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General rules for gas chromatography

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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 0114:2000** is replaced with this Standard.

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General rules for gas chromatography

1 Scope

This Japanese Industrial Standard specifies the general rules applicable to the qualitative and quantitative analysis for organic and inorganic substances using gas chromatography.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Standard. For standards with the year indication, only the editions of the indicated year shall be applied and the revisions (including amendments) made thereafter shall not be applied. For those without the indication of the year, the most recent edition (including amendments) shall be applied.

JIS K 0050 *General rules for chemical analysis*

JIS K 0211:2005 *Technical terms for analytical chemistry (General part)*

JIS K 0214:2006 *Technical terms for analytical chemistry (Chromatography part)*

JIS K 0215:2005 *Technical terms for analytical chemistry (Analytical instrument part)*

JIS K 8251 *Glass wool (Reagent)*

3 Terms and definitions

For the purposes of this Standard, the terms and definitions given in **JIS K 0050**, **JIS K 0211:2005**, **JIS K 0214:2006** and **JIS K 0215:2005**, and the following terms and definitions apply.

NOTE : When necessary, this Standard modifies definitions in **JIS K 0211:2005**, **JIS K 0214:2006** and **JIS K 0215:2005**, by supplementing, adding, etc. The definitions modified are marked with an asterisk (*).

3.1 gas chromatography*

the chromatography in which gas is used as a mobile phase

It separates and detects analytes by using the difference in the interaction with a stationary phase (adsorption, partition).

3.2 gas chromatograph*

the apparatus used for gas chromatography

3.3 gas chromatographic analysis

qualitative and quantitative analysis of compounds using a gas chromatograph

It can be used synonymously with gas chromatography.

3.4 chromatogram*

the record of the results obtained by gas chromatography

It is also called gas chromatogram.

3.5 column*

a tube used for separating sample components, which is filled with column packing or of which capillary inner wall supports a stationary phase

It is also called separation column. Materials of the column tube are, for example, glass, fused silica, stainless steel, copper, and iron.

3.6 stationary phase*

an element of the place where gas chromatography is performed, as well as an immobilized phase in the column

For example, an adsorbent or a liquid kept by the support. Analytes are separated from one another, by using the difference in an interaction with the analyte.

3.7 stationary liquid

the liquid employed for a stationary phase

3.8 mobile phase*

an element of the place where gas chromatography is performed, as well as a gas which develops and elutes the analyte flowing in contact with a stationary phase

3.9 column packing*

granular, adsorbent stationary phase packed in a column, particles which support stationary liquid, etc.

3.10 support*

the granular base used for supporting stationary liquid in the partitionary column packing

3.11 pressure gradient correction factor*, j

the factor used for correcting the retention volume, in order to adjust the pressure difference between an inlet and outlet of the column of a gas chromatograph

It is obtained by the following formula.

$$j = \frac{3}{2} \times \left[\frac{(P_i / P_o)^2 - 1}{(P_i / P_o)^3 - 1} \right]$$

where, P_i : the pressure of carrier gas at an inlet of the column
 P_o : the pressure of carrier gas at an outlet of the column

The above-mentioned formula is applicable only to the column of specific diameter, packed homogenously with column packing.

3.12 phase ratio*, β

ratio of the volume of mobile phase to that of stationary phase inside the column

In the case of a hollow column, it is obtained by the following formula.

$$\beta = \frac{d_i}{4d_f}$$

where, d_i : the inside diameter of column
 d_f : the film thickness of stationary liquid
 The same unit shall be used for d_i and d_f .

3.13 split injection method*

the method of partly injecting some vaporized test samples into a column, by using a branch at the sample introducing port

The sample injection method for capillary column, intended to prevent the electrical overload on the column of a sample and analyse (split introduction system).

3.14 splitless injection method*

sample injection method for capillary column, by opening the outlet for split when most of the vaporized test samples injected are transferred into the column, discharging the solvent which remains in a vaporizing chamber outside the system, and analysing the test samples (splitless introduction system)

3.15 direct injection method*

sample injection method for capillary column, by injecting test samples in a heated vaporizing chamber, instantaneously vaporizing, and introducing all the vaporized test samples into the column

3.16 cold on-column injection method*

sample injection method by introducing test samples directly into a column through the injection port whose temperature is kept below the boiling point of the solvent for test sample (whole-quantity introduction system)

After the injection, raise the temperature of the column and analyse test samples.

3.17 programmed temperature vaporization method, PTV method

sample injection method by programming arbitrary temperature at the sample introducing port, and introducing test samples into a column

It can be used for multiple injection methods (whole-quantity introduction system, split introduction system and splitless introduction system).

3.18 base line*

stable signal in chromatogram, recorded at the part where, without any sample component, only carrier gas passes through the detector

3.19 tailing*

the state in which the end of a peak shows a gently sloping foot

The peak width of the latter part of the peak becomes wider than that of the former part of the peak.

3.20 leading*

the state in which the front part of a peak shows a gentle rise

The peak width of the former part of the peak becomes wider than that of the latter part of the peak.

3.21 peak*

the curved part recorded in chromatogram when the sample component is eluted from the column

3.22 peak height*

the length of a line drawn vertically on a time abscissa, from the top of the peak to the line connecting both feet of the peak

3.23 peak width*

the length between two intersections of each tangent at the inflection point of both sides of the peak with the line connecting both feet of the peak

3.24 peak area*

the size of area surrounded by the peak and the line connecting both feet

3.25 peak width at half height*

the length between the intersections of the peak with the line drawn parallel to time abscissa at the mid-point of peak height

3.26 peak width at half height method*

the calculating method of peak area by multiplying peak height by peak width at half height

3.27 resolution*, R

a measure of indicating how far the peak of target component is separated from the adjacent peak

Resolution is obtained by the following formula, by using peak width or peak width at half height.

$$R = 2 \times \frac{(t_{Rb} - t_{Ra})}{(W_a + W_b)}$$

where,

R : resolution

t_{Rb} , t_{Ra} : retention time of component peak a and b
($t_{Rb} > t_{Ra}$)

W_a , W_b : time of peak width of component a and b

The same unit shall be used for t_{Rb} , t_{Ra} , W_a and W_b .

$$R = 1.18 \times \frac{(t_{Rb} - t_{Ra})}{(W_{a1/2} + W_{b1/2})}$$

where, R : resolution

t_{Rb}, t_{Ra} : retention time of component peak a and b
($t_{Rb} > t_{Ra}$)

$W_{a1/2}, W_{b1/2}$: time of peak width at half height of component a and b

The same unit shall be used for $t_{Rb}, t_{Ra}, W_{a1/2}$ and $W_{b1/2}$.

3.28 retention factor*, k

the numerical value of the retention time of each component's peak corrected by the value of dead volume

It is defined by the following formula using retention time t_R and hold-up time t_M . It is the ratio of the sample component distributed to the stationary phase and the sample component distributed to the mobile phase.

$$k = (t_R - t_M) / t_M$$

3.29 retention time*

the time from introduction of a sample into the column to appearance of peak top of the specific component

3.30 adjusted retention time*

the retention volume t_R' corrected by hold-up time (t_M)

It is obtained by the formula $t_R' = t_R - t_M$.

3.31 retention volume*

the volume of carrier gas required to elute a specific component from a column under specified condition

It is obtained by the formula $V_R = t_R \times F_c$ where, t_R is retention time in this case, and F_c is the carrier gas volume measured at the column outlet, at the temperature of the column.

3.32 specific retention volume*, V_g

the value indicated by the total corrected retention volume per unit mass of stationary liquid under standard condition (V_g)

$$V_g = \frac{V_N}{W_L} \times \frac{273.15}{T}$$

where, V_N : total corrected retention volume

W_L : the mass of stationary liquid

T : the absolute temperature of the column (K)

3.33 adjusted retention volume*, V_R'

retention volume corrected by hold-up volume (V_R')

It is obtained by the formula $V_R' = V_R - V_M$.

where, V_R' : adjusted retention volume

V_R : retention volume

V_M : hold-up volume

3.34 corrected retention volume*, V_N

retention volume obtained by correcting hold-up time, volume and pressure drop in the column

It is obtained by the formula $V_N = j \times V_R'$, that is, multiplying pressure gradient correction factor j by adjusted retention volume V_R' .

3.35 retention value*

general term for retention volume, retention time, adjusted retention volume, corrected retention volume, specific retention volume, relative retention, retention factor, and the like

3.36 relative retention*

the ratio of retention value of the target substance to that of reference substance

The numerical value is obtained by the following formula under the same condition, intended to indicate the retention value of a certain substance.

$$r_{12} = \frac{V_{R1}'}{V_{R2}'} = \frac{V_{N1}}{V_{N2}} = \frac{V_{g1}}{V_{g2}} \neq \frac{V_{R1}}{V_{R2}}$$

where, V_R' : adjusted retention volume

V_N : corrected retention volume

V_g : specific retention volume

V_R : retention volume

The subscripts 1 and 2 stand for the specific substance and reference substance respectively. The same unit shall be used for V_R' , V_N , V_g and V_R .

3.37 hold-up time*

the time from introduction of a sample to appearance of peak top of the component not retained in the column ($k = 0$)

3.38 number of theoretical plates*, N

an index to indicate the efficiency of a column

The number is obtained for the specific component, by the following formula. Depending on the obtaining method of peak width, there are the tangent method, peak width at half height method, area height method and the like.

$$N = 16 \times \left[\frac{t_R}{w_b} \right]^2 \dots\dots\dots \text{Tangent method}$$

$$N = 5.54 \times \left[\frac{t_R}{w_{b1/2}} \right]^2 \dots\dots\dots \text{Peak width at half height method}$$

$$N = 2\pi \times \left[\frac{t_R h}{A} \right]^2 \dots\dots\dots \text{Area height method}$$

If the peak curve shows Gaussian curve, the results of above three formulas become identical.

where, t_R : retention time

w_b : peak width

A : peak area

h : peak height

$w_{b1/2}$: peak width at half height

The same unit shall be used for t_R , w_b , and $w_{b1/2}$.

3.39 analyte*

a component to be tested in analytical sample

3.40 solid phase extraction*

the operation to isolate, purify, concentrate sample components, etc., by passing samples through the solid collector packed with column packing

3.41 carrier gas*

mobile phase gas used for gas chromatography

3.42 programmed temperature gas chromatography*

analytical method of gas chromatography by raising the temperature in a column oven according to the programme set beforehand

3.43 programming rate*

rate of change in the column oven temperature in programmed temperature gas chromatography

3.44 external standard method*

a method to obtain the concentration or quantity of the analyte in the sample using calibration curve prepared based on the peak area or height on the chromatogram which has been obtained from the sample containing the same component of known concentration as the analyte

3.45 internal standard method*

a method to determine an analyte in the target sample, to which known quantity of internal standard is added, using the relation curve prepared by analyzing mixed

samples of known quantity of analyte with known quantity of internal standard and by plotting the quantitative ratio of analyte/internal standard and signal ratio

This method has such advantage that is hardly influenced by the varied introduction amount of sample.

3.46 internal standard

substance used as a standard in the internal standard method

3.47 relative sensitivity*

the ratio of the peak area or height per unit amount of target component to the peak area or height per unit amount of the reference component

The reciprocal of relative sensitivity is called correction factor.

3.48 solvent effects

the phenomenon that the peak width is narrowed because, when the temperature of the column is cooled 20 °C lower than the boiling point of the sample solvent, the sample solvent is vaporized at the sample injection port and condensed at the top of the column, then the components are expanded at the injection port and retained by the solvent

The phenomenon is observed in the gas chromatographic analysis using a capillary column.

3.49 reference material*

the material whose characteristic values are proved at the necessary and sufficient degree, to be used for the calibration of gas chromatograph, evaluation of measuring method or rating of samples

3.50 surrogate

the material being same as or similar to the analyte in chemical constitution, to be added, when the mass spectrometer (MS) is used as a detector, for the correction of yield, confirmation of recovery and the like at the operation stages of pretreatment and analysis of the sample

The element which is partly substituted by a stable isotope such as deuterium d, ^{13}C and the like is used. Surrogate is also called surrogate substance.

3.51 discrimination

the change in composition of a sample having a wide range of boiling points between the sample injected and the sample entered in the column in gas chromatographic analysis

Mainly, the high boiling components in the sample are more difficult to shift to a column than low boiling components, and the composition ratio of high boiling components becomes relatively small. It is produced by the fractional distillation at the needle point of syringe, the heterogeneous vaporization at the injection port, the diffusion and the like.

3.52 McReynolds' constant

the total sum of five values, each obtained by subtracting the retention index to squalane referred to by non-polar stationary phase, from the retention index of corresponding analyte in the stationary liquid of five analytes (benzene, 1-butanol, 2-pentanone, pyridine and 1-nitropropane)

The bigger McReynolds' constant is, the stronger the polarity becomes. As a standard, the different separation behaviour is observed when McReynolds' constants differ by 100 or more.

3.53 thermal desorption

the phenomenon that the surface-adsorbed material is desorbed from the surface to the other phase by heating

3.54 thermal extraction

the operation of shifting the material contained in sample to the other phase by heating

3.55 conditioning

the operation of heating a column to an adequate temperature while letting carrier gas flow, intended to remove the impurities adsorbed or dissolved in stationary phase

3.56 fuel gas*

the gas which causes a phenomenon required for operating a detector such as combustion

3.57 additional gas*

the gas required for operating a detector adequately

3.58 supporting gas*

the gas which supplies oxygen required for combustion

4 Outline of gas chromatography

Gas chromatography is a type of column chromatography, and a type of physico-chemical method for separating complicated mixture, by using the difference of partition equilibrium or adsorbance of sample components between stationary phase and mobile phase packed in the column.

Depending on the type of stationary phase, it is roughly classified into gas-solid (adsorption) chromatography and gas-liquid (partition) chromatography. In gas-solid chromatography, such adsorbents as silica gel, active charcoal, active alumina, and synthesized zeolite are used as stationary phase. In gas-liquid chromatography, stationary liquid homogeneously impregnated with and coated on diatomite or on other inert support particles, or is coated on the inner surface of capillary column or chemically combined. In the former case, particles are packed in the tube of 2 mm to 6 mm in inside diameter and several metres in length. In the latter case, the inert porous support (usually diatomite) impregnated with stationary liquid is packed in the tube. Those tubes, made by hard glass or stainless steel, are called packed columns. On the

other hand, the thin pipe of about 0.1 mm to 1.2 mm in internal diameter and several metres to several tens of metres in length whose inner surface keeps stationary liquid is called capillary column. Column is made of quartz or stainless steel. Generally, gas-solid chromatography is used for inorganic gas or low boiling hydrocarbons, while gas-liquid chromatography is used for the separation of general organic compounds.

Figure 1 shows the example of basic diagram of the apparatus, which is composed of a flow rate controller for carrier gas, sample introducing port, column, column oven, detector and data processing device. Helium, nitrogen gas or others are usually used for carrier gas, and are provided to the apparatus from a high-pressure gas container (cylinder) via a pressure reducing valve. Then, its pressure and/or flow rate is controlled before sending and the carrier gas is sent to the sample introducing port and column at a certain flow rate. Test sample is introduced by a gas sampler or a syringe for liquid or a syringe for gas.

The test sample introduced to the column together with carrier gas is separated into individual components and detected by a detector. The signal from the detector is processed by the data processing device.

Gas chromatographic analysis can employ various detectors including a thermal conductivity detector, flame ionization detector, electron capture detector, flame photometric detector, thermionic ionization detector, and mass spectrometer, therefore it has wide applications to the concentration from a high level of percentage to a low level of ppm. Various detectors such as the one which can analyse the components containing inorganic gas, sulfur in high sensitivity, can be used.

Combining various columns and detectors different in characteristics enables the controlling analysis for manufacturing process in many industries including petroleum, medicines, food, and environment, and also enables the qualitative analysis and quantitative analysis for more complicated samples. The constitution which enables the analysis of samples with complicated composition, by using the different characteristics of the columns and detectors, for example, by using several columns or detectors in parallel or introducing chromatogram in whole or part into the column of other characteristics (multiple dimensional chromatography) is also used.

Furthermore, attaching various accessories (e.g. a sample introducing device for gas or liquid, head space sampler, purge trapping device and apparatus for thermal desorption) to a gas chromatograph enables the analysis of tiny amount of contaminants in the air and water to the level of ppb or ppt. Gas chromatography allows such wide applications that it can, for example, analyse high molecular compounds, which are difficult to analyse directly, from the decomposed products by using a pyrolysis apparatus.

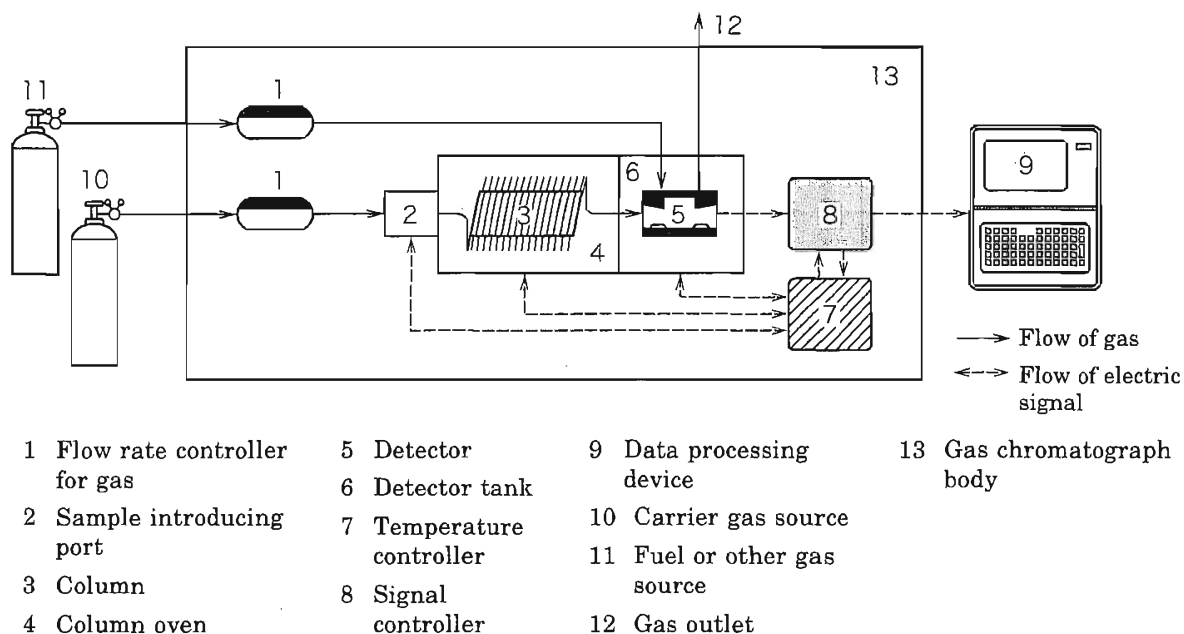


Figure 1 Example of basic diagram of gas chromatograph

5 Operations before sample introduction

5.1 General

When a gas chromatographic analysis is to be operated, a sampling method and sampling device matching the type of sample shall be selected in advance, depending on the purpose of analysis. Test samples taken can be classified into three cases according to the type and analysis purpose: the case in which test samples can be directly introduced to the gas chromatograph, the case in which test samples are introduced to the gas chromatograph via an accessory shown in 6.10, and the case in which pre-treatments (e.g. extraction of target analyte, derivatization, concentration process of target analyte or others) are required.

5.2 Sampling

Take sample which represents the sample population by the sampling method which is most suitable for analysis purpose, properties of sample and items to be tested. Follow individual standards, if any. Samples shall be pretreated or introduced to a gas chromatograph as swiftly as possible so as to prevent those samples from being deteriorated by external influences and time-dependent changes. When storage is inevitable, it shall be confirmed beforehand that the storage or transportation gives no degeneration on the quality of samples. If there is a concern for the degeneration on the quality of samples, the preventive measures shall be taken [for instance, the residual chlorine in city water can affect the concentration of trihalomethan or stimulate the decomposition of some agricultural chemicals. In such case, L (+)-ascorbic acid shall be added to the samples then samples shall be stored]. When a mass spectrometer (MS) is employed as a detector, a substance labelled by stable isotope (surrogate substance) should be added for the accuracy control. When double measurements are required, at least two pieces of the same sample shall be taken simultaneously for the data reliability. When gas is analysed, sampling methods related to the analytical operations