INTERNATIONAL

RECOMMENDATION

OIML R 83

Edition 1990 (E)

Gas chromatograph/ mass spectrometer/data system for analysis of organics polluants in water

Chromatographe en phase gazeuse équipé d'un spectromètre de masse et d'un système de traitement de données pour l'analyse des polluants organiques dans l'eau

OIML R 83 Edition 1989 (E)

ORGANISATION INTERNATIONALE
DE MÉTROLOGIE LÉGALE

INTERNATIONAL ORGANIZATION
OF LEGAL METROLOGY

Foreword

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GAS CHROMATOGRAPH/
MASS SPECTROMETER/DATA SYSTEM
for ANALYSIS of ORGANIC
POLLUTANTS in WATER

1. Scope

1.1. This Recommendation provides requirements, procedures and tests for verifying the performance of a gas chromatograph/mass spectrometer/data system (GC/MS/ DS) when used for measurements of water pollutants in carrying out pollution control programs and in assessing the quality of water as mandated by national laws and regulations. It does not intend to exclude any other equivalent means of measurement or analysis of such substances; however, other instruments that operate on similar technical principles as the gas chromatograph/mass spectrometer systems described, such as the ion trap detector, are not covered by this Recommendation. 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. Only low resolution mass spectrometers are considered in this Recommendation. Such instruments coupled with appropriate gas chromatographs can be used successfully to analyse a variety of water samples, such as ground waters, surface waters, aqueous municipal and industrial effluents, and saline waters. Each sample may require a different preparation prior to analysis by a GC/MS/DS; however, although important to an overall analysis, considerations of sampling, sample preparation and measurement methods are beyond the scope of this Recommendation. Examples of relevant measurement methods are referenced in Annex A.1.

1.2. Sample compounds, present in detectable amounts, may be analysed by a GC/MS/ DS if they can pass through a gas chromatograph column and are not significantly affected by thermal or catalytic decomposition or adsorption. Some difficult compounds, which are non-volatile or thermally unstable, can be converted to derivative compounds that are then able to undergo gas chromatograph separation and detection by mass spectrometer. A list of general compound types that may be analyzed by a GC/MS/DS is given in Annex A.2.

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

2. Application

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

2.1. for a broad spectrum organic analysis having the goal to determine known or unsuspected major or minor components of a sample,

2.2. for routine monitoring of a relatively large number (e.g. greater than 20) of sample components. This monitoring also minimizes interference effects of sample components, experienced in other conventional methods, by producing a unique spectral pattern for most compounds,

2.3. for real time selected ion monitoring (SIM), which is widely recognized as being a very sensitive, accurate, precise, and selective tool in environmental analysis.

3. Terminology

3.1. Carrier gas

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

3.2. Mobile phase

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

3.3. Stationary phase

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

3.4. Elution

The removal of a sample component from the stationary phase by the mobile phase in the gas chromatograph column.

3.5. Column

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

3.6. Solid support

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

3.7. Injection device

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

3.8. Detector

A device that can respond to eluted sample components in the carrier gas emerging from the gas chromatographic column. It is the mass spectrometer in a gas chromatograph/mass spectrometer system.

3.9. Mass spectrum

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

3.10. Detection limit of a gas chromatograph/mass spectrometer system

The minimum amount of a specific compound which, when injected into the gas chromatograph can produce a signal-to-noise ratio of at least 10 for a characteristic molecular ion of that compound subject to the following conditions: in the full scan mode, a scan time (for example, one second) over the appropriate mass range shall be specified; in the selected ion monitoring (SIM) mode, the principal ion characterizing the compound shall be measured. The mode of ionization (electron impact or chemical ionization) shall be considered.

Notes: 1) Methyl stearate is often used as the test compound.

2) The term "sensitivity" is frequently used to have the same meaning as this term within the community of mass spectrometer manufacturers and users.

3.11. Dynamic range of the gas chromatograph/mass spectrometer system

The ratio of the maximum amount of sample (below the saturation level of the mass spectrometer) that can be introduced into the gas chromatograph/mass spectrometer and measured, to the minimum detectable amount. It depends on the gas chromatograph column type (packed or open tubular) used and the mass spectrometer mode of operation (selected ion monitoring or scanning).

3.12. Resolution of a mass spectrometer

The ratio: $R = \frac{m}{\Delta m}$

interpreted by either one of the following definitions:

— m is the mass of a component comprising the first peak of a doublet, and Δm is the difference in 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 *is* the mass of a component within a peak and Δm is the width of the peak at one-half its height.

Note: Unit resolution usually means $R = 2\ |m|$, where $|m|$ is the numerical value when m is expressed in unified atomic mass units.

3.13. Symbols for quantities used in this Recommendation are as follows:

m = mass of an ion in unified atomic mass units, u (or amu in some references)

z = ratio of the charge of an ion to the elementary charge.

Note: For further discussion of terminology and relationship for gas chromatography and mass spectrometry, see [1, 2, 3, 4].

4. Description of the instrument

4.1. The gas chromatograph (GC)

4.1.1. The gas chromatograph is used to separate volatile organic and inorganic mixtures. Its basic components are considered to be 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 sample is introduced through the injection device and usually vaporized just before the column. It is carried through the column by an inert carrier gas flowing at a controlled rate. The eluate from the gas chromatographic column enters the mass spectrometer directly or through an enrichment device or separator.

4.1.2. A gas chromatographic analysis is based on the sample components being partitioned between the gas (mobile phase) and a liquid or solid adsorbent (stationary phase). The liquid or solid adsorbent is held immobile in the column on a solid support or is coated on the walls of the column.

Partition of the sample components depends on column operating parameters including carrier gas flow rate, temperature, vapor pressure, and on properties of the liquid or solid adsorbent.

4.1.3. The important components of the gas chromatographic part of the system are as follows:

4.1.3.1. a carrier gas that is sufficiently pure and inert with respect to the stationary phase; helium is commonly used,

4.1.3.2. an injection device that may be one of the following types: packed column, splitless capillary column, split capillary column, direct capillary column, direct capillary on-column, purge-and-trap, static-head-space, and sample enrichment injection devices,

4.1.3.3. a column that may be either packed or capillary (open tubular). Capillary columns are often connected directly to the mass spectrometer while packed columns are connected either directly or through an enrichment device that selectively eliminates a large portion of the carrier gas.

Note: For a more detailed description and more details on the metrological as well as technical requirements of the gas chromatograph part of the system, see the OIML International Recommendation R 82 "Gas chromatographs for measuring pollution from pesticides and other toxic substances". Also see references [4] through [9].

4.2. The gas chromatograph/mass spectrometer interface

4.2.1. The interface between the gas chromatograph and mass spectrometer is a separator that preferentially removes the gas chromatograph carrier gas and permits a flow of enriched sample gas to enter the mass spectrometer.

4.2.2. A jet separator is commonly used. It fractionates on the principle that gases of different molecular weights diffuse at different rates in an expanding supersonic jet stream.

4.2.3. Direct coupling without a separator is used when the vacuum-pumping system of the mass spectrometer can cope with the total carrier gas flow of packed columns. Capillary columns are usually connected directly to the mass spectrometer.

4.3. The mass spectrometer (MS)

4.3.1. A mass spectrometer is an instrument that ionizes the gaseous eluate from a gas chromatograph column and separates fragment ions formed according to their mass-to-charge ratio.

The charged species are usually detected with an electron multiplier which provides an amplified signal for each specific ion detected. The result is a set of mass ions and intensities that is recorded by the data system. A plot of relative ion intensity vs. the mass-to-charge ratio *(m/z)* gives a typical mass spectral display (see Figure 1).

4.3.2. The ionization techniques most often used are the following:

4.3.2.1. in electron impact ionization (EI), the most common form of ionization, a beam of electrons intersects the molecular sample stream. The internal energy transferred in this process is dissipated through a series of fragmentations in which molecular bonds are broken and charged species (i.e. ions) are generated,

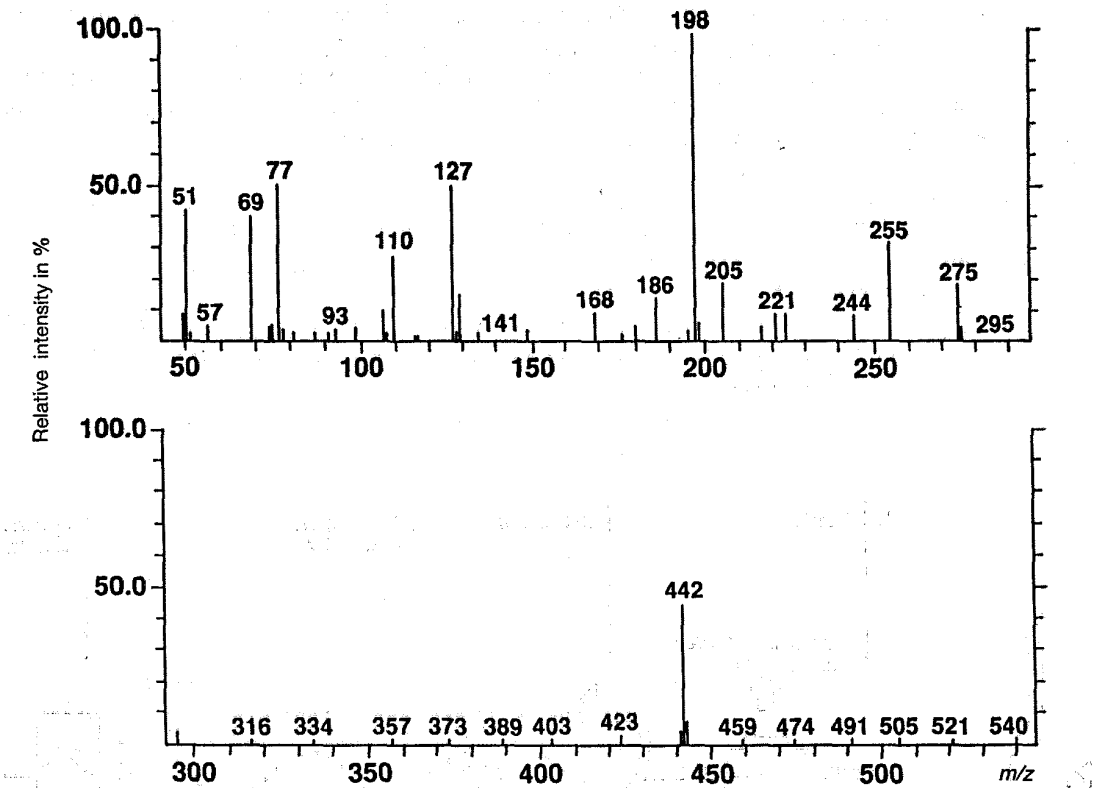

Figure 1. Mass spectrum of decafluorotriphenylphosphine
(In addition such charts should include data that identify
the analysis and its date: see point 6.9.2.4)

4.3.2.2. in chemical ionization (CI), new ionized species are formed when the sample molecules interact with ionized reagent gas. This process may involve the transfer of an electron, proton, or other charged species to or between the reactants. "Chemical ionization" means that positive ions result in the process. If negative ions are formed, the process is called "negative chemical ionization".

Note: An ionization source will generally initiate processes that can be represented as follows:

(a) $M + e \rightarrow M.^{+} + 2e$
(b) $M + e \rightarrow M.^{-}$

where M represents a molecular component and e an electron.

The charged molecular ions then disintegrate into both charged and neutral fragments as in the following example:

(c) $M.^{+} \rightarrow F.^{+} + N$

4.3.3. Separation of ionized fragments can be accomplished by a variety of electronic and magnetic devices. The quadrupole and magnetic sector types are the most commonly used mass separation devices for the analysis of pollutants. Other type are used for special purposes.

4.3.3.1. The quadrupole mass spectrometer: the operation of this type is illustrated in Figure 2, which shows the following steps in analysis:

— the gas chromatograph vaporizes a sample and performs separation of the mixture,

— the gas chromatograph/mass spectrometer interface transfers the gas chromatograph eluate to the mass spectrometer by either a capillary column connected directly or a packed column connected directly or through a jet separator,

— an ion source converts a portion of the molecules to parent and fragment positive and negative ions,

— a quadrupole mass filter separates the ions according to their mass-to-charge ratios by using a radio frequency and direct current voltages,

— an electron multiplier converts the ion current into an electric current, which is amplified for measurement, and

— an output device or data system (DS) plots, or records, ion intensity vs. mass-to-charge ratio (*m/z*). This information is used by the analyst for compound identification [10].

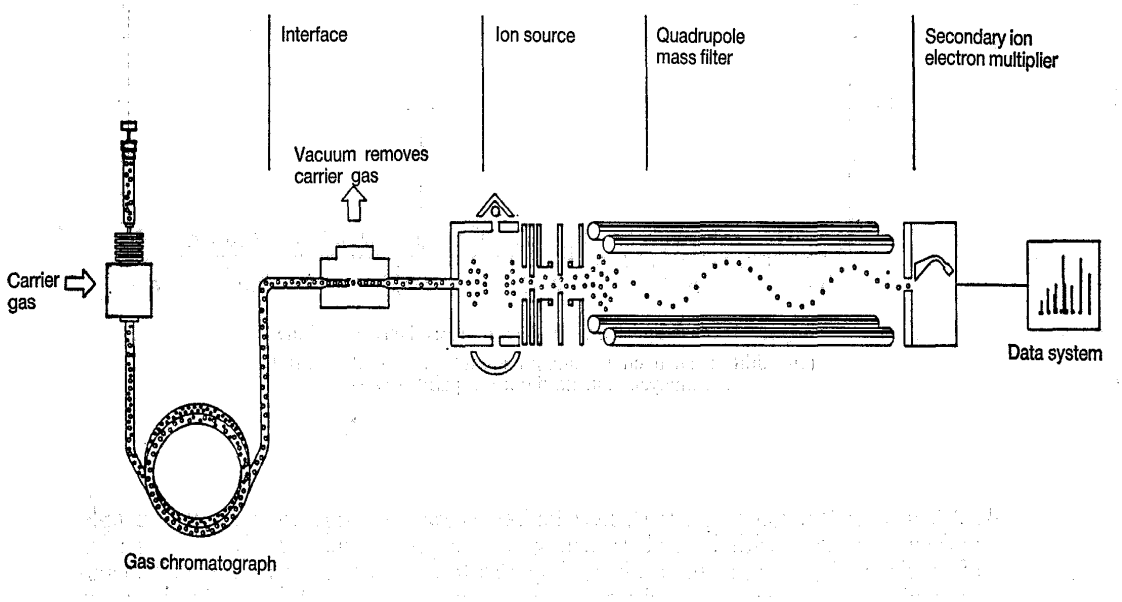

Figure 2. Diagram of a GC/MS/DS comprising a quadrupole mass spectrometer

4.3.3.2. The magnetic sector mass spectrometer: the type illustrated in Figure 3 is double focusing with reversed geometry, i.e. the magnet precedes the electrostatic sector; however, other types are successfully employed, such as Nier-Johnson. The following analytical steps are also illustrated in Figure 3:

— the gas chromatograph vaporizes a sample and separates it into components (note that packed columns often require a separator between the gas chromatograph and the ion source),

— an ion source converts molecules into parent and fragment positive and negative ions,

— an ion slit defines a point source of ions,

— the magnetic field separates the ions of equal velocity according to their mass-to-charge ratio (i.e, ions with different mass-to-charge ratios have paths of different radii of curvature),

— an intermediate slit collimates the ion beam further for energy focusing and detection,

— an electric field focuses the ion beam according to the kinetic energy of component ions,
— a collector slit further resolves ions at each selected mass,
— an electron multiplier converts ion current into an electric current which is amplified for measurement,
— an output device or data system (DS) plots, or records, ion intensity vs. mass-to-charge ratio. This information is then used by the analyst, for compound identification [10].

Note: For a more detailed discussion of the mass spectrometer, see references [4] and [11].

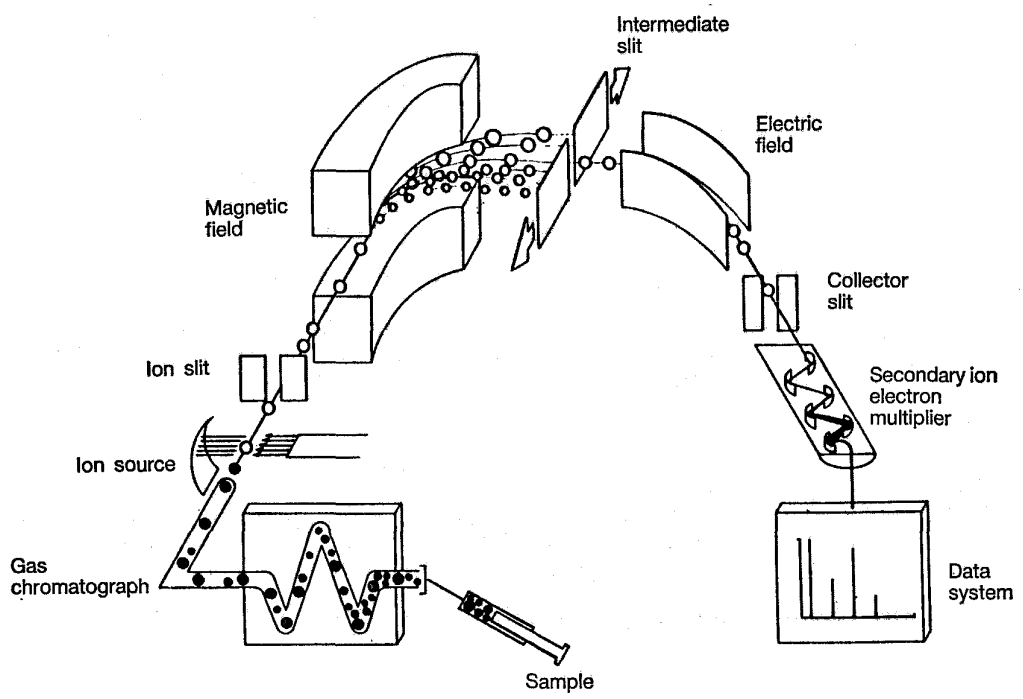

Figure 3. Diagram of a GC/MS/DS comprising a magnetic sector mass spectrometer

4.3.4. The ion detector types most commonly used are multistage and continuous dynode electron multipliers.

4.4. The computer data system (DS)

4.4.1. The DS consists of the following major components: (a) a central processing unit (CPU), (b) a large capacity storage device (hard disk), (c) a video terminal, and (d) a printing device to produce copies of output data.

4.4.2. The DS processes the data relating to the mass spectra stored in its storage device. It is also equipped with analog-to-digital and digital-to-analog interfaces to collect data from and control the gas chrornatograph/mass spectrometer.

4.4.3. The DS can be used in data reduction; that is, in the process of transforming the initial digital representation of a mass spectrometer output into a form that can be interpreted. Examples of such data forms are bar graphs and tables of relative ion intensity vs. mass-to-charge ratio.

5. Metrological requirements

5.1. Temperature control of the gas chromatograph column oven and injection zone

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

5.1.2. Temperature gradients in the column oven measured close to the column shall be within ± 1 °C or ± 1 % of the isothermal temperature selected whichever is greater.

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

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

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

5.2. Gas chromatograph carrier gas

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

5.2.2. The minimum purity of any carrier gas should be 99.995 %.

5.3. Interface temperature control

At the gas chromatograph/mass spectrometer interface, the temperature shall be controlled up to 350 °C.

5.4. The mass spectrometer

5.4.1. The mass range (*m*/z) covered should be at least from 10 to 600 u. If polybrominated biphenyls or other high molecular weight compounds are to be analyzed, the mass range should be increased to at least 1 000 u.

5.4.2. The accuracy of mass values (*m/z*) shall be within ± 0.1 unit over the mass range scanned within an eight hour period.

5.4.3. The minimum resolution shall be unit resolution (see point 3.12). This provides the ability to separate two adjacent mass peaks over the mass range.

5.4.4. The scan speed shall be sufficient to scan from *m/z* = 25 to 500 u within 0.5 seconds. It should be capable of being done without change in mass spectrometer resolution and mass accuracy over the entire range scanned.

5.5. Detection limit and dynamic range

The detection limit and dynamic range shall be specified in accordance with points 3.10 and 3.11 respectively.

5.6. Data system

The data system shall be capable of producing an accurate and referable record of the mass spectra with a resolution and acquisition rate on a continuous basis at least equivalent to the requirements in points 5.4.3 and 5.4.4.

6. Technical requirements

6.1. Carrier gases

6.1.1. A carrier gas appropriate for the method of analysis shall be used. Helium is commonly used.

6.1.2. Traces of unwanted contaminants in the carrier gas shall be removed by means of molecular sieve scrubbers, filters, and filter-dryers. These devices should be inserted in the supply lines as close to the gas chromatographic column as practical.

6.2. Gas chromatograph injection devices

6.2.1. Both packed column and splitless Capillary injection devices should be available.

6.2.2. The packed column injection shall permit injection of the sample onto the column. The splitless injector shall allow for the use of wall-coated-open-tubular (WCOT) glass or fused silica capillary columns.

Note: A capillary on-column injection device may also be useful in some cases.

6.3. Gas chromatograph columns

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

6.3.2. Columns should be those fabricated from non-reacting metal, glass, or fused silica.

6.3.3. Either a liquid or solid stationary phase that provides the desired sample component separation shall be used.

6.4. Temperature control systems

6.4.1. The temperature control of the gas chromatographic column shall be such as to provide fast temperature change at various temperature programming.

Note: The values and programming range of temperatures are determined by the sample and method of analysis.

6.4.2. The mass spectrometer should have its own temperature control system in order to minimize the noise and drift of its output signal.

6.5. Interface material

Gas chromatograph/mass spectrometer interfaces shall be constructed of inert material (for example, glass or fused silica).

6.6. Ionization source

6.6.1. A mode of ionization shall be used such that the spectral pattern of ion species formed are interpretable by using reference data compilations [12, 13, 14].

6.6.2. An electron impact ionization source shall be available, that is capable of producing an electron beam with energies between 60 and 80 eV.

Note: The normal energy of operation is 70 eV.

6.6.3. A chemical ionization source may be useful for the analysis of some compounds. If available, it should use volatile hydrocarbons (such as methane or isobutane) or ammonia as reactant gases.

6.7. Scanning facilities

Automated scanning of ions by the mass spectrometer shall be available under DS control. Selected ion monitoring (SIM) shall also be available.

Note: SIM is the mode of operation in which specific ions are selected to pass through the mass spectrometer. The ion (or ions) is (are) selected to identify a specific target component of interest that may be in a sample at a very low concentration level. The detection limit of the mass spectrometer may be significantly lower using this technique.

6.8. Detection of negative ions

Detection of negative ions is useful in association with chemical ionization.

6.9. Data system (DS)

6.9.1. A large capacity storage device (hard disk) shall be available in the DS for storing at least 6 000 complete mass spectra in order to be able to scan the mass spectrometer from *m/z* of 40 to 500 in 0.5 seconds and to detect up to 460 mass peaks per spectrum.

Note: If the mass range of the GC/MS/DS is exceeded by any mass fragment in the spectrum of a compound, the DS may be capable of identifying the compound by using other fragment ions which are within the mass range of the instrument.

6.9.2. Data display software programs should include the following:

6.9.2.1. presentation of mass spectra in a list and as bar charts (see Figure 1),

6.9.2.2. ability to integrate the area under a plot of the intensity of a single mass fragment or the sum of all mass fragments (see Figure 4),

6.9.2.3. ability to subtract one or more mass spectra from another in order to eliminate contribution of background mass fragments to the sample spectrum,

6.9.2.4. ability to identify all mass spectral data files stored on the large capacity storage device by the year, month, day, hour, and minute of the analysis, along with a description of the sample (see Figure 1),

6.9.2.5. ability to identify any post-acquisition manipulation of mass spectral data (e.g., background subtraction). The display or hardcopy of the data shall contain a description of the type of processing performed, and the original data shall not be altered.

Note: The GC/MS/DS may comprise other features such as:

— the ability of generating small (about 50 spectra) libraries of mass spectra,
— the ability to use small libraries with a reverse library search algorithm [12],

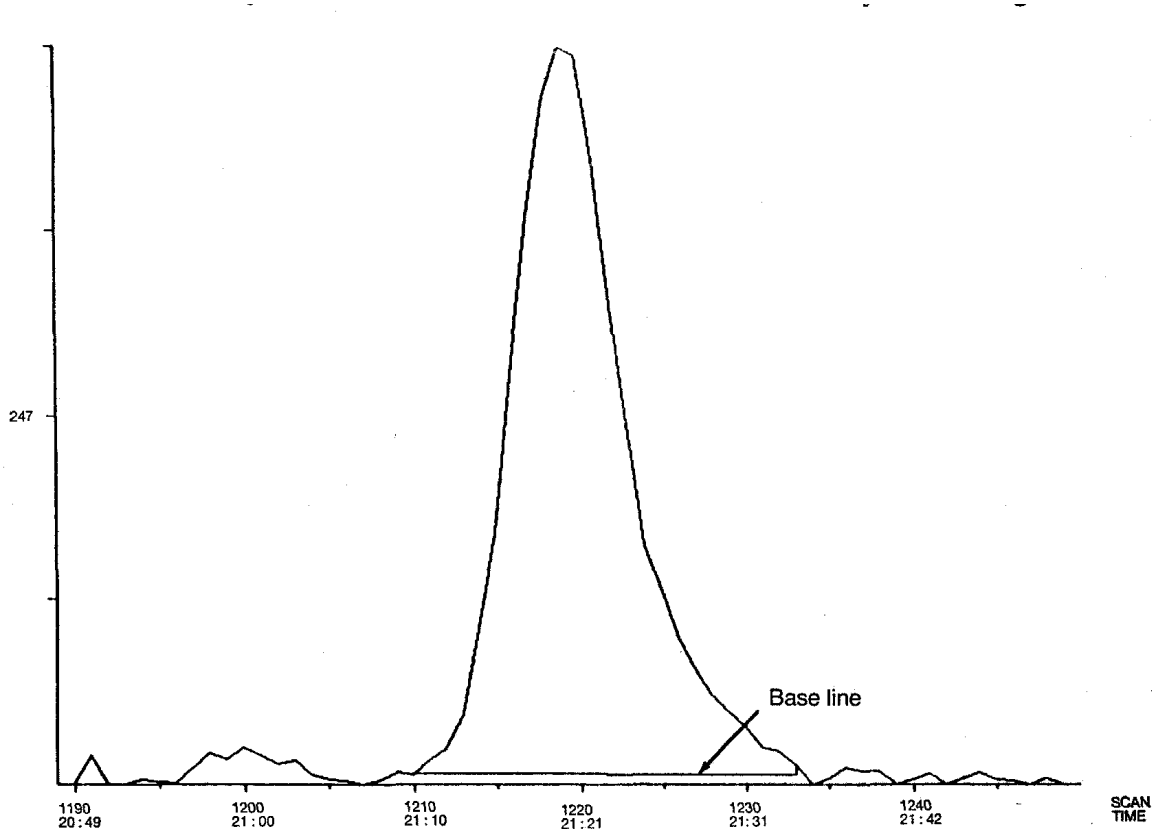

Figure 4. Integration of *m/z* = 247

— the ability to optimize the reverse library search within specific retention times,
— the ability to perform automatic quantitative analysis using integrated specific abundances with either an internal or external standard,
— the ability to perform automatic quantitative analysis using integrated specific ion abundances and regression analysis with more than one internal or external standards,
— the availability of a reference data compilation on a hard disk [13].

6.10. Markings

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

7. Practical instructions

7.1. A GC/MS/DS uses high voltage, high current, high vacuum, compressed gases, and high temperatures during normal operation. Warning labels shall be placed conspicuously on the instrument to alert the user of these potential hazards. These shall be consistent with the national safety regulations.

7.2. Proper venting shall be provided for potentially hazardous and/or toxic exhausts from the gas chromatograph/mass spectrometer which include reagents, carrier gases, and vacuum pump vapors.

7.3. The manufacturer of a GC/MS/DS shall supply a manual that describes its operation and routine maintenance. Service manuals shall be available upon request.

7.4. Before installation of a GC/MS/DS, all environmental factors shall be carefully considered. Manufacturers shall provide specifications for power consumption that include maximum permissible variations for mains voltage and frequency. Specifications shall also include rated operating conditions for temperature, relative humidity, airbone particulate matter, vibration, and heat dissipation requirements.

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

8. Metrological controls

8.1. General considerations

8.1.1. A GC/MS/DS is a complex instrument comprising a variety of major components. Some components used depend on the method specified as appropriate for analysis of a specific sample by the national responsible organization for pollution control. Therefore, traditional legal metrology controls comprising pattern evaluation and approval and initial and subsequent verification may not be practical for these instruments. However, national control should include as a minimum the quality control procedures specified in point 8.2 as a means of assuring the metrological integrity of a GC/MS/DS.

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

8.2. Quality control procedures

8.2.1. An initial test of GC/MS/DS upon installation shall be performed with a suitable test compound provided by its manufacturer. The results of this test shall be within the specifications of the manufacturer.

8.2.2. A test of the entire GC/MS/DS shall be carried out using reference materials, or specifically prepared samples, that are appropriate for the method of analysis. Checks of the calibration of the system shall be carried out at least once per day, or once per each work period.

Annex A.3 gives a test procedure for routine calibration of the GC/MS/DS. Annex A.4 gives a test procedure for establishing the repeatability of the instrument [15, 16]. Appropriate reference materials may be available as indicated in references [17] and [18].

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

8.2.4. A written log shall be maintained that contains the following information in chronological order for each GC/MS/DS:

— results of initial and subsequent routine tests and calibrations,
— identification, for each analysis performed, of the operator, sample, carrier gas, gas chromatograph column(s), gas chromatograph column-oven temperature(s), ionization source (electron beam energy or reagent gas), mass spectrometer scanning mode, and data system and reference data used,
— description of malfunctions and corrective actions taken,
— extent of maintenance and/or repair.

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[18] United States National Bureau of Standards, *NBS Standard Reference Materials Catalogue,* NBS Special Publication *260*, Gaithersburg, MD 20899, USA.

APPENDIX A.1

REFERENCES TO METHODS OF ANALYSIS

A.1.1. Pellizzari, E.P. et al, "Master Analytical Scheme for Organic Compounds in Water", EPA Report No. 600/4-84-0/01 (January 1985).

A.1.2. Budde, W.L. and Eichelberger, J.W. Editors, *United States Environmental Protection Agency Manual for Organic Analysis Using GC/MS.*

A.1.3. *Standard Methods for the Examination of Water and Wastewater,* APHA-AWWA-WPCF, American Public Health Association, Washington, D.C., USA, 16th Edition (Revised every three years).

A.1.4. United States Environmental Protection Agency "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule", *40 CFR Part 136,* Federal Register *49,* No. 209, Friday, October 26, 1984.

A.1.5. United Kingdom Health and Safety Executive (HSE) *Methods for the Determination of Hazardous Substances,* St. Hugh's House, Stanley Precinct, Bootle L20 3QZ, England.

ANNEX A.2

GENERAL COMPOUND TYPES OF POLLUTANTS IN WATER

A.2.1. Strong acids
- — Phosphoric/Phosphonic (Benzene Phosphonic)
- — Sulfuric/Sulfate (Ethyl Hydrogen Sulfate)
- — Sulfonic (Benzene Sulfonic)
- — Group I Phenols (Dinitrophenol)
- — Carboxylic (oleic)
- — Soaps and Detergents

A.2.2. Quaternary nitrogen and phosphonium compounds (Tetramethylammonium Chloride)

A.2.3. Amino acids (Glycine, etc.)

A.2.4. Water soluble alcohols
- — Carbohydrates (Glucose, etc.)
- — Group I Alcohols (Ethanol)

A.2.5. Organometallic compounds

A.2.6. Basic nitrogen compounds
- — Alkyl/Aromatic Amines — 1°, 2°, 3° (Cyclohexyl Amine)
- — Heterocyclic Aromatics (Quinoline)

A.2.7. Weak acids
- — Group II Phenols (o-cresol)
- — Imides (Phthalimide)
- — Enols

A.2.8. Water insoluble alcohols (α-Terpineol)

A.2.9. Polar "neutrals"
- — Aldehydes (Benzoaldehyde)
- — Ketones/Thiones (Acetophenone)
- — Phosphates [Tris(2-chloroethyl)-Phosphate]
- — Phosphinates
- — Phosphonites
- — Sulfones (Diphenyl Sulfone)
- — Sulfoxides (Dimethysufoxide)
- — Sultones (Propane Sultone)

A.2.10. Non-polar "neutrals"
- — Esters, Ethers
- — Phosphites, Phosphines, Phosphinites (Triphenylphosphite)
- — Sulfides (Methyl n-Butyl Sulfide)
- — Non-basic nitrogen compounds: Nitriles, Amides, Isocyanates, Nitro, etc.
- — Aliphatic and aromatic compounds
- — Polynuclear aromatic hydrocarbons

A.2.11. Completely unknown mixtures

Note: Compounds in parenthesis are specific examples for the class. This information is from the reference A.1.1 in Annex A.1. Some of these compound types may not undergo normal GC/MS analysis and, therefore, require conversion to derivative compounds before analysis.

ANNEX A.3

A TEST PROCEDURE FOR ROUTINE CALIBRATION OF THE GC/MS/DS

A.3.1. Test using decafluorotriphenylphosphine (DFTPP)

A.3.1.1. Purpose: this test is to establish that the GC/MS/DS system provides a standard fragmentation pattern by electron impact ionization so that interpretation of spectra can be made through search of historical data bases. [11-14]

A.3.1.2. Experimental: inject in splitless mode (capillary column) 30 ng of DFTPP and scan from *m/z* = 40 to 500 u at a rate of one scan per second.

A.3.1.3. Performance: the spectra obtained should meet the criteria for key ions in Table 1. [15, 16]

TABLE 1

Decafluorotriphenylphosphine key ions and ion abundance criteria

Mass	*Ion abundance criteria*
51	30-60 % of the base peak
68	Less than 2 % of Mass 69
70	Less than 2 % of Mass 69
127	40-60 % of the base peak
197	Less than 1 % of the base peak
198	Base peak, 100 % relative abundance
199	5-9 % of the base peak
275	10-30 % of the base peak
365	At least 1 % of the base peak
441	Present, but less than for Mass 443
442	Greater than 40 % of the base peak
443	17-23 % of Mass 442

A.3.2. Test of stability

A.3.2.1. Purpose: this test evaluates the system's time stability.

A.3.2.2. Experimental: repeat conditions prescribed in point A.3.1.2 after 20-28 hours without adjustments from prior conditions.

A.3.2.3. Performance: the GC/MS/DS should meet criteria as indicated in Table 1.

A.3.3. A secondary test using p-bromufluorobenzene

A.3.3.1. Purpose: if DFTPP is not eluted by the gas chromatograph columns required for a test method, p-bromofluorobenzene should be used to check spectrum validity.

A.3.3.2. Experimental: the test procedure of point A3.1.2 should be carried out for this compound.

A.3.3.3. Performance: the spectra obtained should meet the criteria for key ion abundance according to Table 2.

TABLE 2
p-bromofluorobenzene key ions and ion abundance criteria

Mass	*Ion abundance criteria*
50	20- 40 % of the base peak
75	50-70 % of the base peak
95	Base peak, 100 % relative abundance
96	5-9 % of the base peak
173	Less than 1 % of the base peak
174	Greater than 50 % of the base peak
175	5-9 % of mass 174
176	Greater than 50 % of the base peak
177	5-9 % of Mass 176

ANNEX A.4

A TEST PROCEDURE FOR REPEATABILITY

A.4.1. Introduction

A.4.1.1. The purpose of this test is to establish the repeatability of the entire GC/ MS/DS when applied for continuous, repetitive measurements of ion spectra. This test combines each important measurement component from filling the injection device to integration of a specific ion peak necessary for quantitation.

A.4.1.2. This test should be carried out within one day by the same instrument operator.

A.4.1.3. This test should simulate the step that shall be taken in analysis of samples to follow. For example, manual or automatic sample injection devices shall be used as appropriate.

A.4.1.4. All procedures and tests shall be documented.

A.4.1.5. Test results shall be within established limits of error. Otherwise, the instrument shall not be used for analysis of unknown samples.

A.4.2. Procedure

A.4.2.1. Select a group of seven or more compounds to make up the test (reference) sample. Table 3 provides a recommended list. The concentration of each compound in the reference solution should be 20 μg per milliliter. 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.

TABLE 3
Compounds suitable for making a reference solution
for testing the repeatability

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

Note: (*) B means peaks with widths at half height of more than 45 seconds and
N means peaks with such widths of less than 45 seconds for packed columns.

A.4.2.2. Select an appropriate column

A.4.2,3. Prepare for the following data acquisition variables:

— mass range: *m/z* = 35 to 350 u,

— scan time: approximately from 2 to 6 seconds with packed columns and from 0.5 to 2 seconds with capillary columns,

— electron ionization source energy: 70 eV,

— electron multiplier voltage: not to exceed that recommended by supplier for its condition and age.

A.4.2.4. Inject with a syringe (or automatic sample changer) two microliters (40 ng of each compound) of the test sample and acquire data until all compounds have eluted from the column. Repeat and record data for a minimum of four injections.

A.4.3. Data reduction

A.4.3.1. Plot the total ion current profile and calculate the peak areas at the specified quantitation mass in either arbitrary units or as ratios of peak areas for all compounds.

A.4.3.2. Calculate the standard deviation of the peak area characteristic of each compound of the test sample using the following equation:

$$s = \sqrt{\frac{n\sum_{i=1}^{n}(A_i)^2 - \left(\sum_{i=1}^{n} A_i\right)^2}{n\,(n-1)}}$$

where s = the experimental standard deviation
n = the number of measurements for each compound
A = the peak area representing the quantitation ion mass

A.4.4. For the performance of the instrument to be acceptable, the standard deviation of each characteristic peak in each spectrum of the reference sample mixture shall be within ± 10 percent.

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