ORGANISATION INTERNATIONALE
DE MÉTROLOGIE LÉGALE

INTERNATIONAL RECOMMENDATION

Portable gas chromatographs for field measurements of hazardous chemical pollutants

Chromatographes en phase gazeuse portatifs pour la mesure sur site des polluants chimiques dangereux

OIML R 113

Edition 1994 (E)

CONTENTS

FOREWORD

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Bureau International de Métrologie Légale
11, rue Turgot - 75009 Paris - France
Telephone: 33 (1) 48 78 12 82 and 42 85 27 11
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Telex: 234 444 SVP SERV F ATTN OIML

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This publication - reference OIML R 113, edition 1994 (E) - was developed by the OIML subcommittee TC 16/SC 4 «Field measurements of hazardous (toxic) pollutants». It was approved for final publication by the International Committee of Legal Metrology in 1993 and will be submitted to the International Conference of Legal Metrology in 1996 for formal sanction.

PORTABLE GAS CHROMATOGRAPHS
for FIELD MEASUREMENTS
of HAZARDOUS CHEMICAL POLLUTANTS

1 Scope

1.1 This International Recommendation provides procedures for testing and verifying the performance of a portable gas chromatograph (GC) for use in measuring potentially hazardous chemical pollutants associated with hazardous waste sites as mandated by national laws and regulations. This Recommendation does not intend to exclude any other equivalent means of measurement or analysis of such pollutants. A portable instrument is self-contained, or an integrated compact assembly that is capable of carrying out a complete analysis on site and operates on battery power; however, it may have the option of operating on alternating current (AC) power. Several types of portable gas chromatographs that employ a range of techniques for introducing samples and for detecting individual compounds of interest are available. The major components specified in this Recommendation reflect examples of current technology and are not intended to exclude new developments. Laboratory based GCs are covered in the OIML International Recommendation R 82 *Gas chromatographs for measuring pollution from pesticides and other toxic substances*.

1.2 Sample components of interest for detection by a portable GC are components that can pass through its column in detectable amounts without undergoing significant irreversible adsorption or decomposition and which can be detected. Examples of general compound types of hazardous chemical pollutants that may be detected by a portable GC are listed in Annex A.

1.3 Sampling plans, sample preparation, and measurement methods are beyond the scope of this Recommendation.

1.4 Instruments that meet the requirements of this Recommendation have flexibility in some major components depending on their specific application. The following such components are covered:

- direct air sampling devices and syringe injection devices for either gaseous or liquid samples;
- packed and capillary columns operating under fixed or adjustable temperature control;
- packed and capillary columns operating at ambient temperature and under certain other environmental conditions;
- photoionization detectors (PID), flame ionization detectors (FID), argon ionization detectors (AID), and electron capture detectors (ECD).

Note: The detectors mentioned above have the broadest applicability and therefore those most commonly used in field applications. Other detectors may be appropriate and may also meet the requirements of this Recommendation for specific applications.

1.5 Instrument performance better than the criteria prescribed for these applications may be achieved by optimizing the performance of each major component of the measuring system. In such cases, success depends on the knowledge, skill, and experience of the operator.

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

2 Application

2.1 Portable gas chromatographs may be prescribed in national laws and regulations for use in field assessment and control of hazardous chemical pollutants. Such instruments can provide real-time measurements at hazardous waste sites and may be the basis for prescribing sampling plans, occupational and public health medical surveillance, public access, evacuation zones, and hazardous waste containment and cleanup. Hazardous waste sites are locations containing hazardous chemical wastes that can affect or have the potential to affect a larger surrounding area and include, for example, sites of uncontrolled hazardous waste dumping, sites of licensed hazardous wastes disposal facilities, and sites of accidents, spills, or fires involving hazardous chemicals either in fixed facilities or during transport. Portable GCs may be used for monitoring other sites having hazardous chemical pollutants such as the work place, private homes, apartments, and other buildings, and public transports. These applications of some portable instruments are addressed in OIML International Document D 22 *Guide to portable instruments for assessing airborne pollutants arising from hazardous wastes*.

2.2 In many field applications, interference may occur in a gas chromatographic measurement of a specific volatile organic compound because of the presence of other known or unknown compounds. It is therefore necessary to anticipate the presence of compounds that can interfere with the intended measurement and to select instrument components, sampling plans, and measurement methods that may minimize possible interfering effects.

2.3 Adequate operating instructions shall be available, and appropriate testing of the instrument performance prior to and after field measurements shall be carried out. The instrument performance shall also be checked periodically, especially after maintenance and repair, and under conditions compatible with the anticipated operational environment under extreme seasonal variations. Specific recommendations for routine tests by a user are provided in 8.3. In some cases, field checks may be appropriate to ensure that an instrument is operational.

3 Terminology

3.1 Injection device

The means of introducing a sample into the column.

3.2 Column

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

3.3 Mobile phase

The carrier gas used to elute the sample components through and from the column.

3.4 Stationary phase

The liquid or solid immobile material on a solid support that causes separation of sample components through varying rates of adsorption and elution.

3.5 Solid support

Normally an inert material within a column that holds the stationary phase. This material may consist of porous particles, impenetrable particles, the interior column wall, or a combination of these alternatives over which the carrier gas flows.

3.6 Elution

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

3.7 Detector

A device that responds to sample components in the eluate of the column.

3.8 Noise

A measure of the variation in the detector's output signal when a sample component is not being detected. This can be classified into two types:

- Short-term noise includes all observable random variations of the signal from the detector or other components having a frequency of about one or more cycles per minute.
- Drift is the average slope of the baseline signal measured over an extended time period, for example, one-half hour.

3.9 Detection limit

The smallest quantity of a sample component which yields a detector output signal that is three times greater than the short-term noise.

Note: This term is also referred to as «minimum detectability» or «minimum detectable limit (MDL)» in references and manufacturer's literature. The detection limit is sometimes defined as the output signal equal to some other multiple (for example, two or ten) of the noise level and may depend somewhat on whether the gas chromatograph is being used for quantitative or qualitative analysis [1].

3.10 Linear range

The range of mass flow rates or concentrations of the sample component of interest in the carrier gas over which the sensitivity of a detector remains constant within specified limits and is expressed as the ratio of its upper limit to the detection limit.

3.11 Dynamic range

The range of mass flow rates or concentrations of the sample component of interest over which an incremental change produces a measurable change in the detector output signal. Its upper limit is the highest mass flow rate or concentration at which a further increase in either flow rate or concentration will not give an observable increase in detector output signal. It is expressed as the ratio of its upper limit to the detection limit.

3.12 Sensitivity

The output signal of a detector per unit mass of eluted sample components of interest and is either one of the following categories:

3.12.1 Concentration-dependent detector

Expressed in $A \cdot mL \cdot g^{-1}$ or $V \cdot mL \cdot g^{-1}$, and by the equation:

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

where
S = sensitivity
P = the integrated peak area ($A \cdot s$ or $V \cdot s$)
F = the carrier gas flow rate ($mL \cdot s^{-1}$)
M = mass of the sample in the carrier gas (g)

3.12.2 Mass-flow-rate-dependent detector

Expressed in $A \cdot s \cdot g^{-1}$ or $V \cdot s \cdot g^{-1}$, and by the equation:

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

where the symbols are the same as those defined in 3.12.1.

3.13 Selectivity

An indication of a detector's ability to respond to certain classes of compounds more readily and to a greater degree than to others.

3.14 Chromatogram

A record of the detector output signal versus time that has peaks corresponding to components of a sample.

3.15 Retention time

The elapsed time between injection of a sample and the appearance of the maximum output peak of the component of interest.

3.16 Calibration

The set of operations that establishes, under specified conditions, the relationship between values indicated by a measuring system and the corresponding known values of the measurand.

3.17 Repeatability

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

4 Description of the instrument

4.1 General

4.1.1 Portable gas chromatographs of various design and construction are available for use at hazardous waste sites. In general, a pressurized carrier gas container with a pneumatic control system provides 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 into the instrument 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 at a characteristic retention time. The detector output signal is displayed as a function of time on a chart recorder and/or stored in a data system. A chromatogram (the detector output signal versus time) provides the retention time for each peak component for identification, and peak areas or peak heights can be related to the concentration of the sample components of interest.

4.1.2 A diagram of the instrument is given in Figure 1. The carrier gas regulator may be a pressure and/or flow controller. For liquid samples, the injection device (A) has a means for vaporizing the sample prior to injection. The temperature control device for the column (B) may be either fixed or adjustable; however, some instruments may operate correctly at a relatively stable ambient temperature without temperature control. Under certain conditions of use, a detector (C) will be maintained at a temperature at least equal to that of the column.

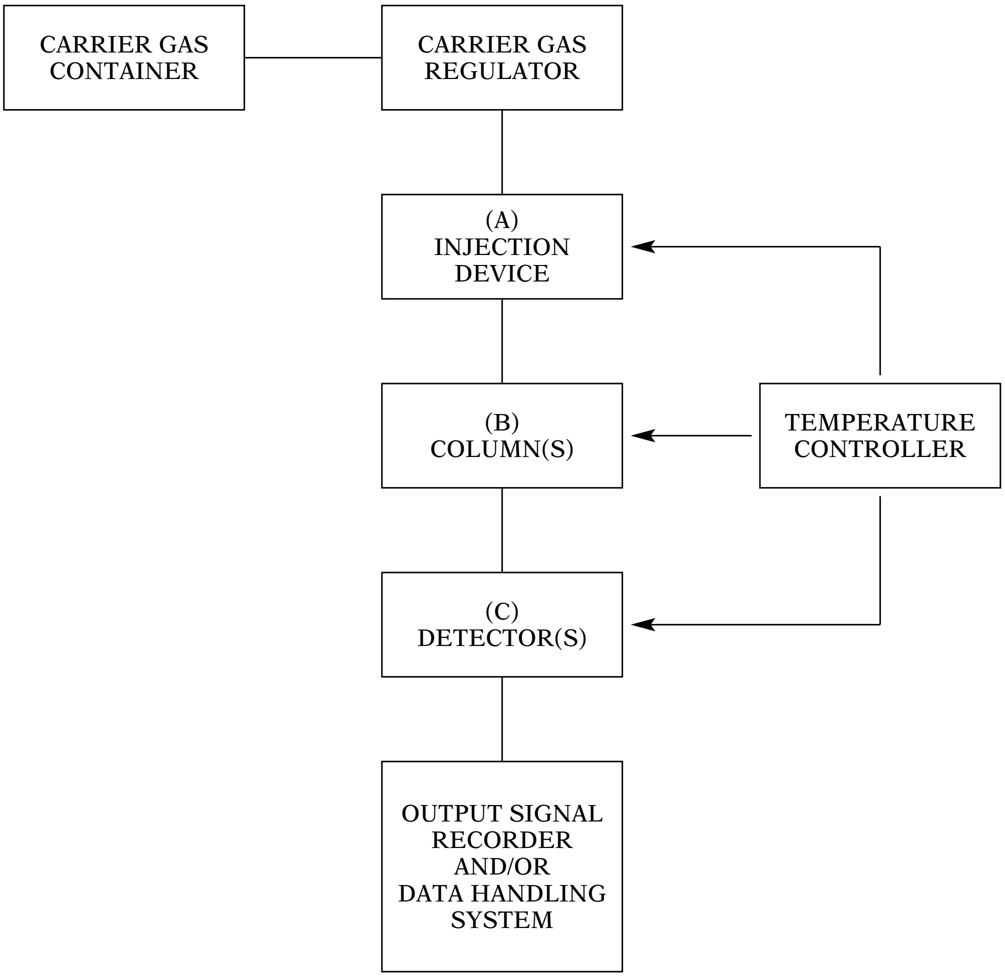

Figure 1. Diagram of a portable gas chromatograph

4.1.3 The principle of gas chromatograph measurements is based on the separation of gaseous or vaporized sample components in the carrier gas (mobile phase) by the column's stationary phase. Sample partition depends 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 either manually or by a computerized data handling system. The identification and quantification depends on a knowledge of the retention times and measuring corresponding peak areas or peak heights of specific chemical components for an instrument operating under reference conditions.

Note: A more detailed description of the instrument may be obtained in references [2–4].

4.2 Instrument components

4.2.1 The pneumatic control system is designed to regulate the flow of the carrier gas through the instrument.

4.2.2 The injection device(s) may be of the following types:

4.2.2.1 A direct and/or (flash) vaporization injection device that allows a gas or liquid syringe to be used to inject a precise amount of a sample into the carrier gas.

4.2.2.2 A gas sampling loop that introduces a precise amount of a continuously flowing gas sample into the carrier gas.

4.2.2.3 A preconcentration and thermal desorption injection device that allows a precise amount of a sample to be concentrated onto a preselected adsorbent after which thermal desorption introduces the sample into the carrier gas.

4.2.3 The column may be either packed or capillary.

4.2.4 If a temperature control device for the column is included, it may be either fixed or adjustable.

4.2.5 The detector(s) may be of the following types:

4.2.5.1 A flame ionization detector (FID) which uses a hydrogen-air flame to produce sample component ions that are subsequently collected on an electrode having a potential difference with respect to the hydrogen jet. The current measured at the collector electrode is proportional to the mass flow rate of the sample component.

4.2.5.2 A photoionization detector (PID) consists of a high energy (ultraviolet) lamp and an ionization chamber. Photoionization of a sample component molecule (R) is usually initiated by the absorption of a high energy photon (hν) from the lamp when the energy of a photon absorbed is greater than or equal to the ionization potential of R; however, in some applications, it may be possible to initiate the ionization of R through an intermediate excited state (R*) by photons with less energy than the ionization potential of R. These two processes respectively may be represented symbolically as follows:

$$R + h\nu = R^+ + e^-$$
$$R^* + h\nu = R^+ + e^-$$

The ions formed are collected in the ionization chamber where the resulting measured current is proportional to the concentration of the sample component being ionized. Lamps with different photon energies are available. For lamps with the high photon energies (e.g., 11.7 eV) the detector response becomes more universal whereas for lamps with lower photon energies (e.g., 10.2 or 10.6 eV), the detector becomes more selective.

4.2.5.3 An argon ionization detector (AID) uses a radioactive tritium (^3H) source to produce argon ions that interact with the sample component of interest eluted from the column. Argon carrier gas is required for this detector. Argon atoms are ionized by the detector sources and some are energized to an excited state (A*). The excitation energy of argon is approximately 11.6 eV; however, the ionization potential of most organic compounds is less than 11.6 eV. Therefore, sample component molecules introduced to the detector from the column can be ionized by the steady stream of excited argon atoms produced by the radioactive source. This interaction may be represented symbolically as follows:

$$A^* + R = A + R^+ + e^-$$

The ions formed are collected in the ionization chamber producing a constant current. The change in that current is proportional to the concentration of the sample component ionized by the excited argon atoms.

4.2.5.4 An electron capture detector (ECD) with a radioactive source, usually nickel (^{63}Ni) or tritium (^{3}H), produces ions in the carrier gas and collects the associated electrons. When the eluate (an electron absorbing compound) enters the detector, the measured constant electron current produced by the radiation source is decreased by an amount proportional to the concentration of the sample component in the eluate. The detector may be operated either in a DC or pulsed mode.

4.2.6 The data system for the instrument usually includes one or more of the following components: direct display, chart recorder, and computer.

5 Metrological requirements

5.1 Carrier gas

5.1.1 The carrier gas flow rate or pressure shall be adjustable to a nominal value that can be maintained to within ± 2.0 %.

5.1.2 The purity of the carrier gas with respect to hydrocarbons shall be specified by the manufacturer.

Note: The level of hydrocarbons present is usually less than 1.0 µL/L.

5.2 Injection device

5.2.1 The injection device shall have a gas sample volume within the range of 10 µL to 5 mL or a liquid sample volume within the range of 0.1 µL to 5 µL; however, a preconcentration thermal desorption injection device shall provide a gas sample volume within the range of 10 mL to 5 000 mL.

Note: The temperature and time of desorption required in the operation of the preconcentration thermal desorption injection device is dependent on the type of sample component(s) to be concentrated and the type of material used in the preconcentrator unit.

5.2.2 When testing the repeatability of the volume delivered by any of the types of injection devices referred to in 5.2.1, the relative standard deviation of peak height or peak area shall meet the requirements of 5.5.2.

Note: It is expected that the use of a gas sampling loop or an automatic injection device would give significantly better performance than a manually operated injection device.

5.3 Column temperature control

5.3.1 For instruments with a fixed temperature control device, the colum temperature shall be maintained at a constant temperature to within ± 2 °C during the period of analysis.

Note: For example, dissolution of sodium azide at 40 °C or an ice bath at 0 °C could provide appropriate fixed temperature points for controlling the temperature of the column.

5.3.2 For instruments with adjustable temperature control devices, the column temperature shall be maintained at a constant temperature to within ± 2°C over the operating temperature range from not more than 10 °C above ambient to the maximum temperature that can be provided by the control device.

5.3.3 For instruments without a fixed or adjustable temperature control device, a means for measuring and recording the change in ambient temperature surrounding the column to within ± 2°C shall be provided (see 8.3.3).

5.4 Detectors shall meet the following minimum requirements for detection limit and linear range under reference conditions after injecting the required concentration of test compound in dry air or nitrogen onto the column. A test procedure is provided in Annex B for gases and liquids in a suitable solvent.

Note: The detection limit is considered to be the maximum permissible value for this quantity with maximum permissible errors of ± 5 % (see Annex B). The linear range is considered to be the working range of the instrument within specified limits although a manufacturer may specify a dynamic range within defined limits.

5.4.1 Flame ionization detector (FID)

- Type: Mass flow dependent
Selective and widely applicable to compounds containing carbon and hydrogen (see Annex A)
- Test compound: Toluene
- Test conditions: Use column type, carrier gas and flow rate, make-up gas flow rate (if necessary), and temperature as specified by the manufacturer
- Detection limit: 2×10^{-9} g injected ± 5 %
- Linear range: 10^4

5.4.2 Photoionization detector (PID)

- Type: Concentration dependent
Selective and widely applicable to organic and inorganic compounds (see Annex A)
- Lamp energy: 10.2 eV, 10.6 eV or 11.7 eV
- Test compound: Toluene
- Test conditions: Use column type, carrier gas and flow rate, make-up gas flow rate (if necessary), and temperature as specified by the manufacturer
- Detection limit: 2×10^{-12} g injected ± 5 %
- Linear range: 10^5

5.4.3 Argon ionization detector (AID)

- Type: Concentration dependent
  Selective and widely applicable to organic and inorganic compounds (see Annex A)
- Test compound: Toluene
- Test conditions: Use column type, carrier gas and flow rate, make-up gas flow rate (if necessary), and temperature as specified by the manufacturer
- Detection limit: 1×10^{-10} g injected ± 5 %
- Linear range: 10^3

5.4.4 Electron capture detector (ECD)

- Type: Concentration dependent
  Selective for halogenated and related compounds (see Annex A)
- Test compound: Sulfur hexafluoride (SF_6)
- Test conditions: Use column type, carrier gas and flow rate, make-up gas flow rate (if necessary), and temperature as specified by the manufacturer
- Detection limit: 3×10^{-13} g injected ± 5 %
- Linear range: 25

Note: This detector may be usable over its dynamic range that is of the order of 10^2.

5.5 Instrument test under reference conditions

5.5.1 During pattern approval and initial and subsequent verification, the repeatability of the output signal of the entire instrument shall be tested in a laboratory using reference standards and under reference conditions as follows:

- ambient temperature: 15 °C to 25 °C and stable to within ± 2 °C
- relative humidity (RH): 40 % to 80 %
- column type: specified by manufacturer
- carrier gas and flow rate: specified by manufacturer
- column temperature: specified by manufacturer
- concentration of the reference sample: inject an appropriate reference standard that gives an output signal of about 300 times the detection limit
- reference standards and associated detector(s):
  - gases: toluene for the FID,PID and AID and SF_6 for the ECD with the reference standard in dry air or nitrogen
  - liquids: toluene for the FID, PID and AID and 1,1,1-trichloromethane for the ECD with the reference standard in a suitable solvent

5.5.2 Under reference conditions and for ten repeated injections of the reference standard within a short period of time, the instrument shall be capable of achieving the following performance requirements:

- a relative standard deviation of the peak height or peak area of the output signal less than 10 %
- a relative standard deviation of retention time less than 2 %

Note: These values of relative standard deviation for peak height or peak area and retention time are considered to be maximum permissible errors.

5.6 Influence factors

5.6.1 During pattern approval, the entire instrument shall be tested using relevant conditions specified in 5.5.1 for the following influence factors:

- vibration (sinusoidal)
- mechanical shock
- electromagnetic fields
- electrostatic discharge
- low voltage indicator for battery power
- variation in mains or portable generator voltage and frequency
- temperature range
- damp heat

5.6.2 The results of the tests specified in 5.6.1 shall meet the requirements of 5.5.2.

6 Technical requirements

6.1 General

6.1.1 The instrument shall be self-contained which means that all instrument components are in a single unit or shall be located together in an integrated compact assembly. The mass of the instrument shall not be more than 30 kg.

6.1.2 The instrument shall be capable of operating over a temperature working range from 5 °C to 35 °C.

6.2 Carrier gases

6.2.1 When necessary, it should be possible to insert in the pneumatic system before the column a means for removing unwanted contaminants, such as moisture and particulate matter in the gas supply lines.

6.2.2 The appropriate carrier gas and detector combination shall be used as follows:

- FID - helium, nitrogen, hydrogen, or air (see note)
- PID - helium, nitrogen, hydrogen, or air (see note)
- AID - argon
- ECD - nitrogen, helium, argon, or argon/methane

Note: At temperatures above ambient, air may damage some stationary phases. The manufacturer's recommendations for the carrier gas and detector combination under such conditions should be considered.

6.2.3 The instrument shall have a self-contained carrier gas supply that allows the instrument to operate for at least four hours.

6.3 Injection inlet

The instrument shall have an injection inlet that provides compatibility between the injection device and column type used.

6.4 Columns

6.4.1 Columns shall be tubular and shall be fabricated from metal, glass, polytetrafluoroethylene, or fused silica. They may be either packed or capillary. The instrument shall be capable of accommodating the column required according to the method of analysis. It shall be possible for the user to replace or install a new column in the instrument in the field as required.

6.4.2 The stationary phase of the column may be either liquid or solid and shall be chosen to optimize the separation of the sample component(s) of interest.

6.4.3 The backflush technique may significantly enhance instrument performance for certain applications and involves a rapid removal of unwanted high-molecular weight sample fractions from the column. This technique may be affected by using a device to reverse the direction of the carrier gas flow through the column. Alternatively, a precolumn may be used.

Note: Annex C provides examples of column types appropriate for use.

6.5 Routine assessment

The instrument shall include a means for routinely introducing reference standards for compounds of interest to obtain a qualitative (retention time) and a quantitative (peak area or height) assessment during either laboratory or on-site field measurements.

Note: Appropriate certified or other reference standards as indicated in references [5–7] may be available for this purpose.

6.6 Battery and AC power

The instrument shall be powered by a battery capable of continuous operation for at least four hours and shall have a means of indicating low battery voltage. It may also have a means for using AC power when available.

6.7 Chromatogram

Data systems shall be capable of producing an accurate and accessible record (chromatogram) of the detector output signal as a function of time. Data systems that can also process data to give a complete qualitative and quantitative analysis on site should be considered.

6.8 Markings

Markings shall be attached conspicuously to the instrument as follows:

- name of manufacturer
- instrument serial and model number
- power requirements as applicable

7 Practical instructions

7.1 Manufacturers of portable gas chromatographs shall provide each instrument with a manual describing its operation and routine maintenance.

7.2 Before using the instrument, all environmental factors should be considered. Manufacturers shall provide specifications for the range of temperature and humidity under which the instrument can be operated successfully.

7.3 Any necessary precautions or warnings for instrument operators shall be indicated explicitly in the manufacturer's operating manual and shall be displayed clearly on the instrument according to national safety requirements.

8 Metrological controls

8.1 Pattern evaluation

8.1.1 Manufacturers shall provide the responsible national body with an instrument operating manual and may provide data and other information on performance tests and calibrations which contribute to determining whether the design of the instrument meets the requirements of this Recommendation.

8.1.2 The instrument manual shall be reviewed for its completeness and clarity of operating instructions. The instrument shall be visually inspected in conjunction with a review of specifications by the manufacturer to determine that requirements in 6.1 through 6.8 are met.

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

- detection limit for detector(s) used (5.4 and Annex B)
- linear range for detector(s) used (5.4 and Annex B)
- ambient reference conditions (5.5 and B.1)
- low voltage indicator for battery power (5.5 and D.2)
- variation in mains or portable generator voltage (5.5 and D.3) and frequency (if applicable)
- mechanical shock (5.5 and D.4)
- vibration (sinusoidal) (5.5 and D.5)
- electrostatic discharge (5.5 and D.6)
- electromagnetic fields (5.5 and D.7)
- temperature working range (5.5 and D.8)
- damp heat (5.5 and D.9)

Note: A reference to the requirements and a brief description of these tests are indicated in parenthesis. Annex D provides a description of the tests associated with influence factors. The tests are based on the requirements of the International Document OIML D 11 *General requirements for electronic measuring instruments*. Appropriate IEC standards referenced in D 11 should be consulted for additional test details and alternatives.

8.1.4 The report on instrument tests carried out during pattern evaluation shall contain at least the items of information according to the format provided in Annex E. A specific form may be developed according to national preference. The manufacturer shall be provided specific comments about any test failures.

8.2 Initial verification

8.2.1 The documentation provided by the manufacturer shall be examined to assure compliance with the requirements of 8.1.

8.2.2 The test under reference conditions specified in 5.5 shall be carried out.

8.2.3 Any other instrument tests not specified in 8.1.2 which may be considered to be critical to the specific application shall be performed.

8.2.4 The period of validity of this verification shall be specified by the responsible national body.

8.2.5 An instrument shall undergo subsequent verification equivalent to initial verification after repair or replacement of component parts or units of the electrical control and readout system. This requirement does not pertain to replacement of the column.

8.3 Routine tests by a user

8.3.1 The responsible national body shall provide information on methods for using instruments to measure specific pollutants. Some measurement methods may be appropriate for use as quality control in assessing an instrument's performance.

8.3.2 An instrument operator shall carry out a test with a reference sample before and after field measurements as well as after replacement of carrier gas supply, injector(s), column(s), or detector(s). The results of these instrument tests shall be within the limits established by the responsible national body.

8.3.3 In addition to the requirements of 8.3.2, the ambient temperature surrounding the column of such instruments not having temperature control devices shall be recorded and a reference gas standard shall be injected before each period of operation to establish the reference measurement condition. The ambient temperature shall also be measured before and after each analysis. If the ambient temperature changes by more than ± 3 °C during a period of operation, the reference gas standard shall be injected again to re-establish a new reference measurement condition. This procedure shall be repeated for temperature changes larger than ± 3 °C from each newly established reference condition.

Note: This requirement is necessary because retention time of a sample component required for identification depends on the column temperature.

8.3.4 In addition to the requirements of 8.3.2, an operator shall carry out a performance test and calibration of the entire instrument before and related to a specific field application (see Annex F).

8.3.5 A chronological written record shall be maintained for each instrument and shall contain at least the following information:

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

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ANNEX A

EXAMPLES OF DETECTABLE COMPOUND TYPES

Compound types	Recommended detector(s)
Alcohols, Aldehydes, and Ketones	FID, PID, AID
Nitro-based explosives	PID, ECD
Fuels and fuel by-products	FID, PID, AID
Fumigants and pesticides	PID, AID, ECD
Chlorofluorocarbons	FID, PID, AID, ECD
Polychlorinated biphenyls	PID, ECD
Chlorinated hydrocarbons	FID, PID, AID, ECD
Haloethers	FID, PID, AID
Organochlorine pesticides	ECD
Amines	FID, PID, AID
Organosulfides	FID, PID, AID
H_2S, COS, and CS_2	PID, AID
Aliphatic/aromatic solvents	FID, PID, AID

ANNEX B

A TEST FOR DETERMINING THE DETECTION LIMIT AND LINEAR RANGE OF DETECTORS

(Mandatory)

B.1 This test provides a procedure for determining whether an instrument's detector meets the requirements of detection limit and linear range specified in 5.4.

B.2 The test shall be carried out at reference conditions specified in 5.5.1 and with a reference sample of the test compound specified for each particular detector type. The following procedure applies for both reference gas and liquid samples taking into account that air samples are diluted with dry air or nitrogen and liquid samples are diluted with a suitable solvent. In addition, the injected volume of reference samples shall be 1 mL for gases and 1 µL for liquids.

B.3 Procedure

B.3.1 Prepare a stock reference sample having a concentration equivalent to the product of the detection limit and the linear range according to that specified in 5.4 for the detector to be tested.

B.3.2 Prepare three to five diluted samples with a middle concentration equal to approximately one-half the concentration of the stock reference sample and the other samples having values at equal intervals from the extremes above and below the middle concentration value.

B.3.3 Select an appropriate injection device (syringe or loop), column, and temperature for the detector to be tested.

B.3.4 Make at least five repeated injections of a blank sample (dry air or nitrogen for gas and solvent used for liquid) and record the retention times and the peak areas or peak heights of any peaks appearing.

B.3.5 Make at least five repeated injections of the appropriate volume of the selected concentrations of the reference sample and record the peak area or peak height of the detector response.

B.3.6 Determine the average peak area or peak height from the data acquired in B.3.5 taking into account any peaks or peaks coeluting with the reference sample as determined in B.3.4. The amount injected shall be expressed in grams of the test compound in each measurement.

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

B.4 Detection limit

B.4.1 From the results of B.3.6, plot the average value of the peak area or peak height versus amount injected in grams. Calculate the slope of the curve that fits the data to a least-squares linear curve. The results of the linear least squares fit of the data shall have a correlation coefficient of 0.98 or better.

Note: The correlation coefficient (r^2) can be calculated from the slope (s) and the standard deviation of the concentration (σ_x) and the detector output signal (σ_y) as follows:

$$r^2 = \left[s \cdot \frac{\sigma_x}{\sigma_y} \right]^2$$

where:

$$s = \frac{\Sigma x_i^2 \, \Sigma y_i - \Sigma x_i \, \Sigma (x_i \, y_i)}{n \, \Sigma x_i^2 - (\Sigma x_i)^2}$$

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

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

$\bar{x}$ et $\bar{y}$ = mean values
n = number of data values

B.4.2 Draw a line parallel to the ordinate that is three times the noise level as determined in B.3.4. The detection limit is the intersection of the parallel line with the slope and shall meet the requirements of 5.4.

B.4.3 The sensitivity of the instrument is the slope of the curve obtained in B.4.1; alternatively, the sensitivity may be calculated using the appropriate equation in 3.12.

B.5 Linear range

B.5.1 Make at least five repeated injections of the appropriate volume of the stock reference sample prepared according to B.3.1.

B.5.2 Plot the average value of the results on the curve obtained in B.4.1.

B.5.3 Compare the value obtained by B.5.2 with the value provided by the curve of B.4.1 for the concentration (or amount in grams) at the end of the linear range. The value of B.5.2 shall not be lower than 5 % of the value defined by the linear range according to the requirements of 5.4 for the detector being tested.

ANNEX C

EXAMPLES OF APPROPRIATE COLUMN TYPES
(Informative)

	PACKED	CAPILLARY		
		Wide diameter open tubular	Wide bore	Narrow bore
Material	glass, ss[a], ptfe[b]	borosilicate glass	fused silica, ss, Ni	fused silica, ss, Ni
Length (m)	0.1 - 6	10 - 80	1 - 60	1 - 60
Inside diameter (mm)	2 - 4	0.9 - 1.5	0.32 - 0.75	0.10 - 0.25
Sample capacity (ng)	10^4 - 10^6	10^4 - 10^6	500 - 6 000	2 - 50
Efficiency[c] (plates/m)	600 - 2 000	500 - 1 000	1 200 - 2 200	2 500 - 10 000[d]

(a) ss = stainless steel

(b) ptfe = polytetrafluoroethylene

(c) Column efficiency is measured by the number of theoretical plates and is related to the peak broadening of an initially compact band as it passes through the column. It is quantitatively described by the height equivalent to a theoretical plate (HETP), which is the length of the column necessary to attain solute equilibrium between the mobile and stationary liquid phases

(d) This range is for a 0.1 mm diameter column

ANNEX D

DESCRIPTION OF PERFORMANCE TESTS ASSOCIATED WITH INFLUENCE FACTORS

(Mandatory)

D.1 Ambient reference conditions

The tests specified in 5.5 shall be carried out, and the requirements specified in 5.5.2 shall be obtained.

D.2 Low voltage indicator for battery power

The instrument's power source shall be replaced by a variable DC power source. The voltage of this source shall initially be set at the DC level specified by the manufacturer and then shall be reduced until a low voltage indicator is activated. Next the voltage shall be increased to a level such that the low voltage indicator is just de-activated. At this last voltage level, the tests specified in 5.5 shall be carried out and the requirements of 5.5.2 shall be met.

D.3 Variation in mains or portable generator voltage and frequency

If applicable, the instrument shall be tested for its susceptibility to changes from the nominal voltage and frequency when operated by an AC source of power. The instrument's power shall be changed from its nominal rated values as specified by the manufacturer as follows: mains or generator voltage by + 10 % and – 15 % and mains or generator frequency by ± 2 %. While the change specified for each nominal power source rated value is maintained in turn for the instrument, the tests specified in 5.5 shall be carried out and the requirements specified in 5.5.2 shall be met.

D.4 Mechanical shock

The instrument shall be placed on a rigid surface in its normal orientation of use. It should then be tilted about one bottom edge to a height of at least 50 mm and allowed to fall once to the surface. After this shock, the tests specified in 5.5 shall be carried out and the requirements specified in 5.5.2 shall be met.

D.5 Vibration (sinusoidal)

The instrument shall be mounted on a rigid surface such that the gravitational force acts in the same direction as it would in normal use. It is then subjected to the following conditions of sinusoidal vibrations in turn on its three mutually perpendicular main axes: frequency range from 10 Hz to 50 Hz, a maximum acceleration level of 2 m/s^2, and 20 sweep cycles per independent axis. After these vibrations, the tests specified in 5.5 shall be carried out and the requirements specified in 5.5.2 shall be met.

D.6 Electrostatic discharge

The instrument shall be tested for its susceptibility to electrostatic discharges from a suitable DC voltage source of 8 kV connected through a capacitor of 150 pF. The instrument shall be grounded or placed on a grounded surface. Electrostatic discharges shall be introduced to the instrument's surfaces, normally accessible to the user, through an electrode with a resistance of at least 150 ohms. The electrode shall be brought in close contact with the instrument until a discharge occurs and shall then be removed quickly before repeating another discharge. At least ten discharges shall be applied with at least ten seconds between each discharge. After this exposure, the tests specified in 5.5 shall be carried out and the requirements specified in 5.5.2 shall be met.

D.7 Electromagnetic fields

The instrument shall be tested for its susceptibility to interference from electromagnetic fields in the range from 0.1 MHz to 1 000 MHz. The field strengths may be generated as follows: (a) by using a «strip line» for frequencies between 0.1 MHz to 150 MHz and «dipole antennas» or «antennas with circular depolarization» for frequencies between 150 MHz and 1 000 MHz, or (b) by using areas of known and precisely measured electromagnetic fields. During exposure to these electromagnetic fields at a field strength of 10 V/m, the instrument shall be subjected to the tests specified in 5.5 and the requirements of 5.5.2 shall be met.

D.8 Temperature range

The instrument shall be placed in an environmental chamber and warmed to a temperature of 35 °C at a relative humidity of 60 % ± 20 % until the instrument is in thermal equilibrium at that temperature. At 35 °C, tests shall be carried out to determine the relative standard deviation of peak height, or peak area, and of the retention time. The instrument shall be cooled down to achieve thermal equilibrium at 5 °C. The rate of cooling shall not exceed 1 °C per minute and the final relative humidity shall be 60 % ± 20 %. After the temperature has stabilized at 5 °C, the same tests shall be conducted as at 35 °C. The tests shall be as described in 5.5 and the requirements specified in 5.5.2 shall be met.

D.9 Damp heat

The instrument shall be placed in an environmental chamber and warmed to a temperature of 35 °C at a relative humidity of 93 % until the instrument is in thermal equilibrium without condensation. Under these conditions, the tests specified in 5.5 shall be carried out and the requirements in 5.5.2 shall be met.

ANNEX E

TEST REPORT FORMAT

Note: This Annex is informative with regard to implementation of this Recommendation in national regulations; however, use of the test report format is mandatory for the application of the Recommendation within the OIML certificate System.

A test report intended for use in the OIML Certificate System and for other purposes shall include the following information.

E.1 The name and address of the testing laboratory(ies)

E.2 A reference (number and year of edition) to this Recommendation

E.3 A unique identification of the pattern to which this test report applies (e.g., the common and trade names, model, and a brief description including drawings, diagrams, and inscriptions)

E.4 The name(s) and address(s) of the manufacturer and of the applicant if other than the manufacturer

E.5 An identification of the instrument tested

E.6 The date of the beginning of testing

E.7 The location at which tests were performed if other than the address identified in E.1

E.8 A summary of the test results carried out according to 8.1.2 and 8.1.3 under conditions specified in this Recommendation

E.8.1 Operating manual has clear and complete instructions: yes no
Comments:

E.8.2 Mass of instrument: kg

E.8.3 Markings: pass fail
Comments:

E.8.4 Self-contained carrier gas supply that operates for at least four hours:
pass fail
Comments:

E.8.5 Detector(s) tested, test conditions, and results:

- type:
- carrier gas:
- column type:
- column temperature:
- reference sample(s) and concentration(s):

- ambient temperature:
- relative humidity:
- relative standard deviation
  - peak height or peak area:
  - retention time:
- detection limit:
- linear range:

Comments:

Note: Provide this information for each detector tested.

E.8.6 Low voltage indicator for battery power:
pass fail

E.8.7 Uses mains power: yes no
Uses portable generator: yes no
Variation on voltage: pass fail
Comments:
Variation on mains voltage and frequency: pass fail
Comments:
Variation of portable generator voltage and frequency: pass fail

E.8.8 Mechanical shock: pass fail
Comments:

E.8.9 Vibration: pass fail
Comments:

E.8.10 Electrostatic discharge: pass fail
Comments:

E.8.11 Electromagnetic fields: pass fail
Comments:

E.8.12 Temperature working range: pass fail
Comments:

E.8.13 Damp heat: pass fail
Comments:

Note: Identify the detector(s) and carrier gas(es) used for each test from E.8.6 through E.8.13.

E.9 A brief statement of conclusions as to whether the instruments tested met the requirements of this Recommendation

E.10 The signature of the responsible person(s), the date signed, and a unique report number.

ANNEX F

AN OVERALL PERFORMANCE TEST FOR THE INSTRUMENT

(Mandatory)

F.1 This test procedure describes the analysis of a sample having a compound or a mixture of compounds that are likely to be present at a hazardous waste site or the analysis of a pre-determined test sample mixture designed to periodically evaluate the overall instrument performance.

F.2 The purpose of this test is to assure that the entire gas chromatographic system is capable of achieving acceptable detection limits of sample components of interest as well as acceptable repeatability of retention times and peak areas or peak heights of the output signal over the specified working range of the instrument. The calibration of the instrument shall be accomplished using these procedures but may require measuring additional concentrations of specific test compounds of interest over the working range of the instrument.

F.3 The test compounds may be selected from the following list for the detectors identified.

	FID	AID	PID 10.2 eV and 10.6 eV	PID 11.7 eV	ECD
Methane	X				
Dichloromethane	X	X		X	X
1,2-Dichloroethane	X	X		X	X
Benzene	X	X	X	X	
1,1,1-Trichloroethane	X	X		X	X
Trichloroethene	X	X	X	X	X
Toluene	X	X	X	X	
p-Xylene	X	X	X	X	
Carbon Tetrachloride		X		X	X
2-Butanone	X	X	X	X	
n-Hexane	X	X	X	X	
n-Pentane	X	X	X	X	
Methanol	X	X		X	
Chloroethene	X	X	X	X	
n-Decane	X	X	X	X	
g-Hexachlorocyclohexane					X
Polychlorinated Biphenyl			X		X
Sulfur Hexafluoride					X

F.4 Gas samples

F.4.1 Select compound or a mixture of compounds from the list in F.3 or other test compound compatible with the detector to be used. Prepare or obtain a gas test sample of the compound or mixture selected having concentrations from 0.1 μL/L to 10 μL/L in dry air or nitrogen.

F.4.2 Select an appropriate injection device, column, and temperature.

F.4.3 For an instrument having a column without a fixed or adjustable temperature control device, record the ambient temperature.

F.4.4 Make at least three injections of a blank (dry air or nitrogen) gas sample and determine the noise level.

F.4.5 Prepare at least three different concentrations of the selected test gas sample specified in F.4.1.

F.4.6 With the instrument under reference conditions, perform at least three injections of 1 mL of each test gas sample prepared according to F.4.5 and record the retention times and peak areas or peak heights of the sample components selected according to F.4.1.

F.4.7 The retention times shall have a relative standard deviation of less than 2 %, and the peak areas or peak heights shall have a relative standard deviation of less than 10 % for the same instrument.

F.4.8 The detection limit, linear range, and sensitivity of the detector for each compound in the test sample can be determined to within specified limits from the data obtained in F.4.6 and following procedures specified in Annex B.

F.5 Liquid samples

F.5.1 Select a compound or a mixture of compounds from the list in F.3 or other test compounds compatible with the detector to be used. Prepare or obtain a stock solution of the selected compound with concentrations from 0.1 mg/L to 10 mg/L in a suitable solvent.

Note: The solvent selected should be compatible with the detector to avoid interferences.

F.5.2 Select an appropriate injection device, column and temperature.

Note: A liquid sample requires a heated injection device.

F.5.3 For an instrument having a column without fixed or adjustable temperature control, record the ambient temperature.

F.5.4 Make at least three injections of a blank liquid sample (the solvent) and determine the noise level.

F.5.5 Prepare by dilution three different concentrations of the stock solution specified in F.5.1.

F.5.6 With the instrument operating under reference conditions specified in 5.5, perform at least three injections of 1 µL of each of the test liquid samples specified in F.5.5 and record the retention times and the peak areas or peak heights.

F.5.7 The retention times shall have a relative standard deviation less than 2 % and the peak areas or peak heights shall have relative standard deviation less than 10 % for the same instrument.

F.5.8 The detection limit, linear range, and sensitivity of the detector for each compound in the test sample can be determined to within specified limits from the data obtained in F.5.6 and following procedures specified in Annex B.

Printed in France

GRANDE IMPRIMERIE DE TROYES
130, rue Général-de-Gaulle, 10000 Troyes