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**General rules for gas chromatography/
mass spectrometry**

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Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee as the result of proposal for revision of Japanese Industrial Standard submitted by Japan Analytical Instruments Manufacturers Association (JAIMA)/ Japanese Standards Association (JSA) with the draft being attached, based on the provision of Article 12 Clause 1 of the Industrial Standardization Law applicable to the case of revision by the provision of Article 14. Consequently **JIS K 0123 : 1995** is replaced with this Standard.

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General rules for gas chromatography/ mass spectrometry

1 Scope This Japanese Industrial Standard specifies the general rules mainly applicable to the qualitative analysis and quantitative analysis of organic compounds [stable organic compounds that are gaseous at the ordinary temperature or have sufficient vapour pressure approximately at not more than 350 °C (including derivatives)], organometallic compounds, inorganic compounds and so on existing in extremely small traces which are carried out by using a gas chromatograph spectrometer.

2 Normative references The following standards contain provisions which, through reference in this text, constitute provisions of this Standard. The most recent editions of the standards (including amendments) indicated below shall be applied.

JIS K 0050 *General rules for chemical analysis*

JIS K 0114 *General rules for gas chromatographic analysis*

JIS K 0133 *General rules for high frequency plasma mass spectrometry*

JIS K 0211 *Technical terms for analytical chemistry (General part)*

JIS K 0214 *Technical terms for analytical chemistry (Chromatography part)*

JIS K 0215 *Technical terms for analytical chemistry (analytical instrument part)*

JIS Z 8202-8 *Quantities and units—Part 8: Physical chemistry and molecular physics*

JIS Z 8203 *SI units and recommendations for the use of their multiples and of certain other units*

3 Definitions For the purposes of this Standard, the definitions in **JIS K 0050**, **JIS K 0114**, **JIS K 0133**, **JIS K 0211**, **JIS K 0214**, **JIS K 0215**, **JIS Z 8202-8** and **JIS Z 8203**, and the following definitions apply.

- a) **analyte** a component for analysis (analyte) in analytical sample or sample solution
- b) **mass-to-charge ratio: m/z** a ratio of ion mass expressed by using atomic mass unit to its charge number
It is used in the abscissa of mass spectrum.
- c) **total ion chromatogram: TIC** a diagram in which the total sum of ion current of mass-to-charge ratio (m/z) is continuously detected and recorded in a certain range
- d) **mass chromatogram** a diagram in which mass spectrums are measured at a definite interval, memorized in a computer and the ion intensity of specified mass-to-charge ratio (m/z) is taken out and expressed
- e) **selected ion monitoring: SIM** a method for detecting continuously the ion of specified mass-to-charge ratio (m/z)

- f) **collision induced dissociation: CID** a phenomenon in which the ion having kinetic energy collides with target gas and a part of collision energy is converted to internal energy and excited, and the dissociation of ion is produced by it
- g) **fragmentation** a reaction in which one or some bonds constituting an ion are cleaved and the ion of smaller mass than the original ion is produced
- h) **fragment ion** an ion produced by fragmentation
- i) **precursor ion** an ion when the different ion is produced from a certain ion
- j) **product ion** all ions produced from the specific ion
- k) **relative sensitivity** a ratio of peak area (or peak height) per unit quantity of analyte to peak area (or peak height) per unit quantity of reference component (internal standard material)

The reciprocal of relative sensitivity is called RRF: relative response factor.

- l) **SOP (standard operating procedure)** a document for specifying the practice method and procedure in detail for test, inspection and so on
- m) **ion source** a part constituting a mass spectrometer and the place where the ionization of sample component and the transfer of produced ion to analyzer are carried out

It consists of ionization chamber, filament, a group of electrodes in which the acceleration, convergence and so on of ion are carried out.

- n) **ionization chamber** a place where a sample molecule interacts mutually with an electron and reaction ion in an ion source and ions are produced
- o) **reagent gas** gas used for ionization of sample molecule in chemical ionization method

Usually, the high purity methane, 2-methyl propane (isobutane), ammonia and so on are used.

- p) **reaction ion** an ion directly concerned in the ionization of sample molecule among the ions produced by ion-molecule reaction of the reagent gas itself

The giving and receiving and so on of proton between sample molecules are carried out.

- q) **quasi-molecular ion** an ion in which proton or hydride is added to molecule, and an ion in which proton or hydride is drawn out from molecule

$(M \pm H)^+$ and $(M \pm H)^-$ correspond to this.

- r) **linked scan** a method in which a magnetic field type mass spectrometer of double-focussing type is simultaneously scanned as keeping the intensity of electric field and magnetic field at a definite relation and the specific ion concerned in the ion and metastable ion in CID is detected

- s) **analyzer** a generic name of mass separating part

- t) **sampling time** a duration in which a mass spectrometer is operated and one data is taken

- u) **scan** to change, for the detection of the ion of a certain range of mass-to-charge ratio (m/z), the intensity of magnetic field and electric field and the voltage to quadruple rod
- v) **resolution** capability of mass spectrometer of separating the two adjoining peaks on mass spectrums

When the two peaks of optional mass-to-charge ratio, $m/z = M$ and $m/z = [M + \Delta M]$, can be distinguished, but the two peaks with the difference of m/z smaller than ΔM can not be distinguished in a mass spectrometer, $R = M/\Delta M$ is taken as the resolution of this apparatus. If the peak can be distinguished here, it means that the separation has taken place at the position of 10 % of peak height in magnetic field type and at the position of 50 % of peak height in other analyzer.

4 Summary The gas chromatograph mass spectrometry (GC/MS method) is the analytical method in which a gas chromatograph mass spectrometer (GC/MS apparatus) consisting of a gas chromatograph (GC) superior in the separation analysis of the mixture, directly connected to a mass spectrometer (MS) superior in the structure analysis and trace analysis for the sample component, is used. Thanks to the respective features of the two components, obtaining the material information in high sensitivity is possible by this method.

When the mixture of the gaseous or liquid sample is introduced into a GC/MS apparatus, the analyte is separated in gas chromatograph, led continuously in the ion source of mass spectrometer and ionized. The produced positive or negative ion enters the analyzer (mass separating part) and is separated according to mass-to-charge ratio (m/z). The separated ion is successively converted to the corresponding electrical signal in the detecting part and recorded as various kinds of chromatogram and mass spectrums. The qualitative analysis is carried out based on the retention time and mass spectrum of analyte on this chromatogram and the quantitative analysis is carried out based on the peak area (or peak height) on the chromatogram.

5 Apparatus

5.1 Construction of apparatus The apparatus shall be composed of gas chromatograph, interface (GC/MS connecting part) and mass spectrometer as shown in figure 1.

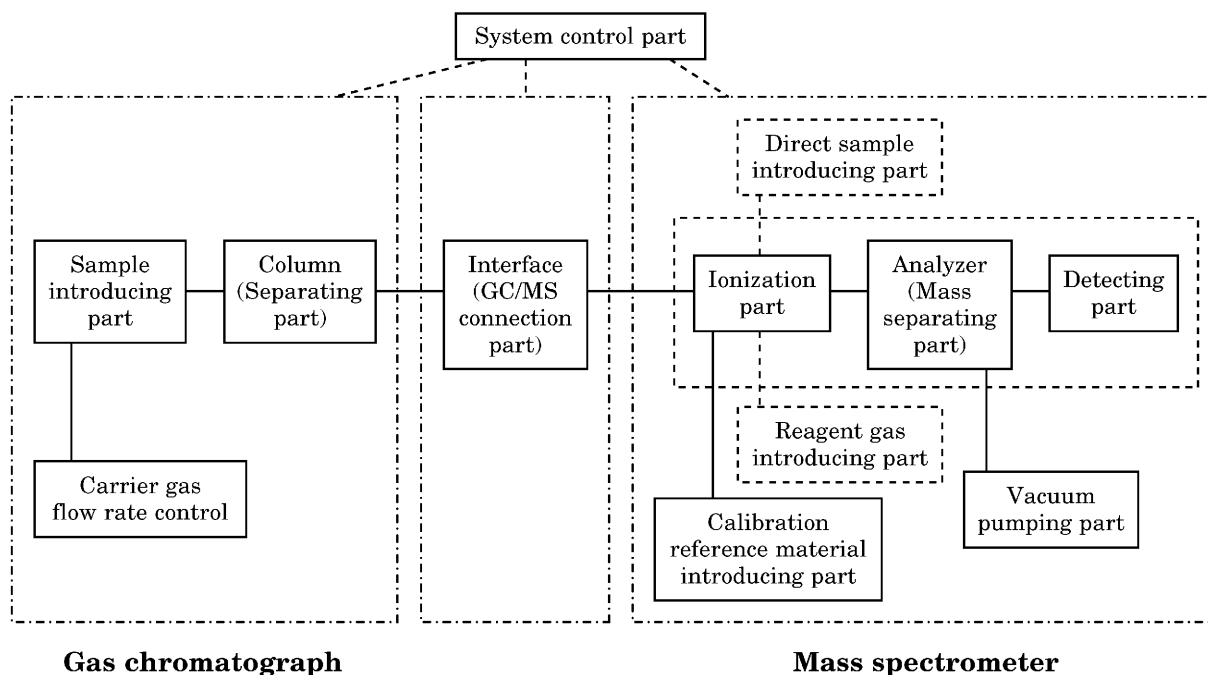


Figure 1 Construction diagram of apparatus (example)

5.1.1 Gas chromatograph The gas chromatograph shall be as follows.

- Controlling part of carrier gas flow rate** It is the part for controlling the flow rate of carrier gas. It is composed of pressure control valve, flow rate control valve, pressure gauge and so on. Some are capable of controlling automatically the carrier gas by flow rate, pressure, linear velocity and so on.
- Sample introducing part** It is the part for introducing the sample in the flow channel of carrier gas. There are those in which gaseous sample is taken in measuring tube and so on to be introduced by valve operation or those in which the liquid or gaseous sample is introduced by syringe. There are the dividing introduction system and the non-dividing introduction system in the sample introducing part for capillary column. One system categorized as the dividing introduction system is the split system, which introduces only a part of injection-evaporated sample in a column. Those categorized as the non-dividing introduction system are the splitless system in which the solvent treatment is devised by utilizing a switchable exhaust opening and almost whole amount of sample is introduced without producing a large tailing of its peak, the whole amount introduction system (direct injection system) which introduces the whole amount of evaporized sample by using a large-bore capillary, the cold on-column system in which the temperature of sample introducing part is set at not more than the boiling point of solvent and the sample is directly introduced to column through injection opening and the programmed temperature vapourization introduction system in which the temperature of sample introducing part is set at not more than the boiling point of solvent, and after the sample is introduced and the solvent is exhausted at low temperature, the sample is rapidly heated and introduced in the column.

- c) **Column** The column can be roughly divided into two types, namely, capillary column and packed column. The length, inside diameter, the kind of stationary phase and so on shall be selected corresponding to the purpose. The capillary column, of which the material is metal, glass, quartz glass, synthetic resin and so on, the inside diameter is 0.1 mm to 1.2 mm, the length is 5 m to 100 m, and the film thickness of stationary phase is 0.1 μm to 10 μm , shall be used. The adsorption type capillary column is the one in which about several 10 μm of adsorbent is coated on the inner wall of column and fixed by using various types of binder. The distribution type capillary column is that which the stationary liquid is chemically bonded or coated on the inner wall of column. The packed column is that which the column packings are packed in a tube of metal, glass, synthetic resin, 2 mm to 6 mm in inside diameter and 0.5 m to 5 m in length. The column packings include adsorption type column packings, distribution type column packings, porous high polymer type column packings or combination of these types.
- d) **Column oven** The column oven shall have the heating mechanism capable of maintaining the inside at the setting temperature and holding the temperature distribution constant. It shall also be capable of an adequate separation, and in the case of the programmed temperature gas chromatography, shall be capable of setting the initial temperature, continuation time (hold time), programming rate, final temperature and continuation time (hold time), with the temperature control precision within $\pm 0.5\text{ }^{\circ}\text{C}$, and the temperature change within $\pm 0.5\text{ }^{\circ}\text{C}$ per 10 % variation in voltage of power source.

5.1.2 Interface (GC/MS connecting part) The interface means the connecting part of GC and MS. It is a device connecting the column outlet of a gas chromatograph, which stays under atmospheric pressure, with the ion source of a mass spectrometer where high vacuum has been applied, and either of the following can be used according to the type of a column and pumping speed of vacuum pump.

- a) **Case of capillary column** In the case of a capillary column approximately 0.3 mm or smaller in inside diameter, one end at its outlet side is connected to as to be positioned very close to the ion source of mass spectrometer. Large bore capillary column approximately 0.3 mm or greater in inside diameter, in some cases, can be used with a dummy column connected at the front stage or rear stage of capillary column. In other cases, the connecting method as shown in **b)** can be used. The GC/MS connecting part has the heating · temperature control mechanism and temperature measurement mechanism capable of maintaining the same or higher temperature as column oven by a small sized thermostatic chamber or heating pipe. The example of connecting part of capillary column is shown in figure 2.

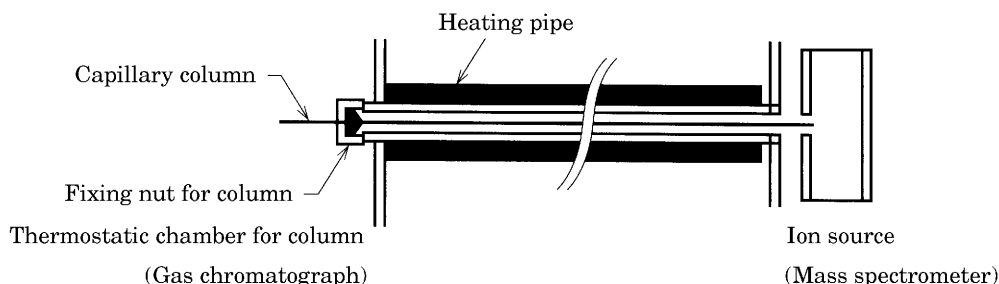


Figure 2 Connection part of capillary column (example)

- b) **Case of packed column and a large bore capillary column** The flow rate of carrier gas for packed column and a large bore capillary column is 5 ml/min to 10 ml/min and the maintenance of vacuum becomes difficult in the system as shown in a). Therefore, a jet separator for separating and removing the carrier gas and concentrating the analyte is used. The material of separator is generally glass and the heating · temperature control · temperature measurement mechanism and exhaust system are provided. The example of construction is as shown in figure 3. This principle utilizes the difference of diffusion coefficient between the helium as the carrier gas and the analyte, and the tip of glass tube is made narrow so as to be part A in figure 3. The carrier gas and the analyte and diffused at this tip part, however the carrier gas in large than the analyte in diffusion coefficient and diffused well to be sucked by oil-sealed rotary vacuum pump. On the other hand, the analyte goes straight on because of its small diffusion coefficient, and the larger the molecular mass of which is, the smaller the loss associated with introduction of which into a mass spectrometer becomes.

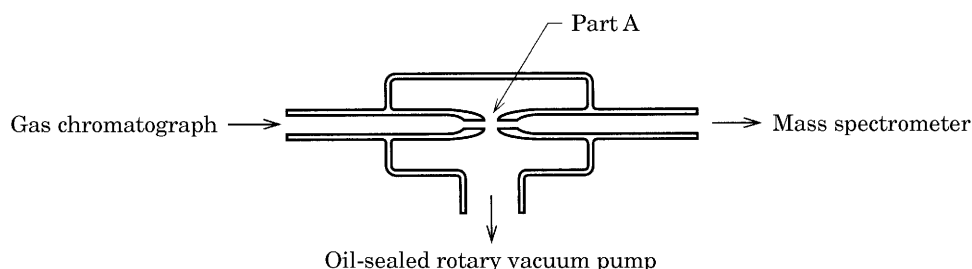


Figure 3 Separator (example)

The connection can be done by open split coupling in some cases. In this method, the carrier gas and sample component flowing out from a column are introduced to a mass spectrometer only by splitting as shown in figure 4. Whereas the separator system has the concentration effect in which the carrier gas of smaller mass is removed and the sample component of large mass is passed. This method only involves splitting and no concentration effect. However, for analysis of small mass gaseous components such as hydrogen, methane, nitrogen or oxygen, which are almost entirely removed in separator system due to their highness in diffusion coefficient, this method will prove more effective because it always leads a certain amount of such small mass gasses into the mass spectrometer.

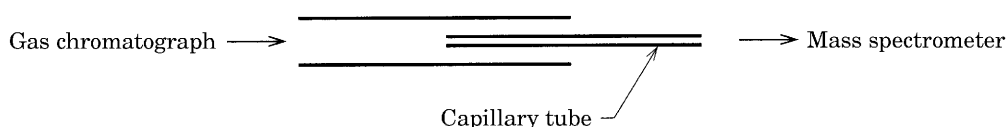


Figure 4 Open split coupling (example)

5.1.3 Mass spectrometer The mass spectrometer is the part in which the analyte separated by gas chromatograph is ionized, separated according to the mass-to-charge ratio (m/z), detected and further data processing is carried out. It is composed of an ionization part, analyzer (mass separating part), detecting part, vacuum pumping part and system controlling part.

a) **Ionization part** The ionization part is the part in which the analyte eluted from gas chromatograph is ionized and introduced to an analyzer. The ionization method to be used includes an electronic ionization (EI) method, positive ion chemical ionization (PCI) method, negative ion chemical ionization (NCI) method and other methods. The ion source in the most general EI method, when the form of analyzer is quadrupole type and magnetic field type, is composed of an ionization chamber, the filament (cathode) for supplying the electron for ionization, an electron trap (anode), an electrode for pushing out or drawing out ion, a group of electrodes carrying out the acceleration of ion, focussing of ion beam, and the magnet for giving magnetic field along the electron flow is fitted outside. It is also provided with a heater for reducing the adsorption of analyte to the inner wall of ionization chamber and for carrying out the degas of air component, the ionization chamber is highly gastight in the ion source of chemical ionization (CI), and when ionized, the introduction of reagent gas is carried out. When the form of analyzer is other than quadrupole or magnetic field type, the structure of ion source is different from the above-mentioned because the ion optical system is different [see **b**].

- 1) **Electronic ionization (EI) method** The method in which the electron having not less than several 10 eV of energy emitted under vacuum from a filament is radiated to the gaseous analyte in ionization chamber and ionization is carried out by giving a part of its kinetic energy in the form of electronic energy. The molecular ion (M^+) is produced at the beginning, however the fragmentation dependant on molecular structure occurs generally by excess internal energy and a fragment ion is produced. The molecular ion does not remain depending on some molecular structures. This ionization method is the one most commonly used in GC/MS apparatus.
- 2) **Positive ion chemical ionization (PCI) method** The ionization chamber is filled under about pressure 100 Pa by using a reagent gas such as high purity methane and the reaction ion originated in reagent gas (for example, CH_5^+ , $C_2H_5^+$ and so on in the case of methane) is produced by radiating electron beam and so on. Next, the analyte is ionized by the ion-molecule reaction between these reaction ions and analyte. The quasi-molecular ion ($M \pm H$)⁺ which is a structurally stable even electron ion is easily produced. A part of reaction heat is stored as the excess internal energy, however the quantity of fragmentation is smaller as compared with EI because of the soft ionization with small reaction energy. In many cases, the presumption of molecular weight is easy by PCI method.

Moreover, for the purity of reagent gas, 99.99 % of purity in the case of methane and not less than 99.9 % of purity in other case are used.

- 3) **Negative chemical ionization (NCI) method** The filling of ionization chamber with a reagent gas such as methane is same as PCI method and the ionization mechanism is roughly divided into two types, the reaction ion type and the electron capture type. In the former, the ionization is carried out by the ion-molecule reaction between the reaction ion (OH^-) produced from water existing in reagent gas or in system and the sample molecule, and the ion such as $(\text{M} - \text{H})^-$ is produced. In the latter, the ionization is carried out by producing the resonance capture reaction of a negative thermion losing kinetic energy in ionization chamber with the sample molecule, and the molecular ion (M^-) and so on are very efficiently produced to the high electron affinity of compounds.
 - 4) **Other ionization method** The other ionization method used by GC/MS apparatus includes the field ionization (FI) method, the laser ionization method, the ionization method by inductively coupled plasma (ICP) and so on. ICP-MS method is originally used for the analysis of inorganic element, however in GC/MS apparatus it is used for the measurement of organic compound and so on.
- b) **Analyzer (mass separating part)** It is the part in which the ion originated in the analyte produced in ionization part is separated according to its mass-to-charge ratio (m/z). There are quadruple type (Q), three-dimensional quadruple type (ion trapping type) (IT), magnetic field type (When electric field is taken as E and magnetic field is taken as B, there are EB type and BE type.), time of flight type (TOF) and other type.
- 1) **Quadruple type** The schematic diagram of quadruple mass spectrometer is as shown in figure 5.

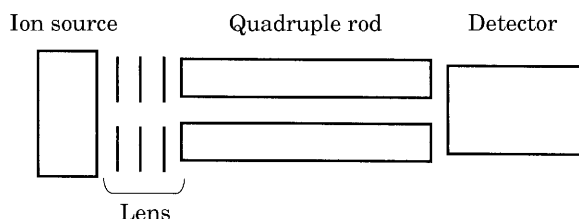


Figure 5 Schematic diagram of quadruple type mass spectrometer

The four columns or rods with hyperboloid made of metal or metallized glass are set in the rear of ion source mutually in parallel. The schematic depiction of the quadruple rods is as shown in figure 6. The same voltage [direct-current voltage (U) is overlapped on high frequency voltage ($V\cos\omega t$)] is applied to the opposite rods and the positive and negative reverse potential are applied to the adjacent rods and switched at high speed. When the ion produced in ion source is entered along the central axis, the ion goes forward to the direction of z-axis as vibrating to the direction of x-axis or y-axis. Moreover, only the ion of specific mass-to-charge ratio (m/z) goes forward stably as vibrating and reaches the detector. There is an apparatus in which a prerod is set in the front of the quadruple rods.