INTERNATIONAL
RECOMMENDATION

OIML R 82
Edition 1989 (E)

Gas chromotographs for measuring pollution from pesticides and other toxic substances

Chromatographes en phase gazeuse pour la mesure des pollutions par pesticides et autres substances toxiques

OIML R 82 Edition 1989 (E)

ORGANISATION INTERNATIONALE
DE MÉTROLOGIE LÉGALE

INTERNATIONAL ORGANIZATION
OF LEGAL METROLOGY

Foreword

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GAS CHROMATOGRAPHS
for MEASURING POLLUTION from PESTICIDES
and OTHER TOXIC SUBSTANCES

1. Scope

1.1. This Recommendation provides the requirements, procedures and tests for verifying the performance of a gas chromatograph (GC) when used for the measurement of pesticides and other toxic substances in carrying out pollution control programs and in assessing the quality of food products as mandated by national laws and regulations. It does not intend to exclude any equivalent means of measurement or analysis for such substances. Many gas chromatographs are available which employ a wide variety of techniques and methods to detect qualitatively and quantitatively sample components [1, 2, 3]. In addition, these instruments are applied in the analysis of a variety of sample types such as ground water, surface water, industrial effluents, soil and sediments, plant and animal tissue, and food. Usually different sample types require different sample preparation techniques prior to an analysis by a gas chromatograph. Sampling techniques and methods of analysis are not specified in this Recommendation; however, examples of relevant methods are referenced in the Annex A.1.

1.2. Sample compounds can be detected by a gas chromatograph if they can pass through a gas chromatographic column and not be significantly affected by thermal or catalytic decomposition or adsorption. Some difficult compounds, which are nonvolatile or thermally unstable, may be converted to derivatives that are volatile and stable and can be separated and detected by a gas chromatograph. Table 1 lists examples of types of compounds that can be detected by a gas chromatograph.

Table 1

Examples of types of compounds detectable by a gas chromatograph

Type of compound (*)	Examples of associated detectors (**)
Organohalogens	Electron capture and electrolytic conductivity
Carbamates	Electrolytic conductivity and thermionic
Organophosphates	Thermionic and flame photometric
Polynuclear aromatics (PNA)	Flame ionization
Benzene	Photoionization and flame ionization
Phthalates	Electron capture and flame ionization
Nitrates and amines	Thermionic

(*) Some sample compounds may have to be converted to derivatives before being analyzed.

(**) Selection of the detector is generally determined by the sample composition, its concentration of compounds of interest, and its matrix.

2. Application

2.1. The application of gas chromatography to environmental measurements are discussed in the references [4] and [5].

2.2. The performance of any specific instrument depends on the quality of its individual components and combinations thereof. Therefore, instrument performance better than specified in this Recommendation may be accomplished by optimizing the performance of the measurement-system components with respect to the associated physical and chemical properties, or anticipated properties, of the samples to be analyzed. In such cases, success depends on knowledge, skill, and experience of the analyst.

3. Terminology

3.1. Carrier gas

That part of the mobile phase used to sweep or elute sample components through the column.

3.2. Mobile phase

The carrier gas together with the portion of the sample entering the column.

3.3. Stationary phase

A phase, either liquid or solid, and composed of active immobile materials that selectively adsorb sample components in the column.

3.4. Elution

The removal of a sample component from the stationary phase by the mobile phase.

3.5. Column

A tube that contains the stationary phase and through which the gaseous mobile phase flows.

3.6. Solid support

Normally an inert material in the column that holds the stationary phase and consists of porous or impenetrable particles, or the interior wall of the column itself, or a combination of these, over which the carrier gas flows.

3.7. Injection device

The means by which a sample is introduced into the gas chromatographic column.

3.8. Detector

A device that can respond to eluted sample components in the carrier gas emerging from the column.

3.9. Retention time

The time elapsed from injection of a sample component to the recording of its peak maximum.

3.10. Detection limit

The mass flow rate (for mass flow-rate-dependent detectors) or the concentration (for concentration-dependent detectors) that yields a signal equal to three times the short-term noise level as determined on a statistical basis.

Note: This term is also referred to as “minimum detectability”, or “minimum detectable limit (MDL)”, in some references and manufacturer's literature. It is sometimes defined as an output signal equal to some other multiple (two or ten) of the noise level and depends somewhat on whether the gas chromatograph is used for quantitative or qualitative analysis.

3.11. Dynamic range of a detector

That range of mass flow rate or concentration of the test sample components over which an incremental change in the mass flow rate produces an incremental change in the detector signal. The lower limit is given by the detection limit, and upper limit is the highest mass flow rate or concentration at which a further slight increase in flow rate or concentration will give no observable increase in detector signal. The value of the dynamic range is the ratio of the upper to the lower limit and is larger than or equal to the linear range.

3.12. Linear range of a detector

The range of mass flow rate or concentration of the test sample in the carrier gas over which its sensitivity remains constant to within 5 %. It is expressed as the ratio of the upper limit of linearity and the detection limit (see Figure 1).

3.13. Noise

A manifestation of variation in the gas chromatograph output signal; it can be divided into two components:

3.13.1. Short-term noise includes all observable random variations of the signal from the detector or other components having a frequency of the order of one or more cycles per minute.

3.13.2. Drift is the average slope of the baseline signal measured over a minimum of one-half hour.

3.14. Sensitivity of the gas chromatograph

The output signal per unit mass of the sample component of interest in the carrier gas; it is expressed in either one of the two following ways:

3.14.1. With a concentration-dependent detector, it is expressed in A · mL/g, or V · mL/g, and by the equation:

$$S = \frac{P \cdot F}{M}$$

where:
P: the integrated peak area,
F: the carrier gas flow rate,
M: the mass of the sample in the carrier gas.

3.14.2. With a mass-flow-rate-dependent detector, it is expressed in A · s/g, or V · s /g, and by the equation:

$$S = \frac{P}{M}$$

where the symbols have the same definitions as in point 3.14.1.

Note: Figure 1 illustrates graphically the concepts of detection limit and linear range for a given range of sensitivity.

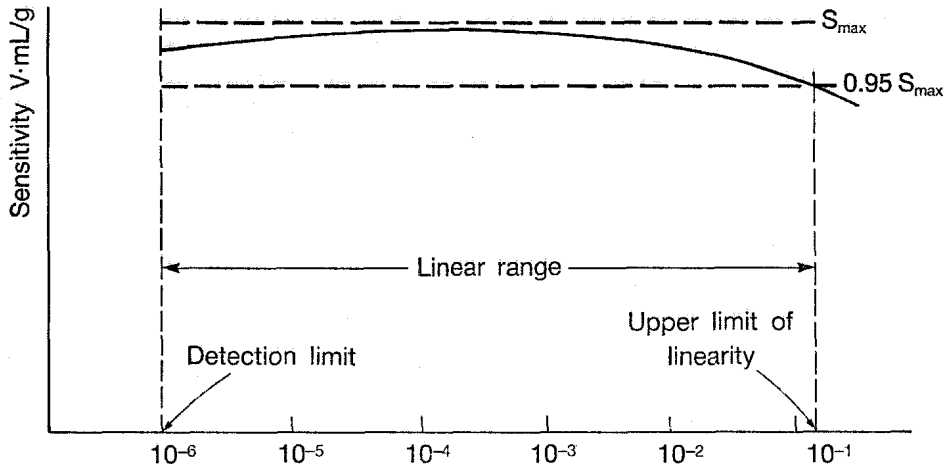

Figure 1. An example of the relationship among the linear range and other GC-detector characteristics

Note: For further discussion of gas chromatograph terminology and relationship, see [1, 6, 7, 8].

4. Description of the instrument

4.1. General

4.1.1. A diagram of a gas chromatograph is shown in Figure 2. An inert carrier gas flows at a controlled rate from the source on the left through a pressure regulator past a sample injection port to the column. The sample to be analyzed is introduced as a solid, liquid or gas through an injection device. If solid or liquid, it is vaporized before being swept into the column by the carrier gas. The eluate from the column passes on to a detector that responds to sample components. The output signal of the detector is displayed instantaneously or stored by a data system. The column effluent is vented into a hood if necessary.

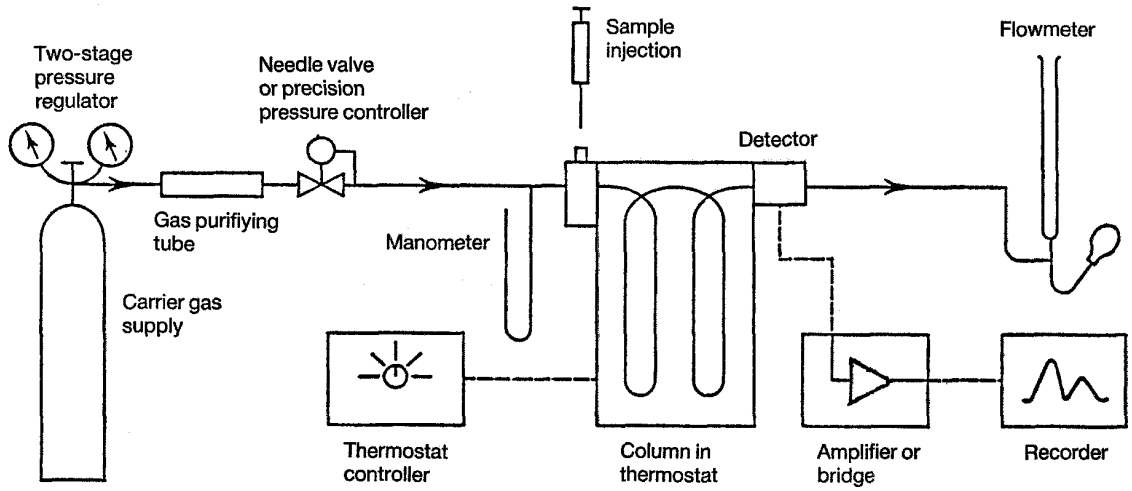

Figure 2. Schematic of a gas chromatographic system

4.1.2. Gas chromatographic analysis depends upon the separation of the sample components by the column. Separation, or partition, of the sample components depends upon column operating parameters such as gas flow rate, temperature, vapor pressure, and properties of the liquid or solid adsorbent.

4.1.3. The concentration of sample components eluted from the column are measured as a function of time by the detector whose output signal is recorded by a data system.

A plot of detector output signal versus time is referred to as a chromatogram. Peak areas, or peak heights, can be related to the concentration of sample components.

Note: For a more detailed discussion of the gas chromatograph, see [1, 2, 7].

4.2. Components

The major components of a gas chromatograph are the following: pneumatic control system for the carrier gas, injection device, column, oven, detector, and data system. A brief description of the components follows.

4.2.1. The carrier gas shall be sufficiently pure, inert with respect to the stationary phase, and compatible with the detector.

4.2.2. Injection devices of the following types are commonly used.

4.2.2.1. A packed column injection device through which the sample is introduced into a region just before the stationary material of a column.

4.2.2.2. A splitless capillary column injection device through which the entire sample is injected into a heated vaporizing region just before the capillary column. At a defined time after injection, most of the carrier gas flow is vented into the atmosphere and the remainder is allowed to enter the column.

4.2.2.3. A split capillary column injection device through which the entire sample is injected into a heated region and vaporized just before the column where it is mixed with the carrier gas and split at a controlled ratio of that entering the column to that being vented to the atmosphere.

4.2.2.4. A direct capillary column injection device through which the sample is introduced directly into a region just before the stationary phase.

4.2.2.5. A direct capillary on-column injection device through which a liquid sample is introduced directly into the column at an ambient or a subambient temperature. This procedure avoids problems of thermal decomposition and adsorptive effects of high-boiling-point compounds experienced in some vaporizing injectors.

4.2.2.6. A purge-and-trap injection device [9, 10] by which, before injection into the column, organic volatile compounds from a wide variety of sample types, including water, waste water, sediments, soil, foods, and biological tissue, are concentrated, using a dynamic headspace sampling chamber and a sorbent (cryogenic or non-cryogenic) trap.

Note: Other types of injection devices may be appropriate depending on the sample form and concentration and include static headspace and sample enrichment injection devices.

4.2.3. The column may be of the following types: packed or capillary (open tubular).

Note: See [11] for a more detailed discussion of applications of capillary columns.

4.2.4. The detector may be of the following, or equivalent, types.

4.2.4.1. The flame ionization detector (FID) [8, 12] uses a hydrogen-air flame to ionize the sample components. Such ions are collected on an electrode which has a potential difference with respect to the hydrogen jet. The measured current at the collector electrode can be related to the mass flow rate of sample components.

4.2.4.2. The electron capture detector (ECD) [13, 14] uses an ion chamber in which the effluent gas from the column is ionized by a radioactive source. The electrons generated are captured by molecules of the sample and cause a change in the current collected in the ion chamber in comparison to that collected with the carrier gas alone. Either a constant or an intermittent negative potential is applied across the reaction chamber to collect the ions from which a resultant differential signal can be related to the concentration of the sample component of interest.

4.2.4.3. The flame photometric detector (FPD) [14] senses light emitted by sample components in a flame. It consists of a hydrogen-air flame, an optical window, an optical filter to select wavelengths of emitted light, and an electrometer to measure the output current of the photomultiplier. By judicious selection of filter, burner geometry and carrier gas flow rates, the FPD can be designed to respond selectively to the optical emissions from certain types of sample molecules while not responding to the emissions from others.

4.2.4.4. The thermionic detector (TID) [15] consists of a heated electrode of an alkali glass or refractory material which selectively ionizes sample components which contain nitrogen and phosphorus. The collected ions produce a differential current signal that can be related to the mass flow rate of such sample components.

4.2.4.5. The electrolytic conductivity detector (ELCD) [16] consists of a reduction furnace and a liquid conductivity cell. Sample components are oxidized or reduced by a reaction gas (such as air or hydrogen) in a high-temperature furnace. The chemical species formed are dissolved in a solvent in the conductivity cell. The differential conductivity of the cell with time can be related to the mass flow rate of sample components. With appropriate choice of the reaction gas, scrubber, and solvent, the ELCD is selective for sample components containing halogens, nitrogen, or sulfur.

Note: This detector is also referred to as the Hall electrolytic conductivity detector or HECD in reference to one of its developers R.C. Hall.

4.2.4.6. The photoionization detector (PID) [11] ionizes the sample components eluted from a column using a sealed UV-light source in an ionization chamber. Those components in the effluent having an ionization energy less than the photon energy of the UV-light source are ionized and collected on an electrode. The resultant differential current is measured with an electrometer and can be related to the concentration of sample components.

4.2.4.7. The thermal conductivity detector (TCD) [17] generally employs either hot wires or thermistors as sensing elements. Both types use two elements, one being in a reference stream of pure carrier gas and the other in the eluate of the column. A difference in cooling, and hence resistance, between the sensing elements gives rise to a differential signal that can be related to the concentration of sample components.

Note: The TCD has a very low sensitivity compared to the other detector types described and is inappropriate for trace pollution measurements.

4.2.5. The data system may consist of one or more of the following three components: direct display (meter), chart recorder, and computer integrating device.

A system may incorporate functions of all three components and usually records the detector output signal as a function of time.

5. Metrological requirements

5.1. Temperature of the column oven and injection zone

5.1.1. Isothermal stability of the column oven shall be within ± 0.5 °C from 10 °C above ambient to 350 °C. Special applications may require temperature stability beyond this temperature range. This stability should be maintained over the entire temperature range for an ambient temperature change of 10 °C or a mains voltage change of 10 percent during analysis.

Note: The requirement for temperature stability of capillary columns should be considered from the point ot view of the dependence of carrier gas flow rate on column temperature and the effect of column temperature variation on the retention time repeatability for sample components. Therefore, for the best performance, the lowest value of temperature instability should be achieved, which may be as low as ± 0.1 °C under appropriate conditions [11].

5.1.2. Temperature gradients in the column oven measured around the column shall be within ± 1 °C or ± 1 percent, whichever is larger, of the isothermal temperature selected.

5.1.3. Temperature programming rates shall be available from 1 °C · min^{-1} to 25 °C · min^{-1} over the temperature range of 50 to 200 °C and at least 1 °C · min^{-1} to 15 °C · min^{-1} over the temperature range of 200 to 350 °C. The standard deviation of the repeatability of temperature at any programming rate shall be within 1 ± °C, or ± 1 percent, whichever is larger.

5.1.4. The temperatures of the injection zone in the range from ambient to 375 °C shall be adjustable at 10 °C intervals and shall have a standard deviation of repeatability within ± 1 °C, or ± 1 percent, whichever is larger.

Note: A heated injection device can be described as having three temperature zones: the injection zone, a temperature gradient to ambient, and a temperature gradient to the oven. Therefore, the temperature over the injection zone of a device will vary depending on the ambient, injection port, and oven temperature.

5.2. Carrier gas

5.2.1. Carrier gas flow rate for packed columns shall be controlled over the range of 5 to 75 mL · min^{-1}, and, for capillary columns, the carrier gas head pressure shall be controlled over the range of 3 to 170 kPa. The value of the flow rate or gas head pressure selected shall be controlled to within ± 1 percent.

5.2.2. The purity of carrier gas used affects gas chromatograph performance. The degree of purity required depends on the detector used and the application (See point 6.1).

5.3. Detectors

Detectors should have the following typical performance characteristics.

Note: The dynamic range is not specified for a detector since it is useful only when special calibration or data handling techniques are applied. Noise and drift are included in the specification of detection limit. Except for point 5.3.7 the current output of a detector is generally connected to the input of an electrometer, which converts the signal to a voltage that is applied to the recording and/or data system. Therefore, the sensitivity of the gas chromatograph output depends on the electrometer used.

5.3.1. Flame ionization detector (FID) [12]

Selectivity	organic carbon
Sensitivity	0.005 - 0.02 A · s/g
Detection limit	1-10 pg/s
Linear range	10^6 - 10^7
Test compound	n-Butane

5.3.2. Electron capture detector (ECD) [13]

Selectivity	electron affinity
Sensitivity	2 - 200 A · mL/g (voltage)
	65 - 500 Hz · mL/pg (current)
Detection limit	0.1 - 1.0 pg/mL
Linear range	10^2 (voltage)
	10^3 - 10^4 (current)
Test compound	Lindane

Note: "Voltage" means operation by the constant d.c. voltage method and "current" means the method in which a constant current controls a variable pulse interval generator. In the latter, a frequency-to-voltage converter is used to transmit the signal to the recording or data system.

5.3.3. Flame photometric detector (FPD) [14]

Selectivity	phosphorus (P)/sulfur (S)
Sensitivity	20 - 200 A · s/g (P)
	2 - 20 A · s /g (S)
Detection limit	0.5 - 5 pg / s (P)
	10 - 100 pg /s (S)
Linear range	10^3 - 10^5 (P)
	10^2 - 10^3 (S)
Test compounds	Tributylphosphate (P)
	Sulfur hexafluoride (S)

Note: In the sulfur mode, the FPD generally exhibits a response that is a non-linear power law function of mass flow rate for sulfur atoms, usually a square law.

5.3.4. Thermionic detector (TID) [15]

Selectivity	phosphorus (P)/nitrogen (N)
Sensitivity	0.4 A · s/g (P)
	0.2 A · s/g (N)
Detection limit	25 pg · s (P)
	50 pg · s (N)
Linear range	10^4 (P)
	10^s (N)
Test compounds	Malathion (P)
	Azobenzene (N)

5.3.5. Electrolytic conductivity detector (ELCD) [16]

Selectivity	nitrogen (N) /sulfur (S) /chlorine (Cl)
Sensitivity	1 A · mL/g (Cl)
Detection limit	2-4 pg/s (N) 2 pg/s (S) 0.5 pg/s (Cl)
Linear range	10^4 (N) 10^4 (S) 10^5 - 10^6 (Cl)
Test compound	Tetrachloroethane

Note: The proper operation and selectivity of the detector depend on the proper combination of reaction gas and furnace composition, temperature, scrubber, and solvent. Heptachlor may also be used as a test compound. The sensitivity specified applies under the following conditions: carrier gas flow rate = 30 mL/min, reaction gas (H_2) flow rate = 100 mL/min, solvent (methanol) flow rate = 20 - 50 μL/min, reactor temperature = 850 °C. These conditions and the specific solvent may differ depending on the instrument manufacturer and whether packed or capillary columns are used.

5.3.6. Photoionization detector (PID) [11]

Selectivity	organic hydrocarbon and some inorganic compounds
Sensitivity	0.01 - 0.1 A · mL/g
Detection limit	1 - 10 pg/mL
Linear range	10^4
Test compound	Benzene
Lamp conditions	10.0 - 12.2 eV at 1.0 mA current

Note: Characteristics given for helium used as carrier gas at a flow rate of 30 mL/min.

5.3.7. Thermal conductivity detector (TCD) [17]

Selectivity	———
Sensitivity	5×10^3 - 15×10^3 V · mL /g
Detection limit	300 - 10^4 pg /mL
Linear range	10^5 - 10^6
Test compound	n-Butane

5.4. Data system

The data system shall be capable of producing an accurate and archiveable record that may be referred to of the detector response and other essential data of the analysis.

6. Technical requirements

6.1. Carrier gases

6.1.1. A carrier gas appropriate for the method of analysis and the gas chromatograph detector shall be used. Examples of common types are the following: hydrogen, helium (He and methane), nitrogen, argon (Ar and methane), and air.

6.1.2. Traces of unwanted vapors and particulates shall be removed by means of molecular sieve scrubbers, filters, and filter dryers which should be inserted in the gas supply lines as close to the column as practical.

6.2. Columns

6.2.1. The instrument should provide for packed and/or capillary columns. The selection of the column depends on the sample and method of analysis.

6.2.2. The columns shall be made of all glass or fused-silica to minimize degradation of pesticides by contact with hot metal surfaces, especially copper.

6.2.3. Either a liquid or solid stationary phase that provides the separation of the sample component(s) of interest shall be used.

6.3. Temperature control systems

6.3.1. The temperature control of the column shall be capable of providing a fast temperature, automatically programmed response. The temperature level and programmed changes depend on the sample components of interest and the method of analysis.

Note: A forced-air oven is the most universally applied method. Insulated electrical heaters at constant temperature may be used but usually are successful only under relatively constant ambient temperature conditions.

6.3.2. The detectors and injection devices used should have a temperature control system separate from the column oven in order to enhance good repeatability of the output signal.

6.4. Markings

Markings shall be attached conspicuously to all major components of the GC/DS as follows:
— name of the manufacturer,
— instrument model and serial number,
— voltage, frequency, and current requirements.

7. Practical instructions

7.1. Operation of a gas chromatograph requires the use of high voltage, compressed gases, high temperatures and may also include ultraviolet radiation and radioactive materials. Warning labels shall be placed conspicuously on the instrument to alert the user of these potential hazards. These shall be consistent with national safety regulations.

7.2. The manufacturer of a gas chromatograph shall supply a manual that describes its operation and routine maintenance. Service manuals shall be available upon request.

7.3. Before installation of a gas chromatograph, all environmental factors shall be considered. Manufacturers shall provide specifications for power consumption that include maximum permissible variations for mains voltage and frequency. Specifications shall also include rated operating conditions for ambient temperature, humidity, airborne particulate matter, vibration, and heat dissipation requirements.

Note: General guidelines to tests for influence factors may be found in the International Document OIML D 11 "General requirements for electronic measuring instruments".

8. Metrological controls

8.1. General considerations

8.1.1. A gas chromatograph is a complex instrument that may comprise for a complete analysis a variety of injection devices, columns, and detectors. Major components used depend on the method specified as appropriate for analysis of a specific sample by the national responsible organization for pollution control. Therefore, traditional legal metrology controls comprising pattern evaluation and approval and initial and subsequent verification may not be practical for these instruments. However, national control should include as a minimum the quality control procedures specified in point 8.2 as a means of assuring the continued metrological integrity of the gas chromatograph.

8.1.2. Quality control procedures for specific analytical methods should also be established by the national responsible organization. Such procedures could include a means for assessing through accreditation of user laboratories and through proficiency testing by comparisons of measurements made by user laboratories.

8.2. Quality control procedures

8.2.1. An initial test of a gas chromatograph upon installation shall be performed with a suitable test compound provided by its manufacturer for each detector. The results of this test shall be within the specifications of the manufacturer.

8.2.2. If at any time the gas chromatograph exhibits performance outside the manufacturer's specifications, it shall be put in a condition conforming with its initial test and retested. This procedure may determine whether the gas chromatograph needs adjustment, replacement of a component, or repair.

8.2.3. A test of the entire gas chromatograph, such as that provided in Annex A.2, shall be carried out routinely using reference materials, or specifically prepared samples that are appropriate for the method of analysis of the class of sample compounds being measured.

Note: Appropriate certified reference materials may be available for such tests as indicated in references [4], [18], [19], and [20].

8.2.4. The quality control procedures published by the national responsible organization should specify gas chromatograph performance tests and calibration procedures that apply for methods of analysis for specific pollutants. The time interval between tests, or calibrations, should also be specified as appropriate.

8.2.5. A written log shall be maintained that contains the following information in chronological order for each gas chromatograph:

— results of initial and subsequent routine tests and calibrations,
— identification, for each analysis performed, of the carrier gas, column(s), column-oven temperature(s), detector(s), and data systems,
— description of malfunctions and corrective actions taken,
— extent of maintenance and/or repair.

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ANNEX A.1

REFERENCES TO METHODS OF ANALYSIS

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A.1.8. ASTM D3086-79, *Test Method for Organochlorine Pesticides in Water,* Annual Book of ASTM Standards, Vol. 11.02, ASTM, Philadelphia, PA (1985).

ANNEX A.2

A PERFORMANCE TEST FOR AN ENTIRE GAS CHROMATOGRAPH USED FOR MEASUREMENT OF PESTICIDES

A.2.1. This test procedure involves assaying a reference solution containing a mixture of halogenated pesticides in water.

A.2.2. The purpose of this test is to assure that the entire gas chromatographic system, including injection device, column, detector, and data system, is capable of the proper separation, detection, selectivity, repeatability of peak area, and repeatability of retention time. The insensitivity to non-chromatographic signals (or sample-spike recovery) may also be checked.

A.2.3. Prepare a reference sample solution by selecting at least 10 of the following halogenated pesticides as sample components:

1) Aldrin
2) Dichlorobenil
3) Heptachlor
4) Lindane (BHC)
5) Endosulfan I
6) Dieldrin
7) Endrin
8) ODD
9) DOT
10) Methoxychlor
11) Hexachlorobenze
12) Tetrasul
13) Tetradifon
14) Chlordane

A.2.4. Prepare a stock solution containing all sample components selected from point A.2.3 in a water miscible organic solvent, such as acetone, methanol, or isopropanol. The concentration of each sample component in the stock solution shall be such that, when one mL of the stock solution is added to pure water to make up a reference sample solution of 1.00 litre, the final nominal concentrations of sample components shall range between 2 to 50 μg/L as indicated in Table 2.

A.2.5. Select an appropriate injection device, column, detector, and temperature programming for the instrument.

A.2.6. Make 10 replicate injections of the reference sample prepared according to point A.2.4. The repeatability of retention times of any of the sample components listed in point A.2.3 should have a standard deviation not exceeding ± 1 percent.

Note: The value of the retention time for any sample component depends on the characteristics of the column used; however, the repeatability of the retention time generally depends on the control of the column temperature and carrier gas flow rate and is best under optimum control of these instrument parameters (see points 5.1 and 5.2). Relative retention of two similar columns for a particular sample component should be constant to within their combined repeatability. A large concentration of a sample component may cause a drift of its retention time.

A.2.7. The instrument's performance shall be acceptable if the requirements of A.2.6 and Table 2 are met.

Note: In order to check the effect of the sample's matrix on measurement results, a reference sample may be added to some of the specimens undergoing analysis. If this effect is studied using the reference sample of point A.2.4, then at least 75 percent of any sample component should be recovered. The concentration of any component in the test sample should be at least one to five times the background concentration of that same component in the specimen undergoing analysis.

Table 2

REPEATABILITY and ACCURACY of the TEST

Sample component	Nominal concentration (a)	Repeatability of peak area (b)	Minimum signal to noise ratio
1	2.0	10 %	500:1
2	–	”	”
3	2.0	”	”
4	–	”	”
5	–	”	”
6	2.0	”	”
7	–	”	”
8	10.0	”	1000:1
9	10.0	”	”
10	–	”	”
11	2.0	”	500:1
12	–	”	”
13	–	”	”
14	50.0	”	100:1

(a) Concentrations in μg/L of sample components to be contained in the reference sample of point A.2.4.

(b) The percent relative standard deviation of the area of the output signal associated with a sample component after 10 replicate injections of the reference sample.

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