

NORMA DE METROLOGIE LEGALĂ

**Sisteme cromatografice gazoase pentru măsurarea
poluării din pesticide și alte substanțe toxice**

Ediție oficială

Chișinău

Sisteme cromatografice gazoase pentru măsurarea poluării din
pesticide și alte substanțe toxice
(OIML R 82:2006, IDT)

Gas chromatographic systems for measuring the
pollution from pesticides and other toxic substances

APROBARE

Aprobată prin Ordinul Ministerului Economiei
nr.41 din 17.03.2009

DESCRIPTORI

Sisteme cromatografice, încercări verificări metrologice

Preambul național

Prezenta normă de metrologie legală reprezintă adoptarea recomandării Organizației Internaționale de Metrologie Legală R 82 „Gas chromatographic systems for measuring the pollution from pesticides and other toxic substances”

Prezenta recomandare a OIML se completează cu un nou capitol, cu următorul cuprins:

„Capitolul 9 Întocmirea rezultatelor verificării metrologice

9.1 Dacă în baza rezultatelor verificărilor metrologice inițiale, periodice sau după reparare mijlocul de măsurare este recunoscut ca utilizabil, atunci pe el se aplică marcajul metrologic de verificare și se eliberează buletin de verificare metrologică de strictă evidență. Rezultatele verificării metrologice sînt valabile pe durata intervalului maxim de timp admis între două verificări metrologice periodice, conform Listei Oficiale a mijloacelor de măsurare supuse controlului metrologic.

9.2 Dacă în baza rezultatelor verificărilor metrologice inițiale, periodice sau după reparare mijlocul de măsurare este recunoscut ca inutilizabil atunci se eliberează buletin de inutilizabilitate.”

Titlul prezentei norme de metrologie legală în limba rusă:

Газохроматографические системы для измерения загрязнения от пестицидов и других веществами

1. Elementele naționale ale prezentei norme de metrologie legală au fost elaborate de Institutul Național de Standardizare și Metrologie.
2. Modificări după publicare:

Indicativul modificării	Revista „metrologie” nr. / an	Punctele modificate

INTERNATIONAL
RECOMMENDATION

OIML R 82

Edition 2006 (E)

Gas chromatographic systems for measuring the
pollution from pesticides and other toxic substances

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



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Foreword

The International Organization of Legal Metrology (OIML) is a worldwide, intergovernmental organization whose primary aim is to harmonize the regulations and metrological controls applied by the national metrological services, or related organizations, of its Member States.

The main categories of OIML publications are:

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- **International Basic Publications (OIML B)**, which define the operating rules of the various OIML structures and systems.

OIML Draft Recommendations, Documents and Guides are developed by Technical Committees or Subcommittees which comprise representatives from the Member States. Certain international and regional institutions also participate on a consultation basis. Cooperative agreements have been established between the OIML and certain institutions, such as ISO and the IEC, with the objective of avoiding contradictory requirements. Consequently, manufacturers and users of measuring instruments, test laboratories, etc. may simultaneously apply OIML publications and those of other institutions.

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Additionally, the OIML publishes or participates in the publication of **Vocabularies (OIML V)** and periodically commissions legal metrology experts to write **Expert Reports (OIML E)**. Expert Reports are intended to provide information and advice, and are written solely from the viewpoint of their author, without the involvement of a Technical Committee or Subcommittee, nor that of the CIML. Thus, they do not necessarily represent the views of the OIML.

This publication - reference OIML R 82, edition 2006 (E) - was developed by the OIML Technical Subcommittee TC 16/SC 3 *Pesticides and other pollutant toxic substances*. It was approved for final publication by the International Committee of Legal Metrology in 2006 and will be submitted to the International Conference of Legal Metrology in 2008 for formal sanction. This Edition supersedes the previous edition of OIML R 82 (Edition 1989).

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Gas chromatographic systems for measuring the pollution from pesticides and other toxic substances

1 Scope

1.1 This Recommendation provides the procedures for testing and verifying the performance of a gas chromatograph (GC) system 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 toxic substances.

1.2 The GC systems covered in this Recommendation are intended to be used in a fixed or mobile laboratory under controlled ambient conditions. Portable GCs for field applications are covered in OIML R 113. GCs coupled with other analytical instruments such as GC-mass spectrometers and GC-Fourier transform infrared spectrometers are also not covered in this Recommendation.

1.3 Instrument performance better than the criteria specified in this Recommendation may be accomplished by optimizing the performance of major components of the measurement system. In such cases, success may depend on the knowledge, skill, and experience of the operator.

1.4 A sample usually requires undergoing a specific preparation technique prior to an analysis with a GC system. Sampling techniques and methods of analysis are beyond the scope of this Recommendation.

1.5 This Recommendation does not address requirements and tests that may be necessary for operator safety. Therefore, users should determine whether instruments meet the safety and labeling requirements specified in national regulations.

2 Application

2.1 GC systems may be applied for 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.

2.2 Sample compounds can be detected by a GC system if they can pass through a gas chromatographic column and not be affected by thermal or catalytic decomposition or adsorption. Some non-volatile or thermally unstable compounds may be converted to derivatives that are volatile and stable and, therefore, can be separated and detected by a GC system.

2.3 Examples of compounds types that can be determined with GC systems are given in Annex A.

2.4 Some specific applications of gas chromatography to environmental measurements are provided in references [1-3].

3 Terminology

3.1 Carrier gas

Gas introduced in order to transport a sample for analytical purposes. In gas chromatography it is the gas which is passed continuously through the column and whose passage promotes the elution of the components of the sample. The carrier gas, together with the portions of the sample present in this phase, constitute the mobile phase.

3.2 Injection device

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

3.3 Column

Tube within the gas chromatograph that contains the stationary phase and through which the gaseous mobile phase flows.

3.4 Mobile phase

Carrier gas and injected gaseous sample that enter and move through the column.

3.5 Stationary phase

Phase in the column composed of active immobile materials, either liquid or solid, that selectively absorbs or adsorbs sample components.

3.6 Solid support

Material in the column (normally inert) 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 Elution

Removal of a sample component from the stationary phase by the mobile phase in the gas chromatographic column..

3.8 Detector

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

3.9 Noise

Manifestation of variation in the gas chromatograph output signal not associated with changes in chromatographic conditions (e.g. temperature gradient), which can be divided into two components:

3.9.1 Short-term noise, which 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.

3.9.2 Drift, i.e. the average slope of the baseline signal measured over a minimum of half an hour.

3.10 Reference sample

Liquid or gaseous reference material containing an accurately known concentration of the sample components of interest and used for testing or calibration of the instrument.

3.11 Detection limit

Mass flow rate (for mass flow rate dependent detectors) or concentration (for concentration-dependent detectors) yielding 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.

3.12 Linear range

Range of mass flow rate or concentration of the analyte in the carrier gas over which its sensitivity remains constant to within specified limits. It is expressed as the ratio of the upper limit of linearity and the detection limit.

3.13 Sensitivity

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:

3.13.1 With a concentration-dependent detector, the instrument sensitivity, S , is expressed in:

$A \cdot \text{mL} \cdot \text{g}^{-1}$, or

$V \cdot \text{mL} \cdot \text{g}^{-1}$, and by the equation:

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

where:

P = the peak area,

F = the carrier gas flow rate,

M = the mass of the sample in the carrier gas.

With the units:

A = amperes,

mL = millilitres,

g = grams,

V = volts.

Note: Peak area is independent of broadening effects caused by variables such as column temperature, eluent flow rate, and rate of sample injection. From this standpoint, therefore, the peak area is a more satisfactory analytical parameter than peak height. On the other hand, peak heights are more easily measured and, for narrow peaks, more accurately determined. Many modern chromatographic instruments are equipped with electronic integrators that provide precise measurements of relative peak areas.

3.13.2 With a mass flow rate dependent detector, the instrument sensitivity, S , is expressed in:

$A \cdot \text{s} \cdot \text{g}^{-1}$, or

$V \cdot \text{s} \cdot \text{g}^{-1}$, and by the equation:

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

where the symbols have the same definitions as in 3.13.1, with the additional unit of:
s = seconds.

3.14 Chromatogram

Record of the detector output signal versus time that has peaks corresponding to specific components of the sample.

3.15 Retention time

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

3.16 Repeatability

Closeness of agreement between results of successive measurements of the same measurand carried out under the same conditions and within a relatively short period of time.

Note: Such conditions include the following: method of measurement, operator, measuring instrument, location, and environmental conditions.

4 Description of the instrument

4.1 General

4.1.1 Gas chromatographs of various design and construction are available for laboratory use. In general, a container with pressurized gas and a pneumatic control system provide a controllable flow rate of carrier gas through a chromatographic column that is maintained at a constant or controlled temperature during the period of analysis. An injection device is used to introduce a known volume of a sample that is swept by the carrier gas through the column to a detector. The detector responds to each sample component as it elutes from the column. The detector output signal is displayed as a function of time (chromatogram) and provides a record on a chart recorder and/or in a data system from which the record may be retrieved.

4.1.2 A diagram of the instrument is given in Figure 1. The flow of carrier gas may be regulated by a pressure and/or flow controller. For liquid samples, the injection device (A) has a means of vaporizing the sample prior to injection. The temperature control device for the column (B) may be either fixed or adjustable; however, some instruments may meet performance requirements at a relatively stable ambient temperature without temperature control. Under certain conditions of use, it may be necessary or desirable for the detector (C) to be maintained under controlled temperature conditions with respect to the column.

4.1.3 Gas chromatographic measurements depend on the separation or partition of gaseous or vaporized sample components in the carrier gas (mobile phase) by the stationary phase in the column. Sample partition depends primarily on the operating parameters of the column such as gas flow rate, temperature, vapor pressure, and the adsorbent properties of the stationary phase. The individual components of the sample resolved by the column and detected are interpreted from a chromatogram or data stored in a data handling system. The identification of components and quantification depends on knowing the retention times and measuring corresponding peak areas of specific sample components for an instrument operating under defined conditions.

Note: A more detailed description of the instrument may be obtained in references [4] – [6].

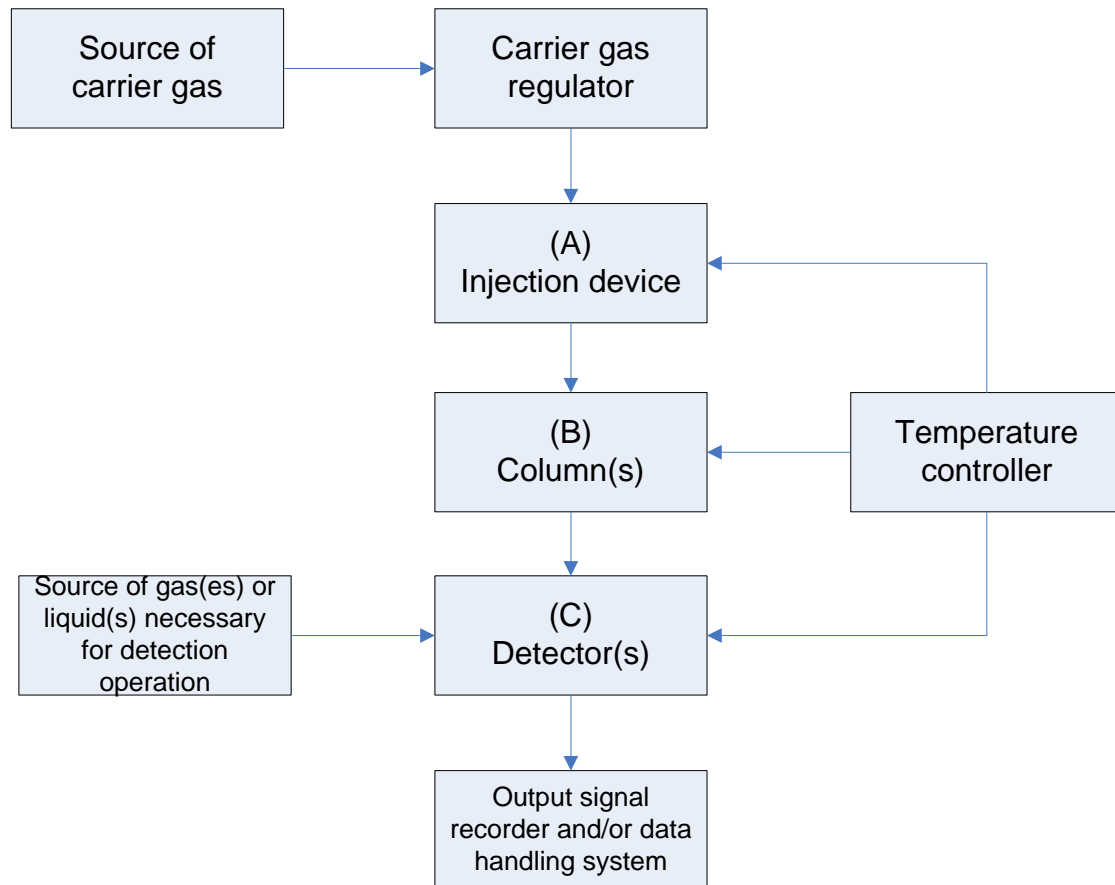


Figure 1 Diagram of a gas chromatographic system

4.1.4 The major components of a gas chromatographic system are as follows:

- pneumatic control system for the carrier gas,
- injection device,
- column,
- temperature control system, and
- detector, and data handling system.

A brief description of some of these components follows.

4.2 Pneumatic control system

The pneumatic control system regulates the flow of gas through the instrument.

4.3 Injection device

Injection devices may be one of the following or other types depending on the form of the sample and its concentration:

- A packed column injection device through which the sample is introduced into a region just before the stationary material of a column.
- A splitless capillary column injection device through which the entire sample is injected into a heated vaporizing region just before the capillary column where it is mixed with the carrier gas and most of the vaporized sample is introduced into the column, and at a specified time after injection, vapors remaining in the liner are vented into the atmosphere.
- 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 between that entering the column and that being vented into the atmosphere.

- A programmed temperature vaporizing injector (PTV) device which is an enhancement to the split/splitless injector and is equivalent except that the injection liner temperature can be rapidly heated or cooled. Sample injection is made into a cool liner, and after the syringe needle has been removed, the temperature of the liner is rapidly increased for more controlled sample vaporization.
- A direct capillary on-column injection device through which a liquid sample is introduced directly into the column at an ambient or a below ambient temperature thereby avoiding thermal decomposition and adsorptive effects of high-boiling-point compounds that occur in some vaporizing injectors.
- A purge-and-trap injection device through which organic volatile compounds from a wide variety of sample types are injected after having been concentrated, using a dynamic headspace sampling chamber and a sorbent (cryogenic or non-cryogenic) trap.
- The column may be of the following types: packed or capillary (open tubular).

4.4 Detector

The detector may be one of the following types:

- The flame ionization detector (FID), a type that is mass flow dependent, nonselective, and widely applicable for organic compounds.
- The electron capture detector (ECD), a type that is concentration dependent, and selective for halogenated and related compounds.
- The flame photometric detector (FPD), a type that is mass flow dependent and selective for phosphorus and sulfur containing compounds.
- The thermionic detector (TID), a type that is mass flow dependent and selective for phosphorus and nitrogen containing compounds. A TID may also be commonly referred as a NPD (nitrogen/phosphorus detector) or NSD (nitrogen selective detector).
- The electrolytic conductivity detector (ELCD), a type that is mass flow dependent and selective for chlorine, nitrogen, and sulfur containing compounds.
- The photoionization detector (PID), a type that is concentration dependent, selective (depending on lamp energy), and widely applicable to organic and inorganic gases.
- The thermal conductivity detector (TCD), a type that is concentration dependent applicable to organic and inorganic gases.

4.5 Data handling system

The data handling system may consist of one or more of the following three components: direct display, chart recorder, and an integrating device with computer. 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 During type evaluation and initial and subsequent verification, the repeatability of the output signal and the retention time of the GC system shall be tested in a laboratory using test compounds and under reference conditions throughout the evaluation as follows:

- ambient temperature between 20 °C and 27 °C and stable to within ± 3 °C during the measurement;
- relative humidity (RH) between 30 % and 80 %;
- carrier gas flow rate as specified by the manufacturer;
- injection device, column, and detector temperatures as specified by the manufacturer.

5.2 The manufacturer shall specify the following components and the conditions under which the instrument is to be tested:

- carrier gas type;
- injector type;
- detector type;
- column type.

5.3 The repeatability of measurements for a GC system shall be checked by 10 repeated injections of a single sample of the relevant test compound with a concentration equivalent to approximately the value at the mid-point of the specified linear range within a relatively short period of time. The manufacturer shall declare whether the instrument uses peak height or peak area as a method of quantification. This Recommendation shall only refer to peak area, but a device may qualify using peak height as a quantification principle (see the note in 3.13.1).

The relative standard deviation of the measurement results shall not exceed:

- 5 % for peak area of the output signal;
- 1 % for the retention time.

Note: The values of relative standard deviation for peak area and retention time are considered maximum permissible errors and are determined according to the procedure provided in Annex B.

5.4 The detection limits and the linear range of a specific detector or detectors to be used with the instrument shall meet the performance requirements specified by the manufacturer for the following relevant test compounds:

Detectors	Test compounds
FID	Mixture of alkanes
PID	Toluene
TCD	Mixture of alkanes
ECD	Lindane
FPD	Malathion
TID	Malathion (P) and azobenzene (N)
ELCD	Tetrachloroethane (Cl), azobenzene (N), and malathion (S)

5.4.1 The detection limit and the linear range for the detectors as specified by the manufacturer shall be verified using the test procedure provided in Annex B.

Note: Achievable detection limits and the linear range for the detectors indicated for the designated test compounds are provided in Annex C.

5.4.2 The detection limit shall be + 5 % or below of the value specified by the manufacturer.

5.4.3 The linear range shall be determined using a minimum of five concentrations of reference gas sample, the maximum concentration being that specified by the manufacturer and the minimum concentration being approximately 10 times the detection limit. Resultant data shall be analyzed by linear least squares, determining the correlation coefficient, r . From this analysis, r^2 shall not be less than 0.95.

6 Technical requirements

6.1 Carrier gas

6.1.1 The manufacturer shall specify the carrier gas and its necessary purity for the specific detector or detectors to be used.

Note: Examples of common carrier gases are the following: hydrogen, helium, nitrogen, and argon (Ar and methane). 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.

6.1.2 The instrument shall have a means for controlling and displaying the carrier gas flow rate.

Note: The flow rate may be indicated by the gas head pressure at or near the entrance to the column.

6.2 Temperature control system

6.2.1 Temperature control shall be provided for the injection device, column and detector.

6.2.2 The range of temperature programming and the rate of changes in temperature achievable in that range shall be specified.

6.3 The manufacturer shall specify the types of column that may be accommodated in the system.

6.4 Data handling system

The data handling system shall be capable of producing an accurate, archivable, and retrievable record of the detector response, sample characteristics, gas composition and flow parameters, temperature profile and other essential data of the analysis.

6.5 Markings

Markings shall be attached conspicuously to all major components of the instrument as follows:

- name of the manufacturer;
- instrument model, serial number and date of manufacture;
- voltage, frequency, and current requirements.

6.6 The manufacturer shall provide a manual that describes the operation and routine maintenance of the instrument.

7 Practical instructions

7.1 Operation of a GC 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 Before installation of a GC system instrument, all environmental factors shall be considered including rated operating conditions at various ambient temperatures and humidity.

7.3 The appropriate means for injecting a sample into the GC system may be selected on the basis of the information available on carrier gas flow rates, or head pressures, and the temperature control available for the various components.

8 Metrological controls

8.1 Type evaluation

8.1.1 Manufacturers shall provide the national responsible body with a GC system and its operating manual and may also provide test data and other relevant information that could support a determination as to whether the system meets the requirements of this Recommendation.

8.1.2 The operating manual shall be reviewed for its completeness and clarity of instructions. The GC system shall be visually inspected in conjunction with a review of specifications provided by the manufacturer to determine that requirements 6.1 through 6.6 are met.

8.1.3 The responsible national body shall carry out the following performance tests, or may accept the manufacturer's test data, that confirm acceptable performance for the following:

- repeatability of peak area (5.3 and Annex B);
- repeatability of retention time (5.3 and Annex B);
- detection limit for detectors (5.4 and Annex B);
- linear range for detectors (5.4 and Annex B).

8.1.4 The report on the tests of the GC system carried out during type evaluation, intended for use within the scope of the *OIML Certificate System for Measuring Instruments*, shall contain as a minimum the items of information according to the format provided in Annex D. A specific form may be developed according to national preference. The manufacturer shall be provided specific information or comments about any test failures.

8.2 Initial and subsequent verification

8.2.1 An initial test of each GC system shall be performed according to the manufacturer's instructions. The result of this test shall be within the manufacturer's specifications that shall be consistent with the repeatability requirements of 5.3 and detection limit determinations in 5.4.1 and 5.4.2.

8.2.2 The test in 8.2.1 shall be carried out under the reference conditions specified in 5.1.

8.2.3 Other GC system tests specified under 8.1.3 that may be considered to be critical to the specific application shall be performed and may be carried out for sample compounds of interest.

8.2.4 The national responsible body shall specify the period of validity of the initial verification. Subsequent verification shall be carried out after the initial period of validity.

8.2.5 A GC system shall also undergo subsequent verification equivalent to initial verification after repair or replacement of critical component parts as specified by the national responsible body. This requirement does not pertain to the replacement of the column.

8.3 Routine tests by a user

8.3.1 The national responsible body shall provide information on methods for using a GC system to measure specific pollutants. Some measurement methods may be appropriate for use as quality assurance procedures for assessing the performance of the system.

8.3.2 The user should carry out frequently (for example, once per work period) a test of the entire GC system using reference samples appropriate for the analytical method used for the class of sample compounds of interest. Reference samples should be used daily along with analytical control charts to verify the working range of the system.

8.3.3 A chronological written record shall be maintained for each GC system and shall contain at least the following information:

- results of all routine tests;
- results of calibrations;
- identification of replacement of major components;
- extent of maintenance and repair.

References

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ISBN 3-527-28042-1 VCH Verlagsgesellschaft.
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Annex A

(Informative)

Examples of compound types detectable by gas chromatography

Compound type *	Examples	Detectors **
Volatile halocarbon solvents	chloroform, carbon tetrachloride, methylene chloride, freons, trichloroethylene, tetrachloroethylene, etc.	ELCD, ECD
Volatile aromatic hydrocarbons	BTEX (benzene, toluene, ethylbenzene, xylenes)	PID, FID
Chlorinated aromatics	chlorobenzenes, dichlorobenzenes, etc.	ECD
Polychlorinated biphenyls	209 congeners containing one to 10 Cl	ECD
Chlorinated hydrocarbon pesticides	endrin, DDE, DDT, dieldrin, aldrin, etc.	ECD
Phthalate and adipate esters	dibutylphthalate, dibutyl adipate, dioctyl phthalate, etc.	PID
Phenols and chlorinated phenols	phenol, chlorophenol, dichlorophenol, etc.	FID
Aromatic amines	Aniline, chloroanilines, N-methylanilines, amino toluenes, etc.	TID
Nitroaromatics, explosives	Nitrotoluene, dinitrotoluene, TNT, etc.	TID
Chlorinated pesticides	2, 4-D, dichlorprop, dinoseb, etc.	ELCD, ECD
Triazine herbicides	Atratron, propozine, atrazine, terbutyn, etc.	TID
Organophosphorus pesticides	Dichlorvos, malathion, parathion, etc.	FPD

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

(**) Selection of the chromatographic detector is dependent on the sample composition, the concentration of compounds of interest, and the sample matrix.

Annex B

(Mandatory)

Test procedure

B.1 This test provides a procedure for determining whether an instrument meets the performance requirements under the conditions specified in clause 5.

B.2 Carry out the test under the reference conditions specified in 5.1 and with a reference sample of the test compound specified by the manufacturer for each particular detector type.

B.3 Select an appropriate injection device (syringe or loop), column, and temperature controls for the detector to be tested with an appropriate reference sample.

B.4 Inject an appropriate volume of reference sample with a minimum being 1 mL for gases and 1 μ L for liquids.

B.5 Reference sample

B.5.1 Obtain or prepare a stock reference sample having a concentration equivalent to the product of the detection limit and the linear range according to that specified by the manufacturer for the detector to be tested.

B.5.2 Use either a reference gas or liquid sample taking into account that air samples are diluted with dry air or nitrogen and liquid samples are diluted with a suitable solvent.

B.6 Repeatability

B.6.1 Determine the repeatability of the reference liquid or gaseous sample tested under reference conditions as specified in 5.1 and whether the requirement of 5.3 for relative standard deviation has been met.

B.6.2 Calculate the relative standard deviation, σ_r , using the following equation:

$$\sigma_r = \left(\frac{\sigma}{x} \right) \cdot 100$$

where:

$$\sigma = \left[\frac{\sum (x_i - \bar{x})^2}{n-1} \right]^{1/2}$$

x_i = the individual result, and

\bar{x} = the average result for n repeated measurements.

B.7 Linear range and detection limit

B.7.1 Make at least ten repeated injections of a blank sample (dry air or nitrogen for gas and solvent used for the liquid) and record the peak areas. Determine the short-term noise level, N_s , (3.11) as the average value of the results.

B.7.2 Make at least five repeated injections at each of at least five selected concentrations of the reference sample from about 10 times the detection limit to the maximum value specified for the linear range. Record the peak area of the detector response.

B.7.3 From the results of B.7.2, calculate the average value of the peak area versus the amount injected in grams taking into account any peaks or peaks coeluting with the reference sample as determined in B.7.1. Plot the results to the mean value determined for each concentration and fit a linear least-squares regression, determining the slope, m , intercept, b , and correlation coefficient, r , parameters from the general linear equation model:

$$y = mx + b$$

Note: If necessary for air samples, correct the concentration injected to values at standard conditions of temperature and pressure.

B.7.4 Calculate the square of the correlation coefficient for the least-squares regression curve using the slope of the curve and the standard deviation of the known concentration values, σ_x , and the standard deviation of the measured peak area values, σ_y , and the following equations:

$$r^2 = \frac{S_{xy}^2}{\sigma_x \sigma_y}$$

where:

$$S_{xy} = n \sum (x_i y_i) - \sum x_i \sum y_i$$

$$\sigma_x = \left[\frac{\sum (x_i - \bar{x})^2}{n-1} \right]^{1/2}$$

$$\sigma_y = \left[\frac{\sum (y_i - \bar{y})^2}{n-1} \right]^{1/2}$$

The results shall meet the requirements of 5.4.3 for the square of the correlation coefficient, r^2 .

Note: The correlation coefficient, r , interprets how well the data fits the least-squares regression curve. A perfect fit would be $r = \pm 1$ or $r^2 = 1$.

B.7.5 Record the sensitivity of the instrument, S , as the slope of the curve obtained in B.7.4; or alternatively, calculate it using the appropriate equation in 3.13.

B.7.6 Draw a line parallel to the abscissa of the curve obtained in B.7.3 that is three times the short-term noise level (N_s in B.7.1). The detection limit is calculated using N_s and the instrument sensitivity, S :

$$\text{Detection limit} = \frac{3 \cdot N_s}{S}$$

Annex C

(Informative)

Achievable detection limits and linear range interval

C.1 Achievable detection limits and linear range intervals are given in Table C.1 for the test compounds and detectors as could be determined under the reference conditions of test specified in 5.1.

C.2 The actual detection limits and linear range interval for a GC system shall be specified by the manufacturer and verified by the overall test provided in Annex B.

Table C.1 Achievable detection limits and linear range interval for GC detectors with indicated test compounds

Detectors	Test compound(s)	Linear range interval	Detection limit
FID	Mixture of liquid alkanes	$10^4 - 10^7$	1 pg/s - 10 pg/s
PID	Toluene	10^4	1 pg/mL - 10 pg/mL
TCD	Mixture of liquid alkanes	$10^4 - 10^5$	300 pg/mL - 10^4 pg/mL
ECD	Lindane	$10^2 - 10^4$	0.1 pg/mL - 1.0 pg/mL
FPD	Malathion	$10^2 - 10^3$ (S) $10^3 - 10^5$ (P)	10 pg/s - 100 pg/s 0.5 pg/s - 5 pg/s
TID	Malathion (P) and azobenzene (N)	10^5 (P) 10^4 (N)	25 pg/s 50 pg/s
ELCD	Tetrachloroethane (Cl), azobenzene (N), and malathion (S)	10^4 (S) 10^4 (N) $10^5 - 10^6$ (C1)	2 pg/s 2 pg/s - 4 pg/s 0.5 pg/s

Annex D
(Mandatory)
Test report format

A test report intended for use within the scope of the *OIML Certificate System for Measuring Instruments* or for other purposes shall include the following information:

Report No. _____

OIML Recommendation R 82, Edition 2006.

D.1 Name and address of the testing laboratory(ies)

D.2 Location at which the tests were performed, if other than that indicated in D.1

D.3 Name and address of the manufacturer

D.4 Name and address of the applicant, if other than the manufacturer

D.5 Identification of the instrument (type) tested

Trade name: _____

Model number: _____

Serial number: _____

Requirements for: Voltage _____ Frequency _____ Current _____

D.6 Review of the operating manual

Acceptable Deficient

Comments: _____

D.7 Summary of the visual inspection in conjunction with a review of the information provided by the manufacturer or in the operating manual and according to clause 6

D.7.1 Means for controlling and displaying the carrier gas flow rate

Yes No

Comments: _____

D.7.2 Temperature controls

Injection device: Yes No

Column: Yes No

Detector: Yes No

Comments: _____

D.7.3 Temperature programming

Yes No

Comments: _____

D.7.4 Types of columns that can be accommodated in the system are specified

Yes No

Comments: _____

D.7.5 Type of data handling system

Comments: _____

D.7.6 Markings

Pass Fail

Comments: _____

D.8 Summary of the results of the tests carried out according to 8.1.3

D.8.1 Conditions for testing (complete information for each detector type tested)

Ambient temperature: _____

Relative humidity: _____

Carrier gas:

 Type: _____

 Purity: _____

 Flow rate: _____

Injection device type: _____

Column type: _____

Detector type: _____

Temperature:

 Injection device: _____

 Column: _____

 Detector: _____

Temperature programming: _____

Data display or readout: _____

D.8.2 Repeatability of peak area and of the retention time

Test compound: _____

Concentration: _____

Note: The TID and ELCD detectors will require more than one test compound and, hence, the tests in D.8.2, D.8.3, and D.8.4 shall be repeated for each required test compound.

Repetition ↓	Peak area	Retention time
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		
\bar{x}		
σ_r		

Relative standard deviation (σ_r)Peak area: Pass FailRetention time: Pass Fail

Comments: _____

D.8.3 Determination of linearity

Test compound _____					
Peak area or height					
Concentration →					
Repetition ↓					
1					
2					
3					
4					
5					
Average					

r^2 (correlation coefficient squared) calculated from B.7.4:

Value: _____ Pass Fail

Comments: _____

D.8.4 Determination of detection limit

Repetition	Blank sample
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
\bar{x}	

\bar{x} (noise level) = _____

Detection limit (specified by the manufacturer): _____

Detection limit (determined according to B.7.6): _____

Pass Fail

Comments: _____

D.9 Brief statement of the conclusions as to whether the GC system tested meets the requirements of this Recommendation

D.10 Person(s) responsible for the testing

Signature(s) and title(s):

Date: _____