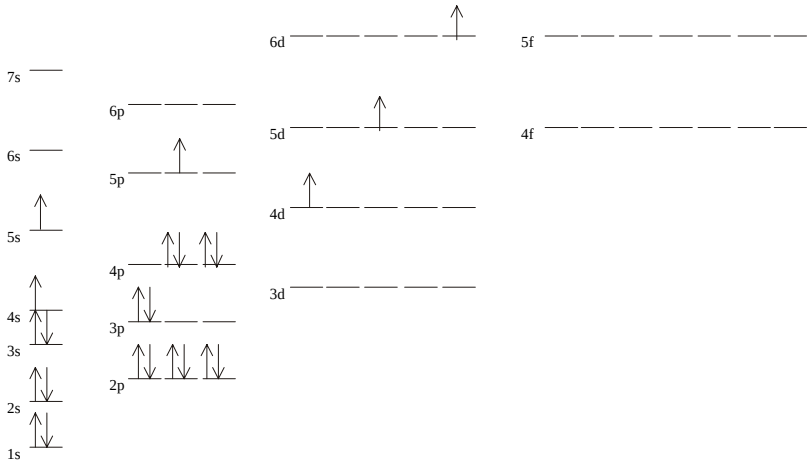
nucleus and increasing energy level. Shell "1" has room for an *s* orbital only. Shell "2" has room for *s* and *p* orbitals but no *d* orbitals. Shell "3" has *s*, *p* and *d* orbitals, but no *f* (level 4) orbitals. The relative energy levels for electrons in these various states are diagrammed schematically below.



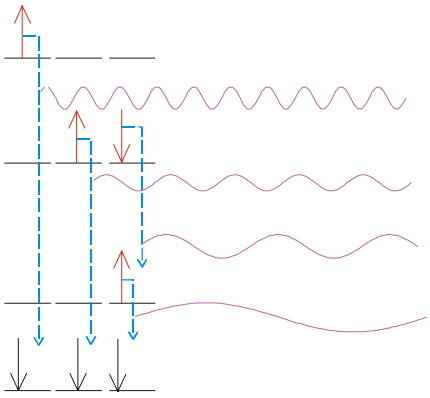
In atoms, electrons fill the 1s orbital first then fill the higher energy levels.
For example, chromium has 24 electrons. Its electron configuration at ground state (when all electrons fill the orbitals of lowest energy) is diagrammed below:



If sufficient energy is added to an atom in its ground state, the electrons absorb the energy and jump to higher orbitals. The electrons in the higher energy orbitals – being further from the nucleus – are the first to undergo transitions. Below is the electronic configuation for a chromium atom in an excited state.



When excited electrons relax to lower orbitals, they re-emit the absorbed energy in the form of a light.

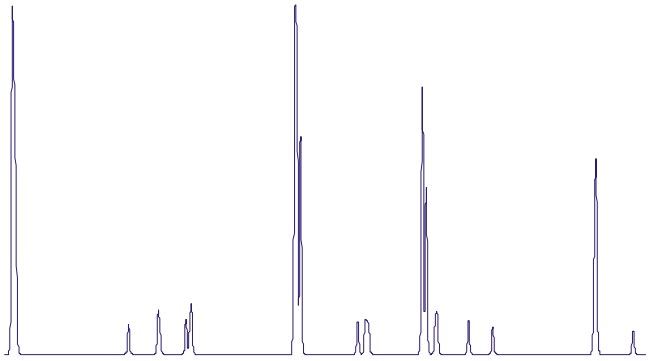


The wavelength of the light emitted is an inverse function of the energy of the transition. Specifically, $\lambda=hc/energy$ where λ is the wavelength, h is Planck's constant, and c is the speed of light.

A given transition, say 5p to 3p, will emit a specific wavelength of light. The wavelength of this transition will vary from element to element, but will be characteristic for a given element.

Emission Spectroscopy

If we add sufficient thermal energy to a population of atoms (or ions), they will collectively transit to various excited states. Some atoms will undergo further excitations and some will relax to lower energy excited states or ground state. The population will be in some dynamic, stochastic state. Light at wavelengths corresponding to the specific electron transitions will be emitted from the system at an intensity related to the number of such transitions. The wavelengths present and their intensities can be measured, yielding a spectrogram. Below is a spectrogram for chromium where the region of the spectrum is between 200 nm and 550 nm (uv range).

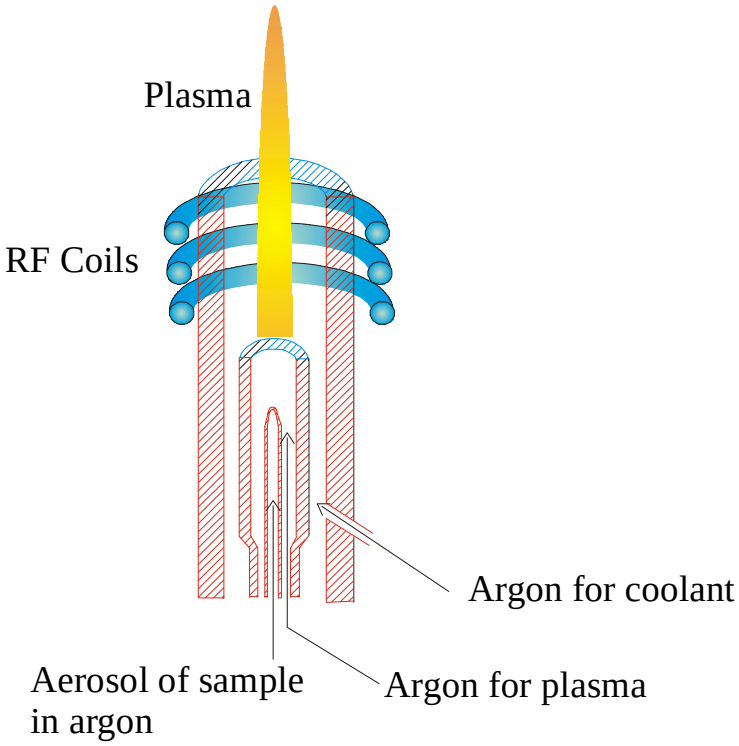


The height of the peak at 267.716 nm could be used to quantify chromium in a sample. We would have to be sure there were no other factors that would affect the height at this wavelength. For example, manganese has a very weak peak at 267.633. If the concentration of manganese was very high, or if the resolution of the spectrometer was poor, manganese would produce an interference in the measurement of chromium at this wavelength.

Inductively Coupled Argon Plasma Atomic Emission Spectrometry (ICP), Techniques and Instrumentation

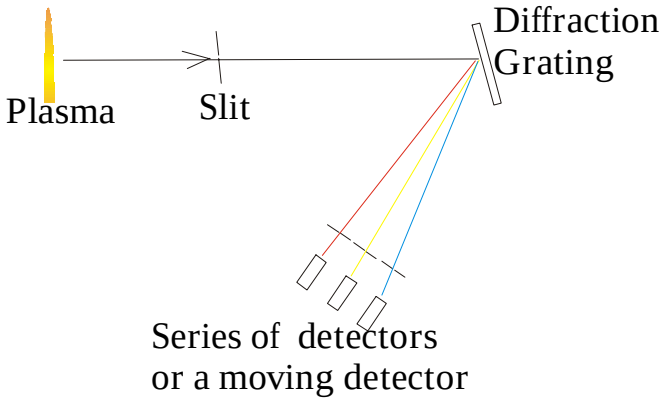
An ICP spectrometer has three basic sections, a plasma torch, an optical grating/detector system, and a data system.

The plasma torch is pictured below. Three concentric quartz tubes are surrounded by a series of RF coils. A flow of argon passes through each tube. The outer flow is a coolant to protect the RF coils. The middle flow provides "fuel" for the plasma. The center tube injects sample aerosol into the plasma for excitation. The RF coils carry a high frequency alternating current, which produces an alternating axial magnetic field. When argon flows through this field it is unaffected until plasma formation is seeded by an ionizing electric discharge (spark). Once initiated, the plasma is conductive. The alternating magnetic field induces a current in the plasma – energizing it sufficiently to maintain continuous plasma generation. This plasma "flame" is 9000°C to 10000°C.



The light emitted from the plasma is directed into an optical system, which spatially separates the wavelengths of the light. Various methods of detecting light

at specific wavelengths are used. One method uses a series of detectors to simultaneously detect several wavelengths. Another uses a moving detector to sequentially detect wavelengths.



Finally, the data system stores/analyzes the detector output and provides instrument control.

Calibration

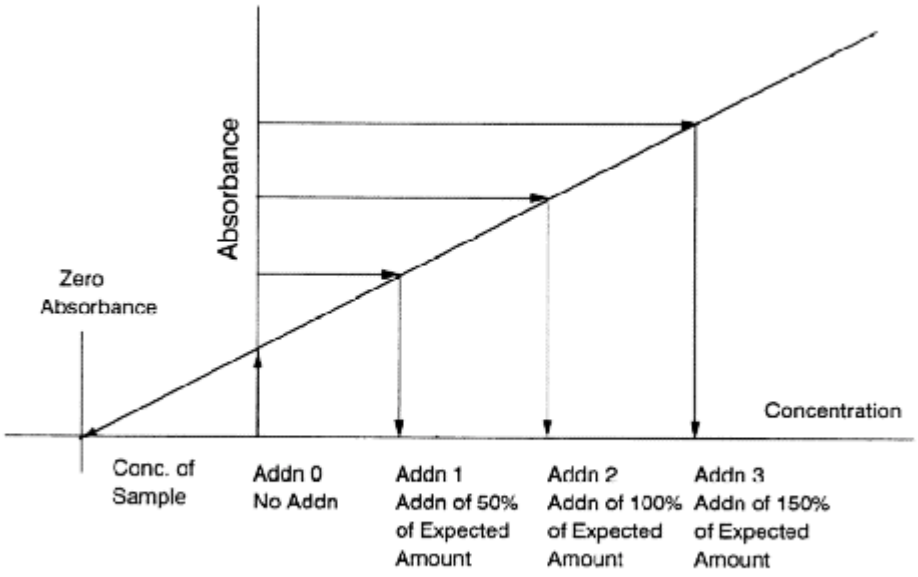
The intensity of light emitted by an element at any of its characteristic wavelengths is a linear function of that element's concentration, provided there are no interferences and the plasma conditions and instrument optics are stable. This linearity extends over several orders of magnitude. A simple linear calibration function is usually used which relates peak height (emission intensity) at a pre-chosen analytical wavelength to concentration.

The ICP technique is extraordinarily linear. Many procedures actually permit the use of sample data obtained by extrapolating concentrations from intensities way above those obtained during a daily, one-point calibration – provided a periodic linear range evaluation is performed.

Another calibration strategy is the method of standard additions. SW846 provides a good functional description of this method:

"To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted

to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected emission from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample emission. The emission of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero emission, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown below. A linear regression program may be used to obtain the intercept concentration."



Basically, what's happening is we are performing the calibration using the matrix of the sample itself. We are recording the responses of the standards as they are attenuated by the matrix and assuming that no emission will result if there is no analyte present.

This process is more easily understood in a sometimes used, limiting case where only one standard fortified sample is analyzed in addition to the sample itself. Let's

say we obtain a result for a sample of 60 ug/l. Let's also say we fortified the sample with 50 ug/l of standard and obtained a result for this *spiked* sample of 100 ug/l. The recovery of the spike equals the spiked sample amount minus the un-spiked sample amount or 40 – 80% of the actual amount added. The assumption in the method of standard additions is: if the matrix suppressed the spike recovery by a factor of 0.8, then the original sample result of 60 is also suppressed by a factor of 0.8. That is, the original result is actually 75.

Interferences

Several factors can interfere with ICP analysis, including:

- The sample's viscosity can change the sample's delivery rate to the plasma relative to that of the standards.
- High concentrations of dissolved solids can suppress ionization in the plasma.
- Strong spectral emissions near the analytical wavelength, caused by high levels of another elemental species, can distort the baseline from which emission intensities are evaluated.
- Broadband radiation from decomposing organics or molecular excitations can raise the baseline from which emission intensities are evaluated.
- The presence of other elements with emission wavelengths coincidental with the measured element's wavelength can cause falsely positive results or high results.

Determining if interference is occurring is usually accomplished in three ways. First, the samples (or a sample chosen to represent a group of samples) are analyzed both with and without a spike added just prior to analysis. If this spike's recovery is poor, an interference is indicated. The method of standard additions corrects these interferences.

A second check involves analyzing the sample at two different dilutions and checking the agreement of the calculated results. Usually, if a sample has a viscosity-related delivery problem, the more highly diluted result will be higher. Obviously, for this technique to work the sample must have the element being measured present at a concentration high enough to be measured confidently at the dilution. Again, the method of standard additions corrects these interferences.

When another element is present with emission wavelengths coincidental with the measured element's wavelength, neither of the above checks will detect the problem. Generally, analytical wavelengths are chosen to minimize these occurrences, and today's spectrometers have adequate resolution to avoid most overlaps. However, a system for evaluating inter-element effects and making inter-element corrections is necessary.

To evaluate inter-element errors and make inter-element corrections, the instrument is calibrated to measure each element, and a series of single component standards for all possible interfering elements is aspirated into the plasma. The false positive result produced by each interferent is used to determine a correction factor. For example, let's say we are evaluating lead. We might determine that a 100 mg/l aluminum standard results in a false-positive lead result of 0.17 mg/l. Later, whenever we analyze lead, we also analyze aluminum. Our final result for lead for any given sample is calculated by subtracting the predicted false-positive lead concentration contributed by the aluminum in the sample from the total lead result. The following table from SW 846 presents potential inter-element interferences.

ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM
INTERFERENCE AT THE 100-mg/L LEVEL[c]

Analyte	Wavelength (nm)	Interferent[a,b] Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

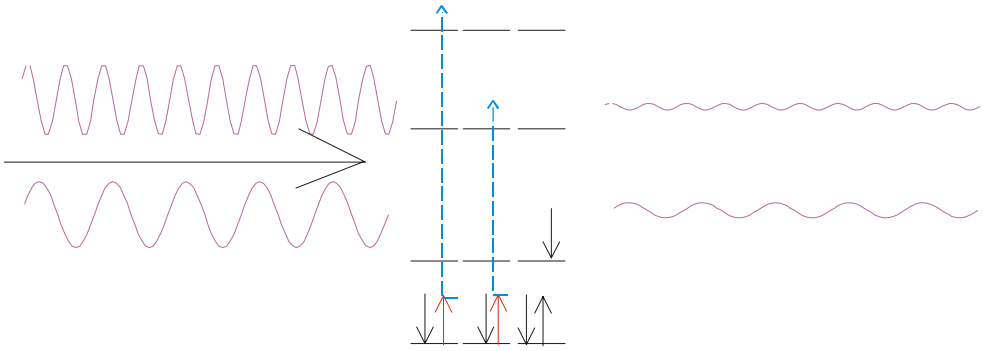
Al - 1000 mg/L
Ca - 1000 mg/L
Cr - 200 mg/L
Cu - 200 mg/L
Fe - 1000 mg/L
Mg - 1000 mg/L
Mn - 200 mg/L
Tl - 200 mg/L
V - 200 mg/L

[b] The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferent figure.

[c] Interferences will be affected by background choice and other interferences may be present.

Absorption Spectroscopy

If we use an excited population of atoms of a given element as a light source and direct that light through an unexcited population of those same atoms, some of the unexcited atoms will transit to excited states – absorbing the light. The reduction in intensity of light at a given wavelength is proportional to the concentration of atoms in the population that was originally at ground state.

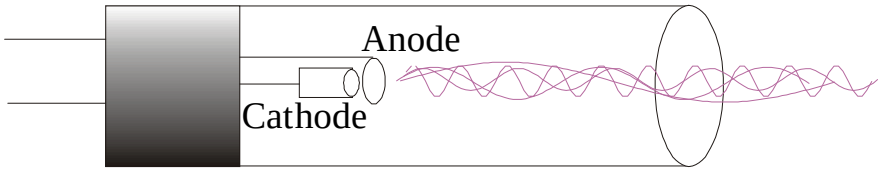


Other factors can reduce the transmitted light and some means for correcting for these interfering absorbances must be employed.

Instrumentation and Techniques

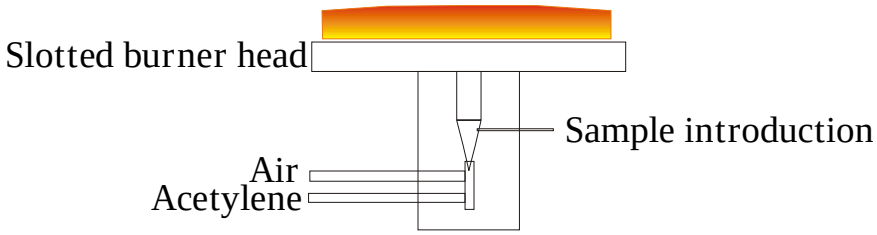
An atomic absorption (AA) spectrometer has four basic components: a source of element-specific radiation, a sample atomization system, an optical grating/detector system, and a data system.

The source of element-specific radiation is a DC lamp where the cathode is constructed using the element of choice. When energized, the cathode material is partially transformed to various excited states.

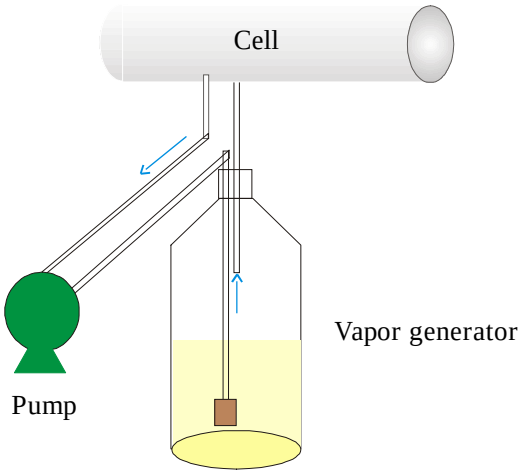


There are several sample atomization systems. One technique uses a burner-head interfaced with a sample aerosol introduction system. The flame is fueled with an air/acetylene or nitrous oxide/acetylene mixture. As the entrained aerosol enters the flame, the elements present are atomized but not ionized. The flame

atomization technique is rarely used for environmental analysis. ICP is more interference free, has better detection limits, and is faster.



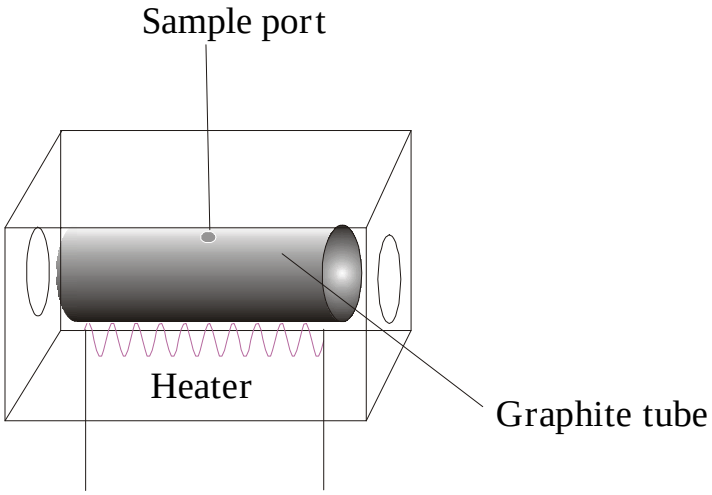
Mercury metal has a high enough vapor pressure to enable presentation of atomic mercury to the lamp beam without a thermal process. Mercury present in an aqueous solution is reduced to metallic mercury in a closed container. The solution is sparged with air and the headspace in the container is pumped to a cell aligned in the lamp beam. This approach is termed the *cold vapor* technique.



Finally, certain metals will form gaseous hydrides under acid conditions in the presence of hydrogen gas. The setup is schematically similar to that shown for mercury. The hydrogen is generated *in situ* by adding a metal like zinc. The gaseous hydride method is occasionally used for environmental samples because it gives good detection limits for those selected metals that form hydrides. However, interferences are frequently a problem.

Another atomization technique is the graphite furnace. In this technique, a graphite tube is clamped into a cell with transparent windows on each side. Sample is

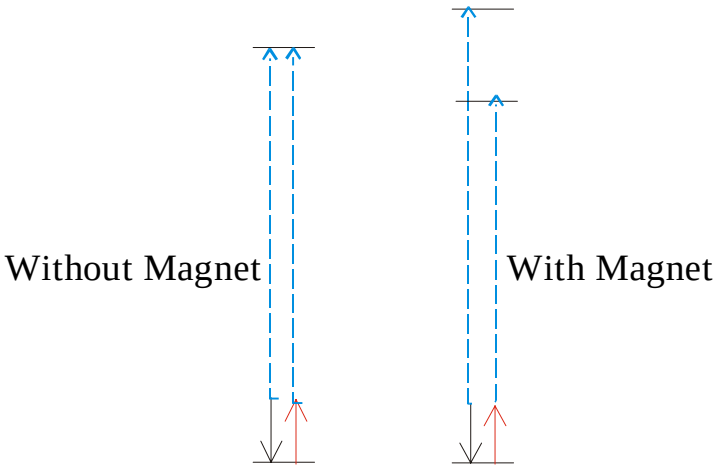
deposited in the tube as an aqueous solution. The tube is heated in a series of steps. First, the tube is heated to just above 100°C to boil away the water. Next, the tube is heated to some temperature high enough to decompose any organic material present, but not so high as to vaporize the element of interest. Finally, the tube is heated to vaporize the element being measured.



Interferences

Naturally, this final atomization step can produce other light-absorbing components in the cell in addition to the element being measured. This background would make the technique unusable if it were not for an ingenious application of the Zeeman effect. Electrons, being moving charges, have a magnetic polarity. (Recall that pairs of electrons in an orbital have opposite magnetic polarities.)

When an external magnetic field is applied to an atom, that field couples (or de-couples) with the magnetic field of the electron, stabilizing it (or de-stabilizing it) from an energy standpoint. The energy required to promote that electron to a higher energy orbital either decreases or increases depending on whether it is coupling or de-coupling with the external field. The wavelength of light associated with the energy of the electron's transition changes when the field is applied.



In the spectrometer, the magnet is applied – in pulses – to the sample area and not the lamp area. The analyte in the sample will only absorb the analytical wavelength emitted from the lamp when the magnet is off. All of the radiation absorbed with the magnet on is being absorbed by background. The absorbance of the analyte is the difference between the absorbance with the magnet off and the absorbance with the magnet on. This technique is called Zeeman background correction.

Although Zeeman background correction is a powerful technique, interferences frequently persist. An additional method for eliminating interferences includes the addition of a matrix modifier, which – through poorly understood mechanisms – alters the atomization temperature of the analyte or alters the interfering substance itself. Optimization of the electrothermal profile for the process sometimes helps.

Occasionally, interferences cannot be removed by any means except dilution, which sacrifices detection limits.

Calibration

A simple linear calibration function is usually used that relates peak height (absorbance) at a pre-chosen analytical wavelength to concentration. Absorbance vs. concentration functions for AA have a limited linear range, so readings must be within the calibration range. The method of standard additions described previously under ICP Calibration is also commonly used (in fact, more so with

AA). When the method of standard additions is not used, samples should be analyzed both with and without a spike added just prior to analysis to verify the absence of interference.

EPA SW846 Methods for Metals Analysis

SW846 metals methods were originally based on wastewater/drinking water methods. These methods were (and still are) documented in "Manual of Methods for Chemical Analysis of Water and Water Wastes," EPA-600/4-79-020 (Revised 1983), USEPA/EMSL. They have 200 series numbers, e.g. 200.7 is the wastewater ICP method. The EPA Office of Solid Waste modified these methods by adding additional detail, specifying further QA/QC, and making provisions for the analysis of solids.

There is one ICP determinative method, Method 6010. AA methods have 7000 series numbers. Each metal has its own group of AA procedures, one for graphite furnace, one for flame, and others for techniques like hydride generation or colorimetric procedures, if appropriate. The cold vapor mercury technique has two methods, one for solids and one for liquids.

Method 6010 refers to other methods (3000 series numbers) for sample preparation. Most of the AA procedures also refer to these preparation techniques, but some have a built-in sample preparation section for water, soil or both. For example, the graphite furnace technique for silver, Method 7761, details sample preparation for water and ignores soil altogether.

Sample Preparation Methods

The primary digestion procedures for metals for subsequent analysis by methods without built-in preparation protocols are the following:

- **Method 3005A:** Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy
- **Method 3010A:** Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy

- **Method 3020A:** Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy
- **Method 3050B:** Acid Digestion of Sediments, Sludges, and Soils

The SW846 summary for each of these methods is presented below.
Method 3005A: Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy

Total recoverable metals - The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

Dissolved metals - The sample is filtered through a 0.45-µm filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards.

Method 3010A: Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy

A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume.

Method 3020A: Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy

A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is cooled and brought up in dilute nitric acid such that the final dilution contains 3% (v/v) nitric acid. This percentage will vary depending on the amount of acid used to complete the

digestion. If the sample contains suspended solids, it must be centrifuged, filtered, or allowed to settle.

Method 3050B: Acid Digestion of Sediments, Sludges, and Soils

For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide.
For GFAA or ICP-MS analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL.
For ICP-AES or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed.

Two other procedures that could be considered preparations – both for metals and organics – are the Toxicity Characteristic Leaching Procedure (TCLP) and the Synthetic Precipitate Leaching Procedure (SPLP). Both techniques are intended to mimic the leaching of contaminants from soils or wastes by rain or runoff. The final sample is aqueous and is subjected to additional preparations and determinative steps for aqueous samples.

TCLP

Application

The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

Summary of Method

For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted (18+/-2hr) with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

Extraction Fluids

Extraction fluid # 1: Dilute acetic acid/sodium acetate. The pH of this fluid will be 4.93 + 0.05.

Extraction fluid # 2: Dilute acetic acid. The pH of this fluid will be 2.88 + 0.05.

Extraction Fluid Determination

The extraction for volatile constituents uses extraction fluid #1

A specialized waste pH check is used to choose the fluid for metals and semivolatiles. If this pH is <5.0, extraction fluid #1 is used, if >5.0 extraction fluid #2 is used.

SPLP

Application

Method 1312 is designed to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes.

Summary of Method

For samples containing greater than 0.5 % solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted (18+/-2hr) with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste, the extraction fluid employed is a pH 4.2 solution. A special extractor vessel is used when testing for volatile analytes. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

Extraction Fluids

Extraction fluid #1: Dilute sulfuric and nitric acids, with a pH of 4.20 + 0.05. The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes.

Extraction fluid #2: Dilute sulfuric and nitric acids, with a pH of 5.00 + 0.05. The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

Extraction fluid #3: This fluid is reagent water and is used to determine cyanide and volatiles leachability.

The Difference Between the Procedures and How To Choose

The primary difference in the procedures is the extraction fluids used. The TCLP method uses acetic acid or acetic acid/sodium acetate solutions. The SPLP method uses nitric acid/sulfuric acid solutions. The final pHs and buffering capacity of the solutions are also different.

The logic for choosing the solutions for the TCLP procedure is based on the sample's pH. The logic for choosing the solutions for the SPLP procedure is based on where the sample comes from if it is a soil. The SPLP procedure has no choice logic for wastes.

SW846 provides no guidance for choosing between these procedures. The TCLP procedure is specified in the Code of Federal Regulations for hazard determination for wastes.

The argument can be made that the extraction fluid used in the SPLP method (nitric/sulfuric) better approximates the chemistry of acid rain than does the fluid used in the TCLP method (acetic/acetate).

Determinative Methods

EPA Method 6010

The current revision of Method 6010 is 6010B. The procedure section of the method requires certain procedural elements and recommends additional elements. A considerable amount of fundamentally important instrument set-up and preparation is not discussed at all. The method simply defers this material to the manufacturer's recommendations.

The method recommends multiple exposures (several readings) for each sample, standard, blank, etc.

Initial Calibration

The 6010 minimum daily initial calibration specifications require an instrument blank and a one-point calibration. The method further recommends that the linear range for each metal be established "periodically". One prudent approach is to perform a multilevel calibration periodically (bimonthly or whenever new standards are prepared or when instrument repairs are performed) using standards that include a point at the reporting limit, one or two intermediate points and one high point – above which all samples will be diluted.

Initial Calibration Verification (ICV)

After initial calibration is complete, it is verified with a second source standard. The result for this standard must be within 10% of true value. Multiple exposure results must have a standard deviation of 5% or less.

Continuing Calibration Verification (CCV)

This is a mid-point check standard. It also must be within 10% of true value and multiple exposure results must have a standard deviation of 5% or less. This standard (or the ICV) must be re-run every 10 samples. Data is not used if it is not "sandwiched" between passing events.

Continuing Calibration Blank (CCB)

This is an instrument blank (no prep steps). It must be free of analyte above the detection limit. It is also re-run every 10 samples.

Inter-element Interference Check Samples (ICSA and ICSAB)

The method requires the analysis of an interference check sample to verify inter-element correction factors. However, the method is vague about just what this standard is. A common practice is to borrow the approach used in the EPA's CLP protocol.

Two standards are prepared from two stock solutions. Stock solution "B" is a mix of elements that are known to be interferents. Stock solution "A" is a mix of analytes that are known to have common interference problems. The two standards made from these stock solutions are:

- ICSAB: A standard containing the interferents and analytes made from stock "A" and stock "B". ICSAB is analyzed at the beginning and end of each run. The results must be within 20% of true value for the analytes in this check.

- ICSB: A standard containing the interferents alone made from stock "B". ICSB is analyzed at the beginning and end of each run. Although there is no formal specification for this analysis, the results should be below reporting limits.

The following table presents the composition of these check standards.

Analytes (A)	mg/	Interferents (B)	mg/l
Ag	1.0	Al	500
Ba	0.5	Ca	500
Be	0.5	Fe	200
Cd	1.0	Mg	500
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	1.0		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

Method Blank

This check sample is a blank that has been carried through all preparation steps. There should be one blank for each preparative batch for each matrix. This blank should be free from analyte above the reporting limit. (CLP protocols require this blank to be free from contamination above the instrument detection limit.)

Laboratory Control Standard (LCS)

This is a standard that has been carried through all of the preparative steps. It is not required by the method but is an element of good practice. There should be one LCS per preparative batch.

Reporting Limit Standard

This audit is also not required (or mentioned) by the method. It is a standard at the reporting limit. The audit provides positive documentation that an analyte will be seen when it is present at the reporting threshold.

Matrix Spike, Matrix Spike Duplicate, Duplicate Samples

The method requires a matrix spike (MS) and matrix spike duplicate (MSD). The MS (and the MSD) is prepared by carrying a sample fortified with known amounts of analytes through all preparative steps. CLP protocols do not require an MSD but do require a sample duplicate analysis. Because laboratory data packages are frequently validated by auditors versed in CLP protocols and not SW846 methods, labs often follow the CLP approach to this precision and accuracy evaluation.

The method provides the following specifications for the MS and MSD analyses:

- A control limit of ± 20% RPD or within the documented historical acceptance limits for each matrix shall be used for sample values greater than ten times the instrument detection limit.

- The spiked sample or spiked duplicate sample recovery is to be within ± 25% of the actual value or within the documented historical acceptance limits for each matrix.

The recovery specification fails to consider the case where the actual analyte concentration in the sample is significantly higher than the spike amount. The CLP protocol does provide for this event by not requiring the flagging of results associated with a non-compliant MS when the original concentration of the analyte is a factor of 4 or more higher than the spike amount.

It must be pointed out that a non-compliant MS, MSD or duplicate analysis does not necessarily indicate a procedural error. Matrix effects are the most common source of these failures. In fact, the purpose of the audit is to evaluate the application of the method to the matrix. Control in the analytical process is evaluated with other audits (blanks, standards, LCS, etc.). A failing MS, MSD or duplicate analysis might be a procedural problem, and when these failures occur, steps should be taken to confirm process control.

Dilution Tests and Post Digestion Spike Tests

Method 6010 has no requirement for running a dilution test or a post digestion spike recovery test to identify possible interferences. The method recommends these tests when a "new or unusual sample matrix is encountered." The specifications for these tests are as follows:

Dilution Test: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

Post Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

The obvious question is, what is a new or unusual matrix? One prudent approach to judging whether these interference tests should be run uses the matrix spike/matrix spike duplicate results. Clearly, when these audits are within control limits, a matrix interference need not be considered. It makes sense to use the

failure of these audits to trigger dilution tests and post digestion spikes to further evaluate matrix interference.

Graphite Furnace Methods

EPA Method 7000A covers general procedures for atomic absorption measurements. Specific analytes are further addressed in separate methods. The furnace technique is most commonly used with arsenic, selenium, lead, thallium, and antimony. ICP does not have adequate sensitivity for these metals. The ICP method can still be used to measure and report these parameters if project-specific detection limit objectives allow, or if the actual sample concentration is well above (5X) the ICP detection limit. The GFAA method numbers for these metals are tabulated below.

arsenic	7060A
selenium	7740
lead	7421
thallium	7841
antimony	7041

The general sequence for GFAA analysis sessions is the same as that for the ICP method, with the following major differences:

- The method recommends multiple injections for all runs to evaluate reproducibility, but no maximum percent difference specification is given.
- Initial Calibration: A minimum of three points and a blank are required for calibration. The method provides no linearity specification for the calibration.
- The Continuing Calibration Verification check standard must be within 20% of true value.
- An LCS is required.
- The use of matrix modifiers and background correction is specified.

Mercury Analysis by the Cold Vapor Method

SW 846 lists two CVAA methods for mercury, 7470A for liquids and 7471A for solids. Both procedures have a preliminary acid digestion and oxidation step for

both standards and samples. Again, the analysis sequence is the same as for ICP except:

- Initial Calibration: A minimum of five points and a blank are required for calibration. The method provides no linearity specification for the calibration.
- The Continuing Calibration Verification check standard must be within 20% of true value.
- An LCS is required.

Typical Method Detection Limits for Metals

Metal	Method	Typical Water MDL, ug/l	Typical Soil MDL, mg/kg (1 g sample)
ALUMINUM	ICP	17	1.7
ANTIMONY	ICP	66	6.6
ANTIMONY	GFAA	4.6	0.46
ARSENIC	ICP	73	7.3
ARSENIC	GFAA	1.6	0.16
BARIUM	ICP	0.23	0.023
BERYLLIUM	ICP	0.11	0.011
BORON	ICP	13	1.3
CADMIUM	ICP	2.7	0.27
CADMIUM	GFAA	0.08	0.01
CALCIUM	ICP	11	1.1
CHROMIUM	ICP	2.9	0.29
COBALT	ICP	3.6	0.36
COPPER	ICP	4.0	0.40
GOLD	ICP	6.3	0.63
IRON	ICP	3.5	0.35
LEAD	ICP	39	3.9
LEAD	GFAA	0.40	0.040
MAGNESIUM	ICP	3.1	0.31
MANGANESE	ICP	0.46	0.046
MERCURY	CVAA	0.16	0.016
MOLYBDENUM	ICP	11	1.1
NICKEL	ICP	6.5	0.65
OSMIUM	ICP	15	1.5
PALLADIUM	ICP	13	1.3
PHOSPHOROUS	ICP	63	6.3
PLATINUM	ICP	47	4.7
POTASSIUM	ICP	320	32
SELENIUM	ICP	76	7.6
SELENIUM	GFAA	2.2	0.22
SILVER	ICP	2.7	0.27
SILVER	GFAA	0.15	0.015
SILICON	ICP	17	1.7
SODIUM	ICP	26	2.6
STRONTIUM	ICP	0.46	0.046
THALLIUM	GFAA	1.3	0.13
TIN	ICP	47	4.7
TITANIUM	ICP	1.4	0.14
TUNGSTON	ICP	34	3.4
VANADIUM	ICP	1.7	0.17
ZINC	ICP	3.0	0.30

Precision and Accuracy

Precision and accuracy evaluations for metals are performed using reagent water for the aqueous matrix and Ottawa sand for the soil matrix. For ICP, these studies

typically show accuracy levels of 90% to 110% and relative percent standard deviations within 10%. GFAA and CVAA accuracy is somewhat lower (85% to 115% typical) and precision is not quite as good (RPD of 15% is typical).

Accuracy and precision for real-world samples is another matter. Several studies have been performed on a wide variety of matrices with mixed results. Generally, the more contaminated or complex the matrix, the more inaccurate and uncertain the results become. The following document provides an excellent review of performance data for the ICP technique.

Jones, C.L. et al. An Interlaboratory Study of Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010 and Digestion Method 3050. EPA-600/4-87-032, U.S. Environmental Protection Agency, Las Vegas, Nevada, 1987.

Requesting Back-up Data

The following elements are necessary and sufficient for data review:

- Sample preparation logs.
- A chronology of the analytical session from beginning to end.
- A chronological printout of instrument results for the session.