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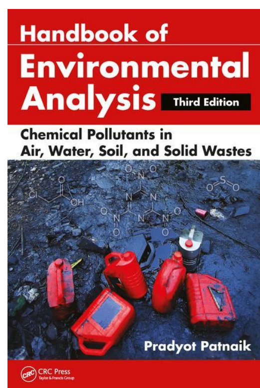

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Pradyot Patnaik

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3 Analysis of Organic Pollutants by Gas Chromatography

GC is the most common analytical technique for the quantitative determination of organic pollutants in aqueous and nonaqueous samples. In environmental analysis, a very low detection limit is required to determine the pollutants at trace levels. Such low detection can be achieved by sample concentration followed by cleanup of the extract to remove interfering substances. Sample extractions and cleanup procedures are described in detail in Chapter 5.

The GC methods, however, can be applied only to determine the presence and quantifications of any specific substance of interest. On the other hand, it cannot be used to identify an absolutely unknown substance which is a limitation of the GC technique. Despite such limitations, GC is an excellent tool for environmental analysis because the list of pollutants to be measured is confined to small numbers for which the compounds in their neat form or certified analytical standard solutions are commercially available. The presence of any substance of interest eluted as a peak in the chromatogram can be confirmed from its retention time matching with that of the same substance in its known standard solution. Furthermore, the retention times of the peaks also have to match identically as well on an alternate GC column to prevent any false identification. Also, there are additional techniques to confirm the presence of a substance if doubt arises on its presence. Some of these techniques are discussed below. There are two other limitations of GC methods that may be cited here. One is the difficulty in separating isomers in many cases, for example, *ortho*- and *para*-xylenes or anthracene and phenanthrene. Also, the substances that have high molecular weights, such as chlorophyll, cannot be determined by GC methods. However, as mentioned earlier, by using appropriate columns, detectors, and chromatographic conditions, a vast number of organic substances, including most environmental organic pollutants, can be conveniently screened and quantified by GC methods.

Aqueous samples containing volatile organics can be directly analyzed by GC (without any separate sample extraction steps) interfaced with a purge and trap setup. The analytes in the sample are concentrated by the purge and trap technique, as discussed in the following section, prior to their analysis by GC or GC/MS. The volatile organics in soils, sediments, and solid wastes may be analyzed in a similar way by subjecting an aqueous extract of the sample to purge and trap concentration. Alternatively, the analytes may be thermally desorbed from the solid matrices and transported onto the GC column by a carrier gas.

At the outset, one must understand certain principles of GC to assess if it is a proper analytical tool for the purpose. If it is so, how do we achieve the best separation and identification of component mixtures in the sample with reasonable precision, accuracy, and speed? In addition, what kind of detector and column should be selected for the purpose? It is, therefore, important to examine the type of compounds that are to be analyzed and certain physical and chemical properties of these compounds. Information regarding the structure and the functional groups, elemental composition, the polarity in the molecule, its molecular weight, boiling point, and thermal stability are very helpful for achieving the best analysis. After we know these properties, it is very simple to perform the GC analysis of component mixtures. To achieve this, just use an appropriate column and a proper detector. Properties of columns and detectors are highlighted in the following sections.

The efficiency of the chromatographic system can be determined from the number of theoretical plates per meter. Although this term primarily describes the property and resolution efficiency of a

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column, other extra column variables, such as the detector, inlet, injection technique, and the carrier gas velocity can also affect the theoretical plates. This is calculated from the following equation:

$$\text{Theoretical plates/m} = \frac{5.54\left(\frac{t}{w}\right)^2}{L}$$

where
t is the retention time of the test compound
w is the width of the peak at half height
L is the length of the column (m)

The number of theoretical plates also depends on the partition ratio k of the test compound and its solubility in the liquid phase. Substances that have higher k values have lower plate numbers. Greater plate numbers indicate greater resolution or better separation of the component mixture.

SELECTION OF COLUMN

A variety of GC columns are commercially available to meet the specific purpose. The selection of columns, their stationary phases, inside diameters, lengths, and the film thickness are briefly discussed below.

A capillary column is usually preferred over a packed column for better resolution and lower detection limit. The efficiency of a column to separate organic compounds depends on the stationary phase and the polarity of the analyte molecules. The polarity of the phase, therefore, is the most important characteristic in selecting a column. While a nonpolar phase most effectively separates nonpolar molecules, a polar phase is required to achieve the separation of polar compounds. Aliphatic hydrocarbons containing C—H single bonds are all nonpolar compounds while those containing carbon–carbon double bonds, such as olefins and aromatics, are polarizable compounds. On the other hand, organic compounds containing oxygen, nitrogen, sulfur, phosphorus, or halogen atoms should exhibit greater polarity. Examples of such polar compounds include carboxylic acids, ketones, aldehydes, esters, alcohols, thiols, ethers, amines, nitroaromatics, nitrosamines, nitriles, halocarbons, PCBs, and organic phosphates. An increase in polarity reduces the thermal stability of the stationary phase. Therefore, a phase of least polarity should be selected, whenever possible, to enhance the life of the column. Table 3.1 lists the polarity of various stationary phases of common capillary GC columns.

Capillary columns are composed of fused silica that has shown remarkable properties of inertness and efficiency in chromatographic analysis. Glass capillaries and stainless steel are sometimes used too; but their applications are nowadays limited.

The inside diameter of the capillary column is another major factor that often dictates the separation of components. The narrowbore columns with internal diameter (ID) 0.20, 0.25, and 0.32 mm provide the best separation for closely eluting components and isomers. The smaller the ID, the greater is the resolution. On the other hand, a major disadvantage of such a narrowbore column, however, is its low sample capacity (i.e., the quantity of sample that can be applied without causing the peak(s) to overload). Wider bore columns of 0.53 and 0.75 mm ID do not have this problem. These wider columns have greater sample capacity than narrowbore columns but relatively lower resolution capacity. Such widebore columns, however, are better suited for environmental samples that often contain pollutants at high concentrations. In addition, widebore columns of 0.53 and 0.75 mm ID provide sufficient sensitivity for minor components' peaks without being overloaded with the major components. The sample capacity of a column may further be increased by temperature programming. It also depends on the polarity of the components and the phase—the polar

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phase has a high capacity for polar components, while the nonpolar phase has a high capacity for nonpolar components (Table 3.1).

The stationary phase can be bound to the tubing either as a physical coating on the wall, or can be chemically immobilized. The former type phases are called nonbonded phases, while the chemically bound phases, cross-linked within the tubing, are known as bonded phases. The latter is preferred because it can be used at high temperatures with less bleeding and can be rinsed with solvents to remove nonvolatile substances that accumulate on the column.

The film thickness of the stationary phase is another major factor that should be taken into account for column selection. A thicker film increases the resolution on a nonpolar column, but decreases the same on a polar column. It also increases the sample capacity, retention of sample components, and, therefore, the retention time and the temperature at which the components would elute from the column and the column bleed. Thus, it has both advantages and disadvantages. A thicker film (>1 μm) should be used to analyze gases or substances with low boiling points or to analyze highly concentrated samples. On the other hand, a thin film (<0.25 μm) should be used to analyze compounds with high boiling points (>300°C) and should be employed with a shorter column (10–15 m length). Film thickness of the stationary phase and the column ID are interrelated, as follows:

$$\text{Phase ratio}, \beta = \text{column radius}, \mu\text{m}/\text{phase thickness}$$

Columns with equal beta value (β) will provide similar separations under the same analytical conditions. For example, a capillary column with 0.32 μm ID and 0.8 μm phase film thickness could be substituted with a column of the same phase with 0.53 μm ID and 1.3 μm film thickness to produce very similar separation. However, standard film thickness (0.25–0.8 μm) should work for most chemical analyses.

Separation of closely eluting components can be efficiently achieved on a longer column. The greater the length of the capillary column, the higher is its resolution efficiency. On the other hand, the long column enhances the time of analysis, increasing the retention times of the components. As mentioned earlier, high resolution can also be attained with narrowbore columns. Therefore, optimizing the column length and ID can provide good separation in the desired analysis time.

TABLE 3.1
Polarity of Stationary Phases

Polarity	Stationary Phase	Examples
Nonpolar	Polydimethylsiloxane	AT-1, BP-1, DB-1, DC-200, HP-1, OV-1, OV-101, RSL-160, Rtx-1, SF-96, SP-2100, SPB-1, ULTRA-1
	Polyphenylmethylsiloxane	AT-5, BP-5, DB-5, HP-5, MPS-5, OV-73, RSL-200, Rtx-5, SE-52, SPB-5, ULTRA-2
Intermediate	Polyphenylmethylsiloxane	AT-20, BP-10, DB-17, HP-17, MPS-50, OV-17, RSL-300, Rtx-20, SP-2250, SPB-20
	Polycyanopropylphenyldimethylpolysiloxane	AT-1301, DB-1301, Rtx-1301
	Polycyanopropylphenylmethylsiloxane	AT-1701, DB-1701, GB-1701, OV-1701, Rtx-1701, SPB-1701
Polar	Polytrifluoropropylsiloxane	AT-210, DB-210, OV-210, QF-1, RSL-400, SP-2401
	Polyphenylcyanopropylmethylsiloxane	AT-225, DB-225, HP-225, OV-225, RSL-500, Rtx-225
	Polyethyleneglycol	AT-WAX, BP-20, Carbowax 20M, CP/WAX 51, DB-WAX, HP-20M, Stabilwax, Supelcowax 10, Superox II
Very polar (acidic)	Polyethyleneglycol ester	AT-1000, FFAP, Nukol, OV-351, SP-1000, Superox-FA

TABLE 3.2
Separation Efficiency and Sample Capacity of GC Columns of Varying IDs

Column ID (mm)	Sample Capacity (ng)	Separation Efficiency (Theoretical Plates/m)[a]	Carrier Gas Flow Rate, Optimum (cc/min)
		Capillary	
0.20	10–30	5000	0.4
0.25	50–100	4200	0.7
0.32	400–500	3300	1.4
0.53	1000–2000	1700	2.5
0.75	10,000–15,000	1200	5
		Packed	
2.0	20,000	2000	20

Note: The data presented are for a 60 m capillary column and a 2 m packed column.
[a] Numbers are rounded off. The higher this number, the greater is the resolution efficiency.

The separation efficiency of a column can be alternatively determined from the number of theoretical plates per meter. The greater the number, the greater is the resolution efficiency of the column. Table 3.2 presents the separation efficiency and the sample capacity of GC columns of varying IDs.

DETECTORS

Selection of GC detectors is very crucial in chemical analysis. Flame ionization detector (FID) and thermal conductivity detector (TCD) can be used for all general purposes. However, the detection limits for analytes are high, especially for the TCD. The latter is commonly used for gas analysis.

When using FID, aqueous samples can be directly injected onto the GC without any sample extraction. The detection limit of an analyte, however, in such a case would be much higher (low ppm level) than what is desired in environmental analysis. When appropriate sample concentration steps are adopted, organic compounds in aqueous and solid matrices and air can be effectively determined at a much lower detection level. Carbon disulfide is commonly used in the air analysis of many organics by GC-FID.

Halogen-specific detectors, such as the electron capture detector (ECD) and Hall electrolytic conductivity detector (HECD) show the best response to compounds that contain halogen atoms. The nitrogen–phosphorus detector (NPD) in the nitrogen mode can determine most nitrogen-containing organics while the same detector in the phosphorus-specific mode can analyze organophosphorus compounds. The flame photometric detector (FPD) is also equally efficient for determining phosphorus compounds. The FPD, however, is primarily used to analyze sulfur-containing organics. The photoionization detector (PID) is sensitive to substances that contain the carbon–carbon double bond such as aromatics and olefins, as well as their substitution products.

CALIBRATION

Prior to the analysis of the unknown, a calibration standard curve is prepared by running at least four standards. Calibration is performed in two ways: the external standard method and internal standard method. The external standard method involves preparation of a calibration curve by plotting the area or height response against concentrations of the analyte(s) in the standards. The calibration factor is then calculated as the ratio of concentrations to area/height response and should be constant over a wide range of concentrations. To determine the concentration of the analyte in

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the unknown sample (extract), the response for the unknown should be compared with that of the standards within the linear range of the curve. Alternatively, an average of response ratios may be calculated which is compared with the response of the analyte. A single point calibration may be used if the area/height response of the analyte is within ±20% of the response of the standard.

The internal standard method is more reliable than the external standard method. Equal amounts of one or more internal standards are added onto equal volumes of sample extracts and the calibration standards. The response factor (RF) is then calculated as follows:

$$\mathrm{RF} = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where A_s and A_{is} are the area (or height) response for the analyte and the internal standard, respectively; while C_s and C_{is} are their concentrations. Thus, the RF for analytes may be determined by running standard solutions of the analytes containing internal standards. If the RF values over the working range of concentrations fall within ±20% of relative standard deviation, an average RF value should be used in the above equation to determine the concentration of the analytes in the sample. Alternatively, a calibration curve may be plotted between response ratio (A_s/A_{is}) versus RF.

The concentration of the analyte in the sample $= A_s \times C_{is} \times D / A_{is} \times \mathrm{RF}$ where D is the dilution factor. For aqueous samples, the concentration of the analyte is usually expressed in μg/L. All concentration terms including those of the calibration standards and internal standards must be in the same unit.

Calculations

The concentration of an analyte in an aqueous or nonaqueous sample may be calculated by one of the following methods.

External Standard Calibration

The area/height response for the analyte peak is compared with that of the standards from the calibration curve or from the calibration factor.

$$\text{Concentration}, \mu\text{g/L} = \frac{A_{unk} \times Q_{std} \times V_{tot} \times D}{A_{std} \times V_{inj} \times V_{sample}}$$

where

- A_{unk} is the area count or peak height of the analyte
- Q_{std} is the amount of standard injected or purged in ng
- V_{tot} is the volume of total extract in μL
- D is the dilution factor, dimensionless
- A_{std} is the area or peak response for the standard
- V_{inj} is the volume of extract injected in μL
- V_{sample} is the volume of sample extracted or purged in mL

For nonaqueous samples, the concentration of the analyte is calculated in the same way except that the weight of the sample W is substituted for the volume of the sample, V_{sample}. Thus,

$$\text{Concentration}, \mu\text{g/kg} = \frac{A_{unk} \times Q_{std} \times V_{tot} \times D}{A_{std} \times V_{inj} \times W}$$

The concentration calculated above is on the sample "as is" and not as dry weight corrected. Concentration on a dry weight basis may be calculated by dividing the above result with the percent total solid expressed as a decimal.

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EXAMPLE 3.1

A 500-mL sample aliquot was extracted with hexane to a final volume of 2 mL. The volume of sample extract and the standard injected were 4 μL. The concentration of the analyte in the standard was 50 μg/L. The area response of the analyte in the sample extract and the standard solutions were 28,500 and 24,800, respectively. Determine the concentration of the analyte in the sample.

$$A_{unk} = 28{,}500$$
$$A_{std} = 24{,}800$$
$$Q_{std} = 4\,\mu L \times \frac{50\,\mu g}{1L} \times \frac{1L}{1{,}000{,}000\,\mu L} \times \frac{1000\,ng}{1\,\mu g} = 0.2\,ng$$
$$V_{tot} = 2\,mL \times \frac{1000\,\mu L}{1mL} = 2000\,\mu L$$
$$V_{inj} = 4\,\mu L$$
$$V_{sample} = 500\,mL$$
$$D = 1, \text{ the extract was not diluted}$$

Concentration of the analyte in the sample, μg/L

$$= \frac{28{,}500 \times 0.2\,ng \times 2000\,\mu L \times 1}{24{,}800 \times 4\,\mu L \times 500\,mL}$$
$$= 0.23\,ng/mL$$
$$= 0.23\,\mu g/L$$

Alternative Calculation

When the aliquots of the sample extract and the standard injected into the column are the same (i.e., 4 μL), the concentration of the analyte in the sample may be calculated in a simpler way as shown below:

$$\text{Concentration of analyte, } \mu g/L = \frac{(C_{extract} \times V_{extract} \times D)}{V_{sample}}$$

where
$C_{extract}$ is the concentration of the analyte, μg/L in the extract determined from the calibration standard curve
$V_{extract}$ is the volume of extract, mL
V_{sample} is the volume of sample, mL
D is the dilution factor

In the above problem the concentration of the analyte in the *extract* is

$$\frac{28{,}500}{24{,}800} \times 50\,\mu g/L = 57.5\,\mu g/L$$

(taking single point calibration) which can also be determined from the external standard calibration curve. Therefore, the concentration of the analyte in the *sample*

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$$= 57.5\,\mu\text{g/L} \times \frac{2\,\text{mL}}{500\,\text{mL}} \times 1$$
$$= 0.23\,\mu\text{g/L}.$$

Internal Standard Method

The concentration of the analyte can be determined from the RF using the equation

$$C_s = \frac{A_s \times C_{\text{is}}}{A_{\text{is}} \times \text{RF}}$$

For this, the internal standard eluting nearest to the analyte should be considered.

ROUTINE ANALYSIS

Routine GC analysis for environmental samples involve running one of the calibration check standards before sample analysis to determine if the area or height response is constant (i.e., within 15% of standard deviation of the RF or calibration factor, and to check if there is a shift in the retention times of the analytes' peaks). The latter can occur to a significant degree due to any variation in conditions, such as temperature or the flow rate of the carrier gas. Therefore, an internal standard should be used, if possible, in order to determine the retention time shift or to compensate for any change in the peak response. If an analyte is detected in the sample, its presence must be ascertained and then confirmed as follows:

1. Peak matching of the unknown with the known should be done, additionally, at a different temperature and/or flow rate conditions.
2. The sample extract should be spiked with the standard analyte solution at a concentration to produce a response that is two to three times the response of the unknown peak.
3. The identification of the peak must be finally confirmed on a second GC column. This may be done either after performing Steps 1 and 2 or by injecting the extract straight onto the second column (confirmatory GC column) without going through Steps 1 and 2.

In addition to determining the presence or absence of pollutants of interest in the sample, the routine analysis must include QC/quality assurance tests to determine the precision and accuracy of the test results and any possible source of errors such as sample contamination, absence of preservative, or exceeding of sample holding time. The QA/QC is discussed at length in Chapter 2.

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