

INTERNATIONAL
RECOMMENDATION

OIML R 83

Edition 2006 (E)

Gas chromatograph/mass spectrometer systems
for the analysis of organic pollutants in water

Système de chromatographe en phase gazeuse/spectromètre de masse
pour l'analyse de polluants organiques dans l'eau



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Foreword

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This publication - reference OIML R 83, edition 2006 (E) - was developed by the OIML Technical Subcommittee TC 16/SC 2 *Measurement of water pollution*. 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 83 (Edition 1990).

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Gas chromatograph/mass spectrometer systems for the analysis of organic pollutants in water

1 Scope

1.1 This Recommendation provides performance requirements and testing procedures for a gas chromatograph/mass spectrometer/data (GC/MS) system when used for measurements in determining water pollutants in pollution control programs and in assessing the quality of water as may be mandated by national laws and regulations. Several types of mass spectrometers are available which employ a wide variety of techniques to achieve separation of ions according to mass-to-charge ratios; however, only low-resolution mass spectrometers are addressed. This Recommendation does not intend to exclude any other equivalent means of measurement or analysis.

1.2 The mass spectrometers addressed and coupled with appropriate gas chromatographs may be used successfully to analyze a variety of water samples, such as ground waters, surface waters, aqueous municipal and industrial effluents, and saline waters. A sample may require specific preparation techniques prior to analysis by a GC/MS system. Although important to an overall analysis, considerations of sampling, sample preparation, and pollutant measurement methods are beyond the scope of this Recommendation.

1.3 Pollutant compounds of interest in a sample may be analyzed by a GC/MS system if they are present in detectable amounts, can pass through the gas chromatographic column, and are not significantly affected by thermal or catalytic decomposition or adsorption. Some compounds that are difficult to analyze, such as those that are non-volatile or thermally unstable, can be converted to derivative compounds that then may undergo gas chromatographic separation and detection by the mass spectrometer.

1.4 Performance criteria better than those prescribed in this Recommendation for these applications of a GC/MS system may be achieved by paying careful attention to optimizing the performance of each component of the measurement system. In such cases, success depends on the knowledge, skill, and experience of the analyst.

2 Application

The application of GC/MS systems for environmental measurements can generally be divided into three distinct categories:

- for a broad spectrum organic analysis having the goal to determine known or unsuspected major or minor components of a sample,
- for routine monitoring of a relatively large number (e.g. greater than 20) of sample components, and
- for real time selected ion monitoring (SIM), which is widely recognized as being a very sensitive, accurate, and selective tool in environmental analysis.

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 portion of a sample is introduced into the gas chromatographic column.

3.3 Stationary phase

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

3.4 Mobile phase

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

3.5 Column

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

3.6 Elution

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

3.7 Detector

Device that can respond to eluted sample components in the carrier gas emerging from the gas chromatographic column and that is contained within the mass spectrometer in a GC/MS system.

3.8 Mass spectrum

Either a graphical or tabular presentation form of the measured mass-to-charge (m/z) ratios of separated ions and corresponding intensities of these ratios.

3.9 Detection limit

Minimum amount of a specific compound which, when injected into the gas chromatograph, produces a signal-to-noise ratio of at least 3 for a characteristic base peak of that compound depending on the mode of ionization and over a specified mass range.

Note: Some compounds do not give a molecular ion, but all amenable compounds have a base peak in their spectra; the base peak is the most intense or abundant ion in a mass spectrum.

3.10 Resolution of a mass spectrometer

The method of calculating instrument resolution is dependent on the instrument's ion analyzer. Two common methods for determining the ratio of m to Δm ($m/\Delta m$) are:

- m is the mass of a component comprising the first peak of a doublet, and Δm is the difference in the mass of the two peaks. The doublet shall be separated by a valley, the value of which shall not exceed 10 % of the value of the highest peak ($m/\Delta m$ is constant (sector type)).
- m is the mass of a sample component within a peak and Δm is the full width at half maximum (FWHM) of the peak (Δm is constant, (quadrupole type)). Thus $m/\Delta m$ decreases as mass decreases. With this type of instrument unit resolution, one can separate each mass from the next integer mass, i.e. one can distinguish mass 50 from mass 51, and distinguish mass 1000 from mass 1001.

3.11 Repeatability

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

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

3.12 Working range

Range of concentrations of a component of interest in solution that can be measured with a repeatability within specified limits.

3.13 Symbols for quantities used in this Recommendation

- m = mass of an ion in unified atomic mass units, u (or amu in some references), and
 z = number of elementary charges on an ion.

4 Description of the instrument

4.1 General

A GC/MS system combines instruments for the purpose of separating and analyzing compounds in a liquid sample of interest. The sample is first injected into the gas chromatograph, which separates the sample components in time. A separator may connect the gas chromatograph and the mass spectrometer and separates the compound of interest from the carrier gas. The sample compounds are ionized in the ion source of the mass spectrometer and the ionized fragments of the compounds are mass analyzed by magnetic or electromagnetic fields in the mass analyzer. The mass analyzed ions interact with a detector that gives signals from which a mass spectrum of the compound can be determined. This spectrum is compared within the data handling system with historical spectra of various compounds. This process of comparison permits the identification of the compound analyzed. Figure 1 shows a block diagram of the GC/MS system.

Note: For further discussion of the GC/MS system and related terminology, see references [1] - [6].

4.2 Gas chromatograph

4.2.1 A gas chromatograph is used to separate volatile organic and inorganic mixtures. Its basic components are a pneumatic control system for the carrier gas, an injection device, a column, a detector (which in this instrument is the mass spectrometer), and a thermal control system. A liquid sample is introduced through the injection device and usually vaporized just before the column. It is

- the injection device which may be one of various types;
- the column, which may be either packed or capillary (open tubular). Capillary columns are often connected directly to the mass spectrometer. Packed columns are connected either directly or through an enrichment device that selectively eliminates a large portion of the carrier gas; and
- the temperature control device for an oven that encloses the column.

Note: More details on the description and the metrological and technical requirements of the gas chromatograph part of the system are given in OIML R 82 *Gas chromatographic systems for measuring pollution from pesticides and other toxic substances*.

4.3 The gas chromatograph and mass spectrometer interface may consist of a separator or be directly coupled.

4.3.1 A separator located at the interface preferentially removes the carrier gas eluting from the gas chromatograph and permits a flow of enriched sample gas to enter the mass spectrometer. A jet separator fractionates on the principle that gases of different molecular weights diffuse at different rates in an expanding supersonic jet stream.

4.3.2 Direct coupling without a separator is used when the vacuum-pumping system of the mass spectrometer can effectively handle the total carrier gas flow of either packed columns or capillary columns.

4.4 Mass spectrometer (MS)

4.4.1 The gaseous compounds of interest in the sample are eluted from the gas chromatographic column and are ionized as they enter the mass spectrometer either by:

- electron ionization (EI), the most common form of ionization, in which a beam of electrons intersects the sample compounds; or
- chemical ionization (CI) that produces ions of the sample compounds through interaction with an ionized reagent gas in which the transfer of an electron, proton, or other charged species may be involved with or between the reactants.

Note: “Chemical ionization” means that positive ions result in the process. If negative ions are formed, the process is called “negative chemical ionization” (NCI).

4.4.2 The fragment ions formed by ionization are separated according to their mass-to-charge ratio usually using a quadrupole or a magnetic-sector type mass spectrometer. They are usually detected with either multistage or continuous dynode electron multipliers that provide an amplified signal for each specific ion detected.

4.5 Data handling system (DS)

4.5.1 The data handling system records the resulting mass spectrum as a set of mass ions and intensities that can be plotted as the relative ion intensity versus the mass-to-charge ratio (m/z) for a typical mass spectral display. The compounds of interest in the sample are identified through comparison of the recorded spectrum with historical data spectra maintained in the data handling system.

4.5.2 The DS consists of the following major components:

- (a) a computer with adequate data storage capability,
- (b) a video monitor, and
- (c) a printer for the output data.

4.5.3 The DS collects data and controls the GC/MS system. It processes the data collected by relating that data to the stored, reference mass spectra, and then presents and stores the analyzed data as appropriate in bar graphs and tables of relative ion intensity versus mass-to-charge ratio stored in its storage device, for example.

5 Metrological requirements

5.1 During type evaluation and initial and subsequent verification, the repeatability, detection limit, and working range of the output signal of the instrument shall be tested in a laboratory using reference standard solutions under reference conditions as follows:

- ambient temperature between 20 °C and 27 °C and stable to within ± 3 °C during the measurement; and
- relative humidity (RH) between 30 % and 80 %.

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

- injector;
- carrier gas;
- reference sample(s);
- column and column oven;
- ion source; and
- scan time.

5.3 The fragmentation pattern by electron impact ionization from the spectra obtained from reference compounds shall be checked to evaluate the historical databases of compounds maintained as references in the GC/MS system. These reference databases may be commercially available databases, such as the NIST or Wiley MS libraries. The average spectrum calculated from all the spectra measured across a GC peak may be used for this test, or a baseline subtracted against spectra from the apex of the peak can be used for searching these databases.

5.3.1 A test of spectrum of the fragmentation pattern using decafluorotriphenylphosphine (DFTPP) shall be carried out. The results shall be consistent with the pattern indicated in Table 1.

Table 1 Ion abundance criteria for decafluorotriphenylphosphine

Mass	Ion abundance criteria
51	10 % - 80 % of the base peak
68	less than 2 % of mass 69
70	less than 2 % of mass 69
127	10 % - 80 % of the base peak
197	less than 2 % of mass 198
198	base peak or > 50 % of 442
199	5 % - 9 % of mass 198
275	10 % - 60 % of the base peak
365	> 1 % of the base peak
441	present but less than mass 443
442	base peak or > 50 % of 198
443	15 % - 24 % of mass 442

5.3.2 If the GC column used in the test does not elute DFTPP, then p-bromofluorobenzene shall be used to check the spectrum of the fragmentation pattern with the results being consistent with the pattern indicated in Table 2.

5.4 The resolution of the GC/MS system shall be checked. The resolution, $m/\Delta m$, of the base peak of either decafluorotriphenylphosphine or p-bromofluorobenzene shall be determined by the methods in 3.10, and the minimum resolution shall be unit resolution. This provides the ability to separate two adjacent mass peaks over the mass range.

5.5 The repeatability of the GC/MS system shall be checked. The reference solution for the test shall be composed of at least seven or more compounds including a chlorinated hydrocarbon that may decompose on a hot metal surface and a polycyclic aromatic hydrocarbon with a molecular weight greater than 200. Table 3 provides a recommended list of test compounds. The relative standard deviation of each characteristic peak of each compound in the reference sample mixture shall be within $\pm 10\%$.

5.6 The detection limit of the GC/MS system shall be determined for a reference solution containing methyl stearate. Its value shall be within 10 % of the value specified by the manufacturer.

5.7 The working range shall be determined by fitting a linear least squares analysis to data obtained for at least five different concentrations of a reference solution containing methyl stearate within the working range specified by the manufacturer. The concentrations selected shall include values approximately equal to 10 times the detection limit and the upper limit of the working range as specified by the manufacturer. At each concentration, 5 replicate measurements shall be performed, and mean value and standard deviation shall be calculated. The linear curve shall be fitted to the mean values calculated for at least three different concentrations. The correlation coefficient, r , of the fitted curve shall be determined, and r^2 shall be greater than 0.95.

Table 2 Ion abundance criteria for p-bromofluorobenzene

Mass	Ion abundance criteria
50	15 % - 40 % of mass 95
75	30 % - 80 % of mass 95
95	base peak, 100 % relative abundance
96	5 % - 9 % of mass 95
173	< 2 % of mass 174
174	greater than 50 % of mass 95
175	5 % - 9 % of mass 174
176	greater than 95 % but < 101 % of mass 174
177	5 % - 9 % of mass 176

Table 3 Compounds suitable for making a reference solution for testing the repeatability of the GC/MS system

Compound	Integration mass	Peak type*
1,3 dichlorobenzene	146	N
naphthalene	128	N
1,2,4 – trichlorobenzene	180	N
n-octadecane	254	N
dimethyl phthalate	163	N
di-n-butyl phthalate	149	N
n-nitrosodiphenylamine	169	N
hexachlorobenzene	284	N
pyrene	202	N
chrysene	228	B
benzopyrene	252	B

- * B indicates peaks with widths at half height of more than 45 seconds;
N indicates peaks for packed columns with widths at half height of less than 45 seconds.

6 Technical requirements

6.1 The manufacturer shall specify the carrier gas used. A means in the supply lines may be provided to remove contaminants of the carrier gas.

Note: Helium is most commonly used as the carrier gas.

6.2 The manufacturer shall specify the injector types that can be used for performance tests and routine analysis.

6.3 The GC oven shall accommodate packed or capillary columns and shall be temperature controlled with temperature control programming during analysis being available.

6.4 The interface between the GC and MS shall be constructed of inert material and shall be temperature controlled.

6.5 An electron impact (EI) ionization source with energies between 60 eV and 80 eV shall be available. A chemical ionization source may be useful for the analysis of some compounds.

6.6 For EI, the detector shall be capable of detecting positive ions. For CI, the detector shall be capable of detecting both positive and negative ions.

6.7 The data handling system shall be capable of storing at least 6 000 complete GC/MS runs.

6.7.1 The data handling system shall be capable of collecting and storing data as follows:

- automated scanning of specific ions of a sample compound of interest;
- scanning the mass spectrum from m/z of 40 to 500 in 0.5 seconds; and
- detecting up to 460 mass peaks per spectrum.

6.7.2 The data handling system shall be capable of displaying and data analysis as follows:

- present mass spectra as a list or as a plot of mass versus abundance;
- integrate the area under a peak to obtain the intensity of a specified mass fragment or the sum of all mass fragments;
- calculate the average mass spectrum from all the spectra measured across a GC peak;
- subtract one or more mass spectra from another for background corrections;
- identify the mass spectra data files obtained according to the time of analysis (year, month, day, hour, and minute); and
- identify any post-acquisition manipulation of the mass spectral data obtained, such as averaging techniques, single ion monitoring, and background subtraction techniques.

6.8 Markings shall be attached conspicuously to all major components of an GC/MS system as follows:

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

7 Practical instructions

7.1 A GC/MS system requires the use of high voltages and high temperatures during normal operation. Instrument installation and operation, particularly with respect to temperature control devices and compressed gases, shall take these requirements into account. Warning labels shall be placed conspicuously on the instrument to alert users of these potential hazards. Such labels shall be consistent with national safety regulations.

7.2 Before installation of a GC/MS system, all laboratory environmental factors shall be considered. Manufacturers shall provide specifications for power consumption that include allowable variations from the rated mains voltage and frequency. Information shall also be provided for rated heat dissipation, operating conditions for ambient temperature and humidity, and any necessary gas venting.

8 Metrological control

8.1 Type evaluation

8.1.1 The manufacturer shall provide the national responsible body with the identified GC/MS system and its operating manual. The operating manual may be electronic, but must contain a defined version identifier. The manufacturer may also provide data and other information that support a determination of whether the system meets the requirements of this Recommendation.

8.1.2 The national responsible body shall review the operating manual for completeness and clarity of instructions. The system shall be visually inspected in conjunction with a review of the manufacturer's specifications to determine whether the requirements of clause 6 are met.

8.1.3 The national responsible body shall carry out tests, or may accept the manufacturer's test data, to check for conformity of the system with the following requirements:

- fragmentation pattern (5.3 and A.3.6);
- resolution (5.4 and A.4);
- repeatability (5.5 and A.5.8);
- detection limit (5.6 and A.6.5); and
- working range (5.7 and A.6.4).

8.1.4 The report of tests on the system carried out during type evaluation and 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 specified in Annex B. A specific form may be developed according to national preference. The manufacturer shall be provided with specific information, including comments on any failures.

8.2 Initial and subsequent verification

8.2.1 For initial verification, the documentation provided by the manufacturer shall be examined for compliance with 8.1.1 and 8.1.2.

8.2.2 Any of the tests specified for the GC/MS system under 8.1.3 that are considered critical to the specific application shall be performed.

8.2.3 The national responsible body shall specify the period of validity of the verification.

8.2.4 An instrument shall undergo subsequent verification equivalent to initial verification after repair or replacement of major component parts of the GC/MS system, including the data handling system or after the period of time specified by the national responsible body.

8.3 Routine tests by a user

8.3.1 The national responsible body shall identify methods for using a GC/MS system to measure specific water pollutants. Some measurement methods may be appropriate for use in assessing the performance of a system.

8.3.2 The operator of a GC/MS system shall carry out a test with a reference standard solution before and after a series of measurements in the laboratory. The results of these tests shall be within the limits established by the national responsible body.

8.3.3 In addition to the requirements of 8.3.2, an operator shall carry out a performance test of the entire GC/MS system related to and before a specific application.

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

- results of all routine tests;
- results of calibrations;
- identification of any major components replaced; and
- details of maintenance and repair.

References

- [1] Budde, William L. and Eichelberger, James W., Organic analysis using gas chromatography/mass spectrometry: a technique and procedures manual, Ann Arbor Science Publishers (1979). ISBN: 0250403188
- [2] Laskens, H.F. and Jackson, J.F., Editors, Gas chromatography/mass spectrometry, Berlin; New York, Springer-Verlag (1986). ISBN: 3540159118
- [3] Message, Gordon M., Practical aspects of gas chromatography/mass spectrometry, New York, Wiley (1984). ISBN: 0471062774
- [4] McFadden, William H., Techniques of combined gas chromatography/mass spectrometry: applications in organic analysis, New York, Wiley (1973). ISBN: 047158338X
- [5] Budde, William L., Analytical Mass Spectrometry: Strategies for Environmental and Related Applications, New York, Oxford University Press (2001). ISBN: 084123664X
- [6] Kitson, Fulton G., Larsen, Barbara S., and McEwen, Charles N., Gas Chromatography and Mass Spectrometry: A Practical Guide, San Diego, CA, Academic Press (1996). ISBN: 0124833853

Annex A

Test procedure

(Mandatory)

A.1 This Annex provides a test procedure for determining whether a gas chromatograph/mass spectrometer system meets the performance requirements under the conditions specified in clause 5 of this Recommendation.

A.2 Carry out all tests under the reference conditions specified in 5.1 and with the components and controls as recommended by the manufacturer for the reference test compound specified.

A.3 Test of the fragmentation pattern

A.3.1 Inject the instrument with 30 ng of decafluorotriphenylphosphine (DFTPP) from a known reference sample. The injector used shall be as specified by the manufacturer.

A.3.2 Scan the ion beam from $m/z = 40$ u to 500 u at a rate of one scan per second.

A.3.3 The spectra obtained shall meet the criteria for key ions as shown in Table 1.

Note: The average spectrum calculated from all the spectra measured across the GC peak may be used for this test.

A.3.4 Use p-bromofluorobenzene to verify the test compound fragmentation pattern if DFTPP cannot be eluted from the gas chromatographic column.

A.3.5 Repeat steps A.3.1 and A.3.2 for p-bromofluorobenzene.

A.3.6 The spectra of ion abundance obtained shall meet the criteria for key ions as shown in Table 2.

Note: The average spectrum calculated from all the spectra measured across the GC peak may be used for this test.

A.4 Resolution

The resolution, $m/\Delta m$, of the base peak of either DFTPP or p-bromofluorobenzene shall be determined and the minimum resolution shall be unit resolution.

A.5 Repeatability

A.5.1 This test shall establish the repeatability of the entire GC/MS system for continuous, repetitive measurements of ion spectra of a test compound. It combines each important measurement component from filling the injection device to the integration of a specific ion peak necessary for quantifying the amount of a specific test compound in a sample.

A.5.2 Select a group of seven or more compounds to make up the test (reference) sample. Table 3 provides a recommended list of test compounds. The concentration of each compound in the reference solution should be 20 µg/mL. The reference solution shall include a chlorinated hydrocarbon that may decompose on a hot metal surface and a polycyclic aromatic hydrocarbon with a molecular weight greater than 200.

A.5.3 Select an appropriate injection device and column and set the operating parameters of the gas chromatograph according to the specifications of the manufacturer.

A.5.4 Set the following data acquisition variables:

- a mass range of $m/z = 35$ u to 350 u;
- a scan time of approximately 2 to 6 seconds with packed columns and from 0.5 to 2 seconds with capillary columns;
- an electron ionization source energy of 70 eV; and
- the electron multiplier detector voltage not to exceed that recommended by the manufacturer according to its condition and age.

A.5.5 Inject 1-5 μL of the test sample in A.5.2 and acquire data until all compounds have eluted from the column. Repeat and record data for a minimum of 10 injections.

A.5.6 Plot the total ion current profile and calculate the peak areas at the specified mass for quantification either in arbitrary units or as ratios of peak areas for all compounds.

A.5.7 Calculate the relative standard deviation, s_r , of the peak area, A , characteristic of each compound of the test sample using the following equation:

$$s_r = \frac{s}{A} \cdot 100$$

where

$$s = \left[\frac{\sum (A_i - \bar{A})^2}{n - 1} \right]^{1/2}$$

n = number of measurements for each compound in the test sample;

A_i = each individual result of determining the peak area representing the characteristic ion mass; and

\bar{A} = the average result for n number of repeated measurements.

A.5.8 For the performance of the instrument to be acceptable, the relative standard deviation of the repeatability of each characteristic peak in each spectrum of the reference sample mixture shall be within $\pm 10\%$.

A.6 Detection limit and working range

A.6.1 Make at least seven repeated injections of a blank sample (dry air or nitrogen for gas and solvent used in the test sample). Record the peak areas, and determine the short-term noise level, N_s , as the average value of the results.

A.6.2 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 or peak height of the detector response.

A.6.3 From the results of A.6.2, calculate the average value of the peak area versus the amount injected, in grams. Plot the results and fit a linear least-squares regression to the mean value determined for each concentration. Determine from the regression the slope, m , intercept, b , and correlation coefficient, r , the parameters from the general linear equation model:

$$y = mx + b$$

A.6.4 Calculate the square of the correlation coefficient for the least-squares regression curve using the slope(s) of the curve and the standard deviation of the known concentration values, s_x , and the standard deviation of the measured concentration values, s_y , using the following equations:

$$r^2 = \frac{S_{xy}^2}{s_x s_y}$$

where:

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

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

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

The results shall meet the requirements of 5.7 for the correlation coefficient.

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 $r^2 = 1$.

A.6.5 Record the sensitivity of the instrument, S , as the slope of the curve obtained in A.6.3 and from the short-term noise level determined in A.6.1 calculate the instrument detection limit:

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

Annex B

Test report format

(Mandatory)

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 83, Edition 2006.

B.1 Name and address of the testing laboratory or laboratories

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

B.3 Name and address of the manufacturer

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

B.5 Identification of the instrument (type) tested

Trade name: _____

Model number: _____

Serial number: _____

Requirements for:
voltage _____ frequency _____ current _____

B.6 Review of the operating manual

Acceptable Deficient

Comments: _____

B.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

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

Yes No

Comments: _____

B.7.2 Temperature controls

Injection device: Yes No

Column: Yes No

Detector: Yes No

Comments: _____

B.7.3 Temperature programming

Yes No

Comments: _____

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

Yes No

Comments: _____

B.7.5 Components of the data system

Comments: _____

B.7.6 Markings

Pass Fail

Comments: _____

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

B.8.1 Conditions for testing (complete information for each test)

Ambient temperature: _____

Relative humidity: _____

Carrier gas:

type: _____

purity: _____

flow rate: _____

Injection device type: _____

Column type: _____

Temperature:

injection device: _____

column: _____

Programming of the column: _____

Interface: _____

Scan speed: _____

Mass range: _____

Data display or readout: _____

Comments: _____

B.8.2 Test of the fragmentation pattern

Test compound: _____

Concentration: _____

Mass	Ion abundance

B.8.3 Repeatability of peak area or peak height

Test compounds and concentration

#1: _____

#2: _____

#3: _____

#4: _____

#5: _____

#6: _____

#7: _____

Repetition	#1	#2	#3	#4	#5	#6	#7
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
\bar{A}							
Φ							

#1: Pass Fail#2: Pass Fail#3: Pass Fail#4: Pass Fail#5: Pass Fail#6: Pass Fail#7: Pass Fail

Comments: _____

B.8.4 Detection limit and working range

Test compound: _____

Measured concentration →	1	2	3
Repetition ↓			
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
\bar{X}			
Φ			
r^2			

Working range: _____

Detection limit: _____

Pass Fail

Comments: _____

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

B.10 Person(s) responsible for the testing

Signature(s) and title(s): _____

Date: _____