

MITSUBISHI
CHEMICAL

Mitsubishi Chemical
Group

KARL FISCHER REAGENTS

TECHNICAL MANUAL



API Corporation

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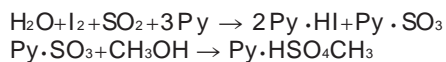
Introduction

The methods used to analyze moisture content in substances range from the loss-on-drying method to physical, electrical and optical systems. Moisture content measurement by means of Karl Fischer reagents is now widely employed as the only reliable chemical method.

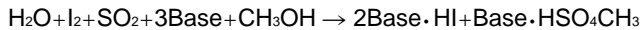
Today the method is widely accepted as a moisture content measurement system for both chemicals and manufactured products. It has been adopted as an international standard by the International Standards Organization (ISO), as an American Standard Testing Method (ASTM) in the United States, and is also included in the German DIN standards and the British BS system. The method has also been incorporated into Japanese standards, including the Japanese Industrial Standards (JIS) and Japanese Agricultural Standards (JAS). It is also included in Japanese pharmaceutical practice, the official food additive manual, and the Japan Petroleum Institute Standards.

Development of Karl Fischer Reagents

The German scientist Karl Fischer (1901-1958) first revealed his new reagent to the world in a paper [NOTE 1] published in 1935. A mixture of iodine, sulfur dioxide, pyridine and methanol, it was named after its inventor. As shown in the following formula, Karl Fischer reagents react selectively to water in specific amounts. Mitchell & Smith subsequently carried out a detailed study of the reaction [NOTE 2] and published findings that indicated a reaction of 1 mole of iodine to 1 mole of water. This basic reaction formula remains in use today.



In recent years, however, the Karl Fischer reaction mechanism has been studied on a more theoretical level. A published paper [NOTE 3] shows that the pyridine acts simply as a buffer and that it is not essential to the reaction. The following reaction formula, in which pyridine is expressed as a base, has been put forward.



Note: Base = Amin. "Base" is sometimes shown as RN.

Characteristics of the Karl Fischer Titration Method

The measurement of moisture content using Karl Fischer reagents is superior to other methods such as loss-on-drying, distillation and infrared absorption, or to electrolysis and other electrical methods, for the following reasons:

- (1) The absolute amount of moisture can be determined without a working curve (in the case of coulometric titration). Moisture content can be determined accurately, even where moisture is present at levels of only a few ppm.
- (2) Measurements can be taken over short periods of time.
- (3) Measurements can be taken using small samples (from a few mg to a few gm).
- (4) The method can be used with liquid, solid and gaseous samples.
- (5) The method is suitable for unstable substances that can alter when heated.

Mitsubishi Chemical Corporation and Karl Fischer Reagents

Mitsubishi Chemical Corporation recognized early on the advantages of the Karl Fischer reagent, when it was introduced into Japan in the postwar era. The company began to investigate this in 1950. It subsequently developed Karl Fischer reagent SS, a single solution with stable titer that could be used by anyone in factory research or analytical laboratories. It also developed and supplied a variety of dehydrating solvents for use with various types of samples. In addition, Mitsubishi Chemical Corporation developed simple methods for measuring the moisture content of various substances and manufactured products. With each new methodology, the company endeavored to promote the use of the Karl Fischer titration method through papers for scientific symposiums and society journals (about 60 to date). In 1985, Mitsubishi Chemical Corporation developed a new Karl Fischer reagent without the pyridine odor. The new pyridine-free products were named the "S-Series". The company continues to respond to the needs of its customers. In 1992, it added the X-Series products, which do not contain carbon tetrachloride or chloroform, to its range of coulometric reagents. This manual has been written to provide basic information on Karl Fischer

reagents and analytical methods. As we want this manual to have immediate application, we have used the Q&A approach to make it easy to find needed information. We hope that this manual will become a useful reference guide and one that will serve to build and improve knowledge of our range of Karl Fischer reagent products.

- (1) Fischer, K.; *Angew. Chem.*, 48,394 (1935).
- (2) Smith, D.M., Bryant. W.M.D., Mitschell; J.; *J.Am.Chem.Soc.*, 61,2407 (1939).
- (3) Verhoef, J.C.; *J. Electroanal.Chem.*, 71,305 (1976), 75,705 (1977).

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Chapter I: Basic Knowledge

Chapter I: Basic Knowledge

I-1. Questions & Answers about Karl Fischer Reagents

1. Karl Fischer Titration

Q1 | What are the other methods currently available for the measurement of moisture content? Please explain how these differ from Karl Fischer titration?

There are many ways of measuring moisture content. Methods based on new principles are still being announced. The following table lists the primary methods in current use. Karl Fischer titration is regarded as the most useful of these methods by virtue of its wide applicability and its capacity to measure absolute values. It is the focus of continuing research.

| Measurement method | Measuring range | Applications | Interfering substances |
|---|------------------|------------------------|--|
| Karl Fischer titration | A few ppm - 100% | gases, liquids, solids | Oxidizing, reducing substances |
| Drying | 0.01% | solids | Volatile substances, unstable substances |
| Azeotropic distillation | 0.05% | liquids | Volatile water-soluble substances |
| Colorimetric method | 0.1-a few % | solids, liquids | Colored substances |
| Infrared absorption | 0.01-a few % | gases, liquids, solids | Alcohol, amine, etc. |
| Gas chromatography | ppm-a few % | gases, liquids | Substances with the same retention capacity |
| Dew point method | ppm-a few % | gases | Condensable substances |
| Electrolysis | 1-1000ppm | gases | ROH, RCHO, NH ₃ , HF |
| Electric resistance (Conductimetric method) | 0.3%-a few % | gases, liquids | Conductive substances |
| Dielectric constant method | 1-a few % | gases, liquids | Substances with high dielectric ratios |
| Neutron scattering method | a few % | solids | Substances containing hydrogen |
| Quartz oscillation method | 1-1000ppm | gases | Substances that react with sensing membranes |

Q2 | Please explain briefly how moisture content is measured using Karl Fischer reagents?

1. Methods

There are two methods based on the use of Karl Fischer reagents, or Karl Fischer titration, to measure moisture content.

- (1) Volumetric titration
- (2) Coulometric titration

Your choice should reflect a proper understanding of each method. It is also essential to use the appropriate reagent in each case. The following table compares the characteristics of each method.

| Item | Volumetric titration | Coulometric titration |
|--------------------|---|---|
| Principle | A method of volumetric analysis used to determine moisture content from the titrated amount of Karl Fischer reagent | Iodine produced through electrolytic oxidation undergoes a KF reaction with water. Moisture content is determined by measuring the amount of electricity required to the point where excess iodine is produced. |
| Titration reagents | Karl Fischer reagent and titration solvent (dehydrated solvent) | Analyte and catholyte |
| Characteristics | <ul style="list-style-type: none"> 1) Since a Karl Fischer reagent is used as the titration agent, the titer must be known in advance. 2) A wide range of reagents can be used as various dehydrating agents are available. 3) The method can be used to measure moisture content across a wide range. However, it is not suitable at the microgram level. | <ul style="list-style-type: none"> 1) The factors measured are current and time. Since electrons act as the titration agent, a standard solution is not required. The method allows measurement of absolute quantities based on the Faraday constant. 2) The same analyte can be used repeatedly. 3) The method is effective for measuring minute amounts of water. Electricity can be measured in tiny increments, so it is possible to measure water in quantities of a ug |

2. Titration Equipment

With Karl Fischer titration, electrical detection methods are used to determine the end point. It is important to use the following types of titration equipment.

Volumetric titration : Automatic volumetric moisture meter

Coulometric titration : Automatic coulometric moisture meter

There are now convenient automatic moisture measurement systems designed for ease of operation.

As Karl Fischer reagents are affected by atmospheric moisture, an airtight titration cell must be used.

For your information

1. Unlike standard volumetric analysis, it is not possible with Karl Fischer titration simply to fill a buret with Karl Fischer reagent and add it one drop

- at a time to a flask or beaker that is exposed to the air. Since Karl Fischer instantly reacts with atmospheric moisture, the end-point would never be reached.
2. At present there is no method that allows the color change at the end-point of Karl Fischer titration to be detected visually. The only method is to detect minute amounts of surplus iodine electrically.

Helpful hint -1

How is the end-point detected electrically?

The volumetric and coulometric titration systems currently on the market employ controlled current voltage detection (constant-current polarization voltage detection). A constant current of 1-30 μ A is applied to two platinum electrodes, and the end-point is detected by measuring the voltage (polarization voltage) between the electrodes. If the titration solution has a relatively high water content, a polarization voltage of 300-500mV will be produced. The voltage varies according to the type of solvent used and the sample. In general, high voltages are produced in the case of substances with low conductivity, such as hydrocarbons.

As the Karl Fischer titration continues and the end-point approaches, the voltage will suddenly drop to 10-50mV. With volumetric analysis, the end-point is deemed to have been reached after the voltage has remained at this level for a specific period of time. With commercially available titration systems, the period is 30-60 seconds. With coulometric analysis, an end-point voltage is specified, and the end-point is reached when the voltage falls below that level.

Q3 | Could you outline the principle and procedures involved in volumetric titration?

[Principle]

Karl Fischer titration is a volumetric analysis method that takes advantage of the fact that iodine contained in Karl Fischer reagents reacts quantitatively and selectively with water, as shown in the following formula.



The quantification is based on the stoichiometrical principle that 1 mole of iodine (254g) reacts with 1 mole of water (18g). In practice, the titer of a Karl Fischer reagent is expressed as a water equivalent. Unlike normal volumetric analysis methods, the concentration of iodine is not shown. For example, Mitsubishi Chemical's SS-X Karl Fischer reagent is adjusted so that 1ml will react with approximately 3mg of water, which means that the solution contains approximately 42mg of iodine and has a 3mg titer. Once the water equivalent of a Karl Fischer reagent is known, it is possible to determine moisture content from the amount used (titrated).

Memo "Titer"

This value is used to determine the quantity of a substance from the amount of reagent titrated. It shows the equivalent amount of water per unit of volume and is usually expressed as mgH₂O/ml.

[Procedures]

- A dehydrated solvent suitable for the sample is placed in a flask attached to an automatic volumetric moisture meter (Figure 1).
- The Karl Fischer reagent is titrated until all water has been eliminated from the titration flask. (It is not necessary at this time to read the amount titrated.) The titer of the Karl Fischer reagent is determined using water, etc.
- The sample is added.
- The Karl Fischer reagent, the titer of which (mgH₂O/ml) has now been determined, is titrated until the end-point is reached. The end-point is detected electrically by means of a detection circuit built into the titration system.
- Moisture content is determined from the amount titrated according to the

following formula:

$$\text{Moisture content (\%)} = \frac{\text{Titration quantity (ml)} \times \text{titer (mgH}_2\text{O/ml)}}{\text{Sample quantity (g)} \times 1000} \times 100$$

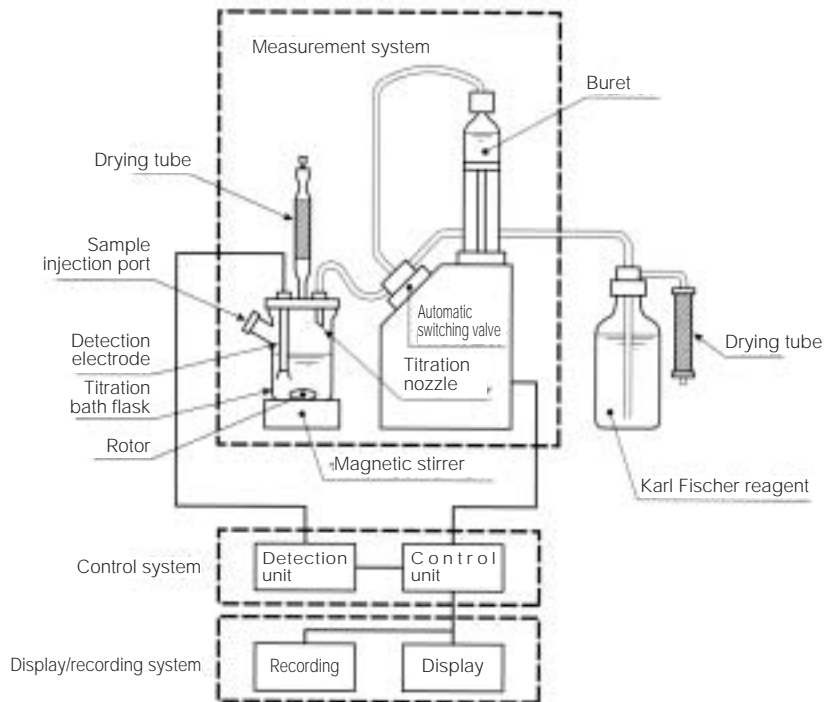


Figure 1: Automatic Volumetric Moisture Titration System

Q4 | Please outline the principles and procedures involved in coulometric titration.

[Principle]

With coulometric titration, electrolytic oxidation is achieved by adding the sample to an iodide ion solution, instead of the iodine contained in the Karl Fischer reagent and used as the titration agent for volumetric titration. As shown in the following formula, electrolytic oxidation produces iodine at the anode. The electrolytic solution immediately begins to act as a Karl Fischer reagent and reacts with the water in the sample. At the end of the process, the excess iodine can be detected electrically.



According to Faraday's laws, the iodine is produced in proportion to the quantity of electricity. This means that the water content can immediately be determined from the Coulombs required for electrolysis. To produce 1 mole of iodine requires 96485×2 Coulomb {current (amperes) \times time (seconds)}. Since 1 mole of iodine reacts with 1 mole of water, the amount of electricity required to cause a reaction with 1mg of water will be as follows.

$$96485 \times 2/18020 = 10.71 \text{ Coulombs}$$

This means that if electrolysis takes 1 second with a current of 107mA, the amount of water can be quantified as 10ug. Normally, titration systems sold over the counter carry out electrolysis at 300-400mA. This design allows titration at the rate of about 30ug per second.

Memo " Faraday's Laws "

The laws relate to electrolysis.

- (1) The mass of an electrolyzed substance deposited on an electrode is proportionate to the amount of electricity.
- (2) The quantity of a substance deposited by a given amount of electricity is proportionate to its chemical equivalent weight.

Faraday constant = 96485 C/mol

[Procedures]

- Electrolyte solutions (Aquamicron AX and CXU) are introduced into the anode and cathode chambers of an electrolysis cell (Figure 3) attached to an automatic coulometric moisture meter (Figure 2).
- An electrolytic current is passed through the anolyte as it is stirred in the anode chamber. All water is removed from the electrolysis cell by producing iodine until the end-point is reached. (It is not necessary at this time to read the amount titrated.)
- The sample is then introduced, and the electrolysis process is started again. Coulometric titration is continued until the end-point is reached. The end-point is detected electrically by means of a detection circuit built into the titration system.
- Moisture content is automatically calculated from the amount of electricity required for electrolysis in the automatic coulometric moisture meter. The amount of water is expressed in ug units.

$$\text{Moisture content (ppm)} = \frac{\text{Measured value (ug)}}{\text{Quantity of sample (g)}}$$

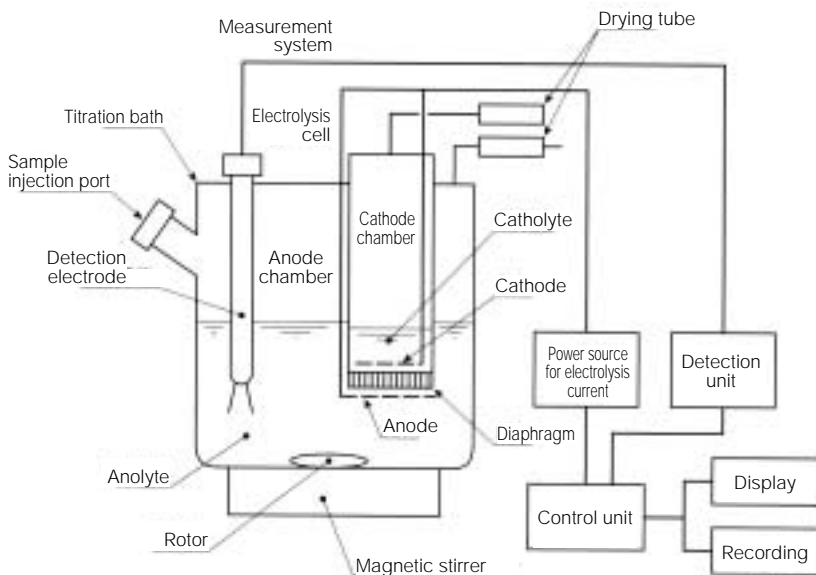


Figure 2: Automatic Coulometric Moisture Meter

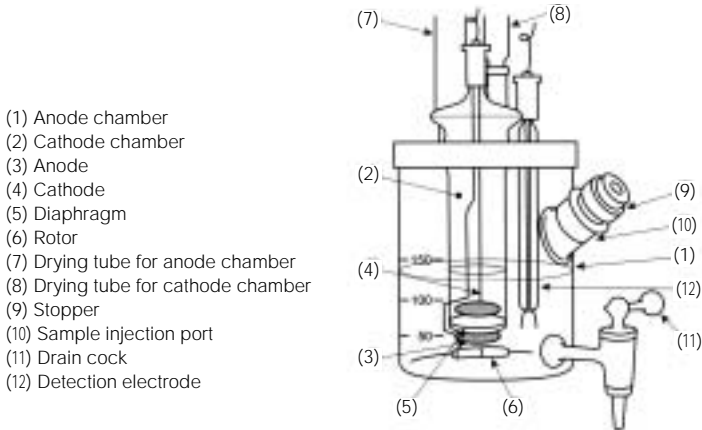


Figure 3: Electrolysis Cell

Helpful hint - 2

Are there any criteria to guide the choice between volumetric and coulometric titration?

The following factors should be taken into account when making this decision.

(1) Using the characteristics of coulometric titration

The need to check titer is eliminated, since it is not necessary to standardize the Karl Fischer reagent. This feature is very useful for reducing the work involved in everyday analysis tasks.

(2) Moisture content as a criterion

Coulometric titration should be used if the moisture content is 1% or lower. It is especially useful for measuring moisture content at the ppm level within tolerances of a few ppm.

Coulometric titration can still be used if the moisture content is higher than about 1%, but it is necessary to use small samples, and analysis results will be influenced by weighing error. Normally volumetric titration is used in such cases.

(3) Electrode reactions

Coulometric titration is not used for substances that react with

electrodes, such as anilines, diamines and some phenols. Volumetric titration is carried out using a suitable dehydrated solvent.

(4) Solids that do not dissolve in electrolyte

Solids that do not dissolve in organic solvents can reduce current efficiency by obstructing electrodes and diaphragms. In principle, coulometric titration should be avoided in such cases. Use volumetric titration with a suitable dehydrated solvent, or the moisture vaporization method.

Q5 | What is the moisture vaporization method, and when is it used?

[Outline]

The moisture vaporization method is used to measure samples of solids that cannot be dissolved in dehydrated solvents or electrolytes, or samples that include interfering substances. The moisture content is vaporized by heating the sample in a flow of dried nitrogen gas. It is then captured in a dehydrated solvent or electrolyte and subjected to Karl Fischer titration. Either coulometric or volumetric titration is used.

This method is commonly used with natural substances, such as minerals and rocks, and with macromolecules such as polymers and rubber. New areas of use include electronic materials, including printed circuit boards and wafers, and printing materials, such as toners. This method is also useful for petroleum products containing additives, such as lubricants.

Convenient moisture vaporization systems are available commercially to suit various purposes. They can be connected to either volumetric or coulometric titration systems and used to measure moisture content.

[Procedures]

- a) Solid samples
 - i) Nitrogen gas (or air) is first passed through a drying tube (filled with silica gel or phosphorus pentoxide, etc.) and then supplied at a rate of approximately 300ml/min. to an oven that is maintained at a suitable temperature for vaporization.
 - ii) The sample boat is placed in the heating tube and exposed to the flow of nitrogen gas to ensure that the heating system is free of moisture.
 - iii) The sample is immediately placed in the sample boat and inserted into an oven that is maintained at the required temperature.
 - iv) The vaporized moisture is absorbed into a dehydrated solvent in a titration flask (or into an electrolyte in an electrolysis cell).
 - v) The absorbed water is subjected to Karl Fischer titration.

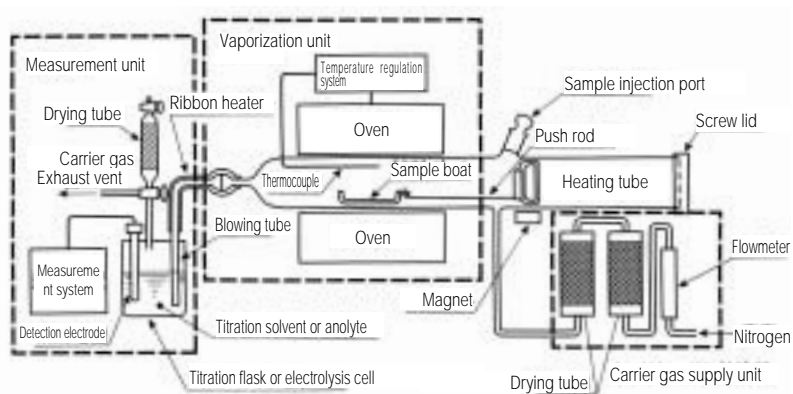


Figure 4: A Moisture Vaporization System (for Solid Samples)

- b) Liquid samples, such as lubricating oils
 - i) Approximately 20ml of a base oil (mineral oil, vacuum pump oil, etc.) is placed in the heating unit of a moisture vaporization system and heated to 100-150°C.
 - ii) The moisture content of the base oil is totally removed by introducing a flow of dried nitrogen gas into the moisture vaporization system at the rate of approximately 300ml/min.
 - iii) 1-10g of the sample is added to the base oil, which is now free of moisture.
 - iv) The vaporized moisture is absorbed into a dehydrated solvent in a titration flask (or into an electrolyte in an electrolysis cell).
 - v) The absorbed water is subjected to Karl Fischer titration.

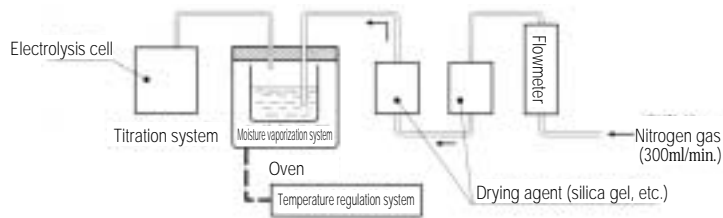


Figure 5: A Moisture Vaporization System (for Lubricating Oils)

! *Helpful hint - 3*

How can we check for accuracy when a moisture vaporization apparatus is added to the system?

The accuracy of capture is an important concern, since moisture vaporized in the moisture vaporization apparatus is carried through the heating tube and blowing tube by means of dried nitrogen gas before being absorbed into a dehydrated solvent (or into an electrolyte in an electrolysis cell). The capture ratio (recovery ratio) can be checked using the following three methods.

(1) Using water

With the water method, which is usually the simplest, 5 or 10ul (5 or 10mg) of water is placed directly into the sample boat using a microsyringe (capacity: 10ul).

(2) Sodium tartrate dihydrate method (theoretical moisture content: 15.66%)

When using this method, the sodium tartrate dihydrate must first be dried at 105°C.

(3) Glass capillary pipette method

The glass capillary pipette method is simple and is suitable for checking amounts in the order of 1,000ug. Glass capillary pipettes are commonly used in biotechnology fields, and their capacities are extremely precise. They provide an easy way to obtain a required volume of water by means of the capillary phenomenon.

Reference:Bunseki, p587, 1995

2. Karl Fischer Reagent Products

Q6 | What volumetric titration reagents are available? Please explain the types of reagents and their uses, and the methods employed.

Mitsubishi Chemical Corporation has a range of products to suit every purpose. Its products can be broadly divided into the following four categories.

- Mitsubishi Karl Fischer Reagents
Titrant
Can be used in various titer according to anticipated moisture content
- Mitsubishi Dehydrated Solvents
They are suitable as titration solvents for the Karl Fischer reaction, to dissolve or disperse a sample in order to extract water.
- Mitsubishi Standard Water Methanol
This is used to determine the titer of a Karl Fischer reagent.
The type used depends on the titer. Water methanol can also be used a titration agent for back titration.
- Mitsubishi Standard Liquid
This is used to determine the titer of a Karl Fischer reagent.

Karl Fischer reagents and dehydrated solvents have traditionally been available in both pyridine types and pyridine-free types, which do not have the pyridine odor. There is no significant difference in performance between the two types, and they can be used interchangeably.

1. Karl Fischer Reagent SS-Z, SS

Initially the titer of Karl Fischer reagents was unstable, and it was necessary to use them in the extremely inconvenient form of binary solutions. Mitsubishi Chemical was the first manufacturer in the world to perfect a single solution version, which it called "Karl Fischer Reagent SS". In the 50 years since that time, Mitsubishi Chemical has continued to enhance and expand its technology, and today enjoys an excellent reputation for its superior products.

Mitsubishi Chemical has also developed Karl Fischer Reagent SS-Z, which is pyridine-free and does not contain chloroform or methyl cellosolve. Users can choose from an extensive product range, as listed below.

| Product | Purpose | Titer | Applications | Packaging |
|--------------------|--|--------------|--|-------------------|
| SS 10mg | Samples with high moisture content (40% or higher) | 8-12mg/ml | Foodstuffs, Cosmetics Detergents, etc | 500ml bottles |
| SS-Z 5mg | General normal samples | 4.5-5.5mg/ml | General samples, Organic solvents | 500ml, 1L bottles |
| SS-Z 3mg SS 3mg | General normal samples | 2.5-3.5mg/ml | General samples, Organic solvents | 500ml bottles |
| SS-Z 1mg SS 1mg | Samples with low moisture content (0.1% or lower) | 0.7-1.2mg/ml | Organic solvents, Petroleum products, Gas products | 500ml bottles |

Karl Fischer Reagent SS-Z: Pyridine-Free and Methyl Cellosolve-Free Types

Instead of pyridine, Karl Fischer SS-Z contains a solid amine. As a result, the product is free of the pyridine odor. All the ingredients required to implement Karl Fischer reactions stoichiometrically are included in a single solution. The product is available in either 5mg/ml, 3mg/ml or 1mg/ml titer.

[Characteristics]

- a) The titer is stable. Even when stored properly under air-tight conditions, Karl Fischer reagents tend to lose titer due to self-reaction. With SS-Z, the titer remains extremely stable and changes at less than 0.05% per day even when stored at room temperature.
- b) SS-Z is suitable even for moisture titration of ketones, which have an interfering effect. SS-Z does not contain methanol, which reacts with ketones. The moisture content of ketones can be measured easily by using SS-Z in combination with the Dehydrated Solvent KTX. (For aldehydes, use SS in combination with CP or PP Dehydrated Solvent).
- c) SS-Z Karl Fischer reagent is available in three titers to suit samples with different moisture contents. The 3mg/ml product is generally regarded as a standard type and should be used first.

KarlFischer Reagent SS: Pyridine Type

Karl Fischer Reagent SS is the traditional product containing pyridine. Its performance is similar to that of Karl Fischer Reagent SS-Z. It is available in a titer of 10mg/ml, making it suitable for samples with a high moisture content.

For Your Information

Mitsubishi Chemical's series of Karl Fischer reagents are supplied in brown glass bottles sealed with lids containing packing. Provided that the bottles are sealed, they can be stored for long periods with only a minimal decline in titer due to moisture absorption. Once the seal is broken, however, moisture absorption could cause titer to decline unless storage conditions are optimal. Care should be taken to close caps tightly.

Karl Fischer Reagent SS is a high-titer product and maintains a stable titer over long periods. Depending on the storage environment, however, minute amounts of sediment may be observed. This has no effect on the effectiveness of the reagent, which can be still used.

 Helpful hint - 4

What is the difference between traditional pyridine products and non-pyridine products?

Pyridine-free types use another amine in place of pyridine as the base. Pyridine requires special handling because of its strange odor. Pyridine-free products use a liquid or solid amine with a high boiling point in place of pyridine.

Apart from the base, the composition of pyridine-free types is virtually the same as traditional products, and safety requirements are identical. Furthermore, it has been confirmed that the performance of pyridine-free types is not significantly different from that of traditional types.

The speed of the Karl Fischer reaction varies according to the pH of the titration liquid, the concentration of sulfur dioxide, the type of organic solvent used, the amount of sample added, and changes in the matrix. It is not possible to generalize about the relative speeds of traditional and pyridine-free products, which should be considered on a case-by-case basis.

2. Mitsubishi Dehydrated Solvents

Moisture content measurement using Karl Fischer Reagent SS or SS-X involves the extraction of moisture from a liquid, solid or gaseous sample into a dehydrated solvent from which all moisture has been removed, followed by titration. Ideally, titration solvents should have low moisture content and contain no impurities. However, it is extremely troublesome and time-consuming to refine solvents through distillation and dry them before each use. Mitsubishi Chemical has solved this problem by developing a range of dehydrated solvents so that a solvent suitable for each type of sample will always be available.

In terms of applications, dehydrated solvents can be broadly categorized into those used to dissolve samples and those used to prevent interference reactions. These are shown in the following table. Users should select a solvent that is suitable for the samples.

(1) Mitsubishi Dehydrated Solvents for Use in Dissolving Specimens

A commonly used titration solvent is methanol, which has a large polarity and considerable capacity to extract water. However, a titration solvent to which other solvents have been added is desirable for substances that do not readily dissolve in methanol. Mitsubishi Chemical offers a range of blended solvents to suit user requirements. Please choose the type that is suitable for the characteristics of the sample. With some exceptions, most of the products are blended at 0.2mg/ml or lower.

| Principal ingredients | Name | Use | Packaging |
|-----------------------------|---------------------------------|-------------------------------------|---------------|
| Methanol | GEX (pyridine-free) MS ML | General samples | 500ml bottles |
| Methanol Chloroform | OL II (pyridine-free) CM | Petroleum products Oils and fats | 500ml bottles |
| Methanol Formamide | SU (pyridine-free) FM | Sugars, proteins Food additives | 500ml bottles |
| Methanol Ethylene glycol | ME | Gases Inorganic salts | 500ml bottles |

Dehydrated Solvents GEX and MS

The solvent most commonly used to extract water from samples is methanol. The main ingredients of Dehydrated Solvents GEX and MS is methanol that has been thoroughly dehydrated. In general, these products can be used immediately to measure moisture content. In addition, a reaction accelerator has been added to make the reaction between Karl Fischer reagent and water occur more rapidly than with ordinary methanol. This allows measurements to be taken quickly and with a clear titration end-point.

[Uses]

Organic solvents (n-heptane, cyclohexane, xylene, toluene, benzene, ethyl acetate, N,N-dimethylformamide, etc.), inorganic chemicals, pesticides, pharmaceutical products, fertilizers, synthetic detergents, refrigerants, foodstuffs, etc.

[Characteristics]

- a) Minute amounts of water can be measured accurately.
- b) The reaction between water and the Karl Fischer reagent occurs rapidly.
- c) The end-point can be readily determined and measured over a short period of time.
- d) By first adding salicylic acid, it is possible to measure the moisture content of amines (strong basicity).

Reference: Muroi, K., Ono, M., Bunseki Kagaku 20, 975 (1971).

Dehydrated Solvents OL II and CM

Dehydrated Solvents OLII and CM are mixtures of dehydrated chloroform and dehydrated methanol, to which a reaction accelerant has been added. Applications include petroleum-related JIS and ASTM tests. These dehydrated solvents are ideal as solvents for petroleum products. They can also be used to dissolve resins, pharmaceutical products, rubber and other substances and can sometimes be used as titration solvents for these items.

[Characteristics]

- a) Petroleum products, resins and adhesives dissolve well in these products.
- b) The reaction between water and the Karl Fischer reagent occurs faster than with ordinary solvent mixtures.
- c) The end-point can be readily determined and measured over a short period of time.

[Applications]

Crude oil, electrical insulating oil, refrigerator oil, diesel oil, naphtha, gasoline, resins, adhesives, pharmaceutical products (caffeine, lecithin, ointments), printing inks, etc.

Dehydrated Solvents SU and FM

In the past the moisture content of sugars and foodstuffs was measured through drying at normal or low pressures. Measurement required long periods of time with these methods, however, and samples were frequently affected by heat decomposition. These drawbacks meant that the results did not always reflect the true moisture content. Measurements could not easily be taken even with the Karl Fischer method, since there was no suitable extraction solvent. Dehydrated Solvents SU and FM developed by Mitsubishi

Chemicals are mixtures of dehydrated formamide and dehydrated methanol, to which a reaction accelerant has been added. Substances that dissolve well in the main ingredient, formamide, include casein, glucose, starch and lignin. These solvents are therefore ideal for use in the extraction of moisture from sugars and foodstuffs.

[Characteristics]

- a) Sugars and protein dissolve well in these products.
- b) The reaction between water and the Karl Fischer reagent occurs rapidly.
- c) The end-point can be readily determined and measured over a short period of time.

[Applications]

Sugars (sugar, drops, caramel, butter sweets, black sugar sweets, malt syrup, syrup), gelatin (medical capsules, etc.), nucleic acid food additives, pharmaceutical products, dried vegetables, cereals, animal feeds, wool, etc.

Reference: Muroi, K., Tsutsui, C., Koizumi, H., Nihon Shokuhin Kogyo Gakkaishi 16, 39 (1969).

Dehydrated Solvent ME

The moisture content of gases can be measured indirectly using the physical or physical-chemical characteristics of water (see Q1), or by means of the Karl Fischer method, which involves a direct reaction with the water. The Karl Fischer method is the more reliable, since the water is captured directly. It is widely used as the standard method and has been included in the JIS system and other systems.

Dehydrated Solvent was created as a moisture capturing solvent for use with gases. It is a mixture of dehydrated methanol and dehydrated ethylene glycol, to which a reaction accelerant has been added. Moisture content can be measured easily and accurately by passing a certain amount of gas through about 100ml of Dehydrated Solvent ME, followed by immediate titration using a Karl Fischer reagent.

Similar measurements can be obtained with a solvent prepared simply by mixing Dehydrated Solvent GEX or MS with propylene glycol in the ratio of 3:1 (by volume).

[Characteristics]

- a) The moisture content in gases can be captured completely, and there is minimal vaporization of the solvent even when large volumes of gas are passed through it.
- b) The reaction between water and the Karl Fischer reagent occurs rapidly.
- c) The end-point can be readily determined and measured over a short period of time.

[Applications]

Inorganic gases (hydrogen, nitrogen, oxygen, argon, helium, etc.)
 hydrocarbons (ethylene, acetylene, propylene, propane, butane, etc.)
 Vaporization solvent for plastics, minerals, greases, lubricants, etc. Also excellent for use with inorganic salts, which dissolve readily in this product.

Reference: Muroi, K., Ono, M., Sekiyu Gakkaishi [Journal of Japan Petroleum Society] 11 (No. 6), 440 (1968).
 K. Muroi, Bunseki Kagaku 20, 975 (1971).

(2) Dehydrated Solvents used to Prevent Interference Reactions

Aldehydes or ketones that include active carbonyls cause interference reactions by reacting with methanol to produce water (see Q8). To prevent such reactions and measure moisture content accurately, it is necessary to use a dehydrated solvent designed for use with ketones. The same dehydrated solvent can be used with lower carboxylic acid, which causes a similar reaction. Reactivity varies according to the specific substance and users should be aware that there are limitations on the size of the samples that can be measured.

| Principal ingredients of solvent | Name | Use | Packaging |
|--|--------------------|---|---------------|
| Propylene carbonate Diethylene glycol monoethyl ether | KTX(pyridine-free) | Ketones Lower carboxylic acid | 500ml bottles |
| Chloroform Propylene carbonate | CP | Ketones Lower carboxylic acid Silicone oils | 500ml bottles |
| Pyridine Ethylene glycol | PE | Special-purpose paints and varnishes | 500ml bottles |
| Pyridine Propylene glycol | PP | Aldehydes | 500ml bottles |

Dehydrated Solvents KTX and CP

The method usually employed to measure the moisture content of substances that react with alcohol, such as ketones and silicon oils, involves the use of glycolic solvents which show relatively low reactivity, where generally used, at low temperatures. Dehydrated Solvent KTX is a pyridine-free titration solvent produced by mixing dehydrated propylene carbonate and diethylene glycol monoethyl ether. It should always be used in conjunction with Karl Fischer Reagent SS-Z. It cannot be used with aldehydes.

The main ingredients of Dehydrated Solvent CP are chloroform and propylene carbonate. With this blended solvent, the moisture content of substances such as ketones, aldehydes (except acetaldehydes) and silicone oils can be measured easily at room temperature.

[Characteristics]

- a) These solvents limit interference reactions with methanol, allowing ketones, aldehydes (except acetaldehydes), carboxylic acid, etc., to be measured at room temperature.
- b) These products can be used with aminobenzene group and are especially suitable for direct titration of aniline.
- c) These products can be used to measure trace moisture in silicone oils.

[Applications]

Acetone, methyl ethyl ketone, methyl isobutyl ketone, etc.

Propionaldehyde, butyraldehyde, crotonaldehyde, etc.

Aniline, cresidine, toluidine, anisidine, etc.

Silicone oils

Dehydrated Solvent PE

Dehydrated Solvent PE is a mixture of dehydrated pyridine and dehydrated ethylene glycol, to which a reaction accelerator has been added. It is used at the amount of no more than 15ml of sample to 30ml of PE, accompanied by direct titration using Karl Fischer Reagent SS. With this product it is possible to suppress the interference reaction that is caused by ketones and to measure moisture content accurately. The solubility of pyridine, which is one of the main ingredients, also allows the product to be used for special applications, such as paints.

[Characteristics]

- a) This solvent allows direct titration of ketones and lower carboxylic acid.
- b) PE can be used as a titration solvent for paints, varnishes, etc.
- c) With this product the reaction between water and the Karl Fischer reagent occurs rapidly.
- d) The end-point can be readily determined and measured over a short period of time.

[Applications]

Acetone, cyclohexanone, methyl ethyl ketone, methyl isobutyl ketone, acetic acid, paints, varnishes, etc.

Reference: Muroi, K., Ogawa, K, Bunseki Kagaku 12, 963 (1963).

Dehydrated Solvent PP

Dehydrated Solvent PP is a mixture of dehydrated pyridine and dehydrated propylene glycol. As a result of work carried out by Mitsubishi Chemical in relation to active aldehydes, which present the greatest problem in terms of accurate measurement of moisture content, it is now possible to suppress two interference reactions (see Q9) and achieve precise measurement through direct titration with Karl Fischer Reagent SS, simply by adding no more than approximately 1ml of sample to 25ml of Dehydrated Solvent PP. In the case of acetaldehydes, which are the most active, about 5ml of sample is added to 25ml Dehydrated Solvent PP. The resulting mixture is then expelled with dried nitrogen and titrated.

[Characteristics]

This solvent allows direct titration of active aldehydes.

[Applications]

Acetaldehydes, n-butyraldehyde, iso-butyraldehyde, propionaldehyde, crotonaldehyde, other higher aldehydes

Reference: Muroi, K., Bunseki Kiki 3 (No.11), 40 (1965).

3. Standardization Reagents of Karl Fischer reagents

The titer of Karl Fischer Reagent SS-Z and SS can be standardized using water, standard water-methanol, standard water solution and sodium tetrataurate dihydrate. The most commonly used methods are those involving water, standard water-methanol and standard water solution. Standard water-methanol is also used as a titration agent for back titration. The following three standard water-methanol and standard water solution products are available.

| Product | Application | Packaging |
|-------------------------------------|---|------------------|
| Standard water-methanol 2.0mg/ml | Standardization of Karl Fischer reagents with titer of 3~10mg/ml, reverse titration | 250ml bottles |
| Standard water-methanol 0.5mg/ml | Standardization of Karl Fischer reagents with potency of 1mg/ml | 250ml bottles |
| Aquamicon standard water 10mg | Standardization of Karl Fischer reagents with titer of 1~10mg/ml | 10-ampoule cases |

- a) Standard water-methanol must be stored in such a way that it cannot absorb moisture from the atmosphere.
- b) Once the seal is broken the moisture content may change because of atmospheric humidity.
The product should be re-standardized before use as a back titration.

Helpful hint -5

Why is salicylic acid used to suppress the interference reaction caused by amines with strong basicity (pKa9 or higher)?

Interference reactions are observed when amines with strong basicity (pKa9 or higher) undergo direct Karl Fischer titration. Consequences of these reactions can include unstable end points and higher than normal analytical readings. To suppress these reactions, samples are first treated with acids to reduce the basicity. Traditionally, acetic acid was used, but this tended to trigger a reaction producing esters. Other problems include the fact that acetic acid itself has a high moisture content. Studies concerning the use of salicylic acid yielded promising results and the following advantages were identified.

- a) No esterification reaction during normal titration.
- b) Since methanol can be used as the titration solvent, Karl Fischer titration yields good results.
- c) Salicylic acid has a low moisture content.

The fact that salicylic acid is a solid, is a drawback. However, preparation simply involves the measurement of about 10g of salicylic acid into a titration flask and the addition of 50ml of Dehydrated Solvent GEX (or MS), then stirring until dissolved. Up to 70mmol of amines can be measured with 10g of salicylic acid.



Q7 | What coulometric titration reagents are there? Please explain the types of reagents and their uses, and the methods employed.

Mitsubishi Chemical Corporation offers a range of coulometric titration reagents to suit user requirements. These products can be broadly categorized into the following four types.

- General-purpose electrolytes (two types)
These are general-purpose reagents for use with normal samples.
- Ketone electrolyte (one type)
This is used with ketones and lower carboxylic acid, etc.
- Check solution (one type)
This product is used for end point checking.
- Standard liquid (two types)
This reagent is used to check the moisture meters used in coulometric titration.

Advice to Users

Electrolytes are of two types; anolyte, which is placed in the anode chamber of the electrolysis cell, and catholyte, which is placed in the cathode chamber. Both these products form one pair.

Characteristics of the Aquamicron Series

When using the Aquamicron Series of electrolytes it is important to understand the following characteristics of the products.

- a) Very small quantities of water (about 10ug) can be measured accurately.
- b) Titration procedures are very simple.
- c) Measurements can be carried out quickly (1-10 minutes).
- d) It is not necessary to assess the titer of the reagent.
- e) The reagent can be used repeatedly.
- f) The composition of the solvents has been enhanced to make them suitable for immediate use with various samples. This eliminates the troublesome task of adding other solvents.

1. General-Purpose Electrolytes

The general-purpose Aquamicron Series of products are ideally constituted to facilitate Karl Fischer reactions with solvents, including methanol and propylene carbonate. Sample solubility is excellent, and even trace amounts of moisture can be extracted and titrated coulometrically with ease. These products also offer superior reagent stability, which is the most important requirement when measuring minute amounts of water. This means that measurements can be taken with good reproducibility.

The Aquamicron Series is suitable for a wide range of products including aromatics and other organic solvents, petroleum products, inorganic products and gas products.

They are also the ideal reagents for the water vaporization method. A particularly convenient feature is the fact that they can be used immediately without the need to add other solvents. Aquamicron products have an excellent reputation for use in day-to-day moisture measurement for plastics and other solid samples.

| Product | Type | Packaging |
|---|----------------------|---|
| Pyridine-free, chloroform-free Aquamicron AX Aquamicron CXU | Anolyte Catholyte | 500ml glass bottles 5ml ampoules (10 per case) |
| Pyridine-free Aquamicron AS Aquamicron CXU | Anolyte Catholyte | 500ml glass bottles 5ml ampoules (10 per case) |

2. Electrolytes for use with Ketones

Ketones are used as industrial solvents and for many other purposes. Specially prepared Aquamicron products that do not contain methanol must be used for ketones because they trigger an interference reaction with the methanol in general-purpose Aquamicron products. The same specially prepared products are also excellent for use with lower carboxylic acid, which causes an esterification reaction with methanol.

Aquamicron products prepared for use with ketones can also be used with usual chemical substances such as alcohols. They should not be used with non-polar hydrocarbons or halogenated hydrocarbons which have low permittivity.

| Product | Type | Packaging |
|---|----------------------|---|
| Pyridine-free, chloroform-free Aquamicron AKX Aquamicron CXU | Anolyte Catholyte | 500ml glass bottles 5ml ampoules (10 per case) |

[Applications]

Acetone, methyl isobutyl ketone, methyl ethyl ketone, cyclohexanone, silicon oils, acetic acid, dichloroacetic acid, etc.

Reference: Muroi, K., Fujino, H., Sekiyu Gakkaishi [Journal of Japan Petroleum Society] 26, 97 (1983).

3. Check Solution P

Check Solution P is a solution of organic solvent containing a trace amount of water (approximately 4mg/ml). It is used to adjust the end point of coulometric titration by providing surplus water when free iodine is produced in the electrolytes. It can also be used for day-to-day inspections of coulometric titration systems. Since methanol is not used as the organic solvent, this product can also be used with both general-purpose Aquamicon products and products prepared for use with ketones.

| Moisture Content | Packaging |
|------------------------------|--------------------------------------|
| 3.8-4.2mgH ₂ O/ml | 100ml glass bottles with septum caps |

[Method of Use]

A red tinge in the anolyte solution indicates the presence of free iodine. Normally, the measurement of moisture content cannot be initiated. In such cases, Check Solution P is added to the anolyte as required (until the red tinge disappears) to supply surplus water and turn all of the iodine into iodide ions. The end point for the anolyte solution can be fine-tuned by adding Check Solution P in 100ul increments until the red tinge disappears. Titration is then started.

Check Solution P can also be used for day-to-day verification of moisture meter. This is done by precisely measuring the moisture content of the Check Solution P itself.

4. Water Standard Solution

Aquamicon Water Standard Solution is a water solution containing a standard amount of water. It is used to verify coulometric moisture meters and to determine the titer of KF reagents when used in volumetric moisture meters. The following products are available.

| Product | Application | Packaging |
|--------------------------------|--|----------------------------|
| Aquamicon Water Standard 0.2mg | Verification of moisture meters (coulometric titration) | 5ml ampoules (10 per case) |
| Aquamicon Water Standard 1mg | Verification of moisture meters (coulometric titration) | 5ml ampoules (10 per case) |
| Aquamicon Water Standard 10mg | Determination of titer of KF reagents (volumetric titration) | 8ml ampoules (10 per case) |

3. Applicability of Karl Fischer Titration

Q8 | What substances is Karl Fischer titration suitable for?

One of the most useful characteristics of Karl Fischer titration is its extremely wide range of applications.

○Organic compounds:

Karl Fischer titration can be used with almost all compounds.

○Inorganic compounds:

The scope of application is limited for a number of reasons, including the fact that inorganic compounds are generally difficult to dissolve in organic solvents and the fact that many react with Karl Fischer reagents. For this reason, the measurement of moisture content in inorganic compounds is commonly carried out using either the drying method or other procedures. However, the Karl Fischer method is useful for compounds that contain volatile substances and for compounds that are amenable to thermal decomposition.

The following are typical compounds that can be measured directly.

1. Organic compounds

(1) Hydrocarbons

Saturated hydrocarbons, unsaturated hydrocarbons, aromatic hydrocarbons

(2) Alcohols

Monohydric alcohols, polyhydric alcohols, phenols

(3) Ethers

(4) Acids

Monobasic acids, polybasic acids, sulfonic acids, hydroxy acids, amino acids

(5) Esters

Organic acid esters, inorganic acid esters, carbamate esters

(6) Aldehydes

Formaldehyde, chloral

(7) Ketones

I-1. Questions & Answers about Karl Fischer Reagents

Normal ketones, diisopropyl ketone, benzophenone, benzoin, alizarin, quinalization, dibenzalacetone, camphor, etc.

(8) Acetals $\text{RCH}(\text{OR}')_2$

(9) Acid anhydrides $(\text{RC}=\text{O})_2\text{O}$

(10) Peroxides

Dialkyl peroxide

(11) Nitrogen compounds

Amines (pKa9 or lower)

Aminoalcohols

Amides RCONH_2

Nitriles RCN

Azo compounds $\text{RN}=\text{NR}'$

Imines RCHNR' Cyanhydrine $\text{RCH}(\text{OH})\text{CN}$

Oximes $\text{R}_2\text{C}=\text{N}'\text{OH}$

Lactam $\text{NH}(\text{CH}_2)_n\text{CO}$

Isocyanide compounds

Nitroso compounds $\text{R}_2\text{N}-\text{N}=\text{O}$, nitro compounds RNO_2

Cyanic acid derivatives $\text{HOC}=\text{N}$

Hydroxamic acid $\text{RC}-\text{NH}$
 $\begin{array}{c} \parallel \quad | \\ \text{O} \quad \text{OH} \end{array}$

Anilides $\text{C}_6\text{H}_5\text{NHCOR}$

Purines, proteins

(12) Halogenated hydrocarbons

(13) Halogenated acyls

(14) Sulfur compounds

Thioether RSR , disulfides RSSR , thiocyanate compounds RSCN ,
isothiocyanates RNCS , thioesters RCOSR

2. Inorganic compounds

(1) Organic salts and their hydrates

Sodium acetate, potassium oxalate, sodium tartrate, Ammonium acetate, barium acetate, lead acetate, ammonium oxalate, etc.

(2) Inorganic salts and their hydrates

Alkaline salts of strong acids, sulfates, acidic sulfates, disulphates, dithionates, phosphates (I), phosphates (II)

(3) Acids

Sulfur dioxide, hydriodic acid, hydrochloric acid, hydrofluoric acid, nitric acid, sulfuric acid (92% or lower), phosphoric acid

(4) Chelate compounds

Cobalt complexes

(5) Polytungsten salts

Q9 | What is interference in the context of the Karl Fischer titration? Please explain what is meant by interference reactions.

Karl Fischer reagent reacts selectively with water, but its other constituents may react with substances other than water. In such cases, titration may fail to reach an end point, or an abnormal amount of Karl Fischer reagent may be consumed, leading to negative or positive errors in the analysis values. This type of phenomenon is called an interference reaction. It is necessary to be aware of this problem when using Karl Fischer titration.

Interference reactions can be broadly divided into the following two types.

- Reactions with iodine (or iodide ions)
- Reactions with other ingredients of Karl Fischer reaction (mainly methanol, sulfur dioxide)

The following are examples of substances that cause interference, and descriptions of the reactions that occur.

1. Reactions with iodine (or iodide ions)

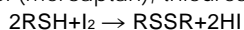
The Karl Fischer method is a form of non-aqueous oxidation-reduction titration. Since the reaction between Karl Fischer reagent and water is a kind of iodometry, it is subject to interference by substances that trigger an oxidation-reduction reaction with iodine and iodide ions. Samples containing substances that react with iodine and iodide ions will therefore produce positive errors in measurements, while those that contain iodine produced through the oxidation of hydriodic acid, which is a reactive substance, will produce a negative error.

(1) Substances that consume iodine (reduction reaction) and cause a positive error

These are substances that react directly with free iodine in the Karl Fischer reagent. Because they consume iodine, they have the same effect as water, which means that the analysis results will be correspondingly higher.

1.1 Organic compounds

- (a) Thiol (mercaptan), thiourea and their nitrogen substitutes



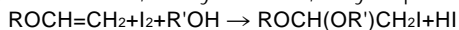
- (b) Hydrazine hydrochloride

Hydrazine hydrochloride reacts on a mole by mole basis with iodine.

- (c) Thio acid



(d) Vinyl ether and 2,3-dihydrofuran, dihydroprane



(e) Ascorbic acid (Vitamin C)

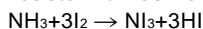
(f) Amines and aminoalcohols (pKa9 or higher)

These consume iodine gradually.

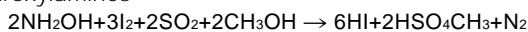
1.2 Inorganic compounds

(a) Ammonia

This reacts with iodine to produce nitrogen iodide

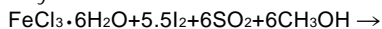


(b) Hydroxylamines



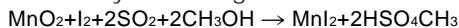
(c) Ferric chloride

Iron(III) salt causes the following reaction, with the result that only 5.5 molecules of water are titrated.

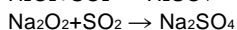
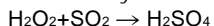


(d) Metal oxides

Manganese dioxide, ferric oxide and lead dioxide react with Karl Fischer reagent. However, the reaction is not quantitatively constant, since these substances do not dissolve readily in the reagent.

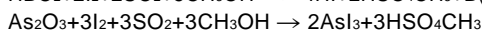
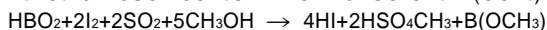
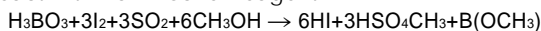


However, interference does not occur with hydrogen peroxide, sodium peroxide, barium peroxide, potassium persulfate or ammonium persulfate, since these substances react selectively with sulfur dioxide.



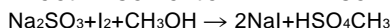
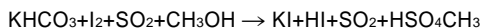
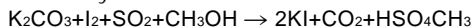
(e) Weak acids and oxides

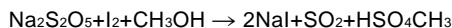
Boric acid, metaboric acid, boron oxide and arsenic trioxide all react with Karl Fischer reagent.



(f) Salts

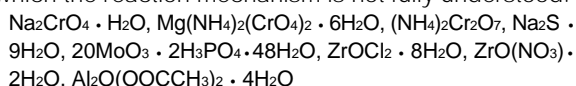
In general, the weakly acidic salts of alkaline metals react with Karl Fischer reagent in the same way as oxides. Carbonates, bicarbonates, sulfites and pyrosulfites react in approximately constant amounts.





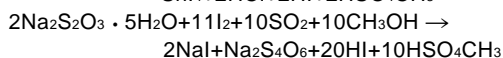
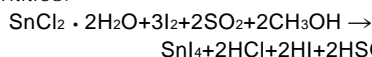
Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) and sodium metaarsenite react in approximately the same quantities as shown in (d).

The following are examples of salts that cause non-quantitative reactions with Karl Fischer reagent, and salts for which the reaction mechanism is not fully understood.

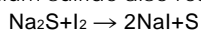


(g) Reducing agents

When strong reducing agents are titrated, the amount of moisture will be higher. Stannous chloride and sodium thiosulfate react with Karl Fischer in approximately constant quantities.



Sodium sulfide also reacts with iodine.



(2) Substances that produce iodine (oxidation reactions) and cause a negative error

(2.1) Organic compounds

(a) Dichloroisocyanuric acid

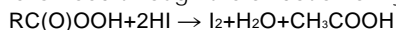
Iodine is freed through the oxidation of hydriodic acid.

(b) Quinone

Iodine is freed through the oxidation of hydriodic acid.

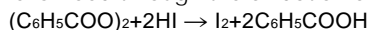
(c) Peroxy acid

Iodine is freed through the oxidation of hydriodic acid.



(d) Peroxides (dialkyl)

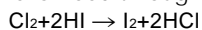
Iodine is freed through the oxidation of hydriodic acid



(2.2) Inorganic compounds

(a) Chlorine

Iodine is freed through the oxidation of hydriodic acid



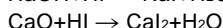
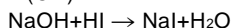
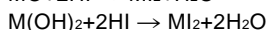
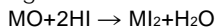
(b) Oxidizing agents

Moisture content appears lower when strong oxidizing agents are measured.

(3) Substances that react with hydriodic acid and produce water

Metal oxides and hydroxides.

Oxides and hydroxides of alkaline metals and alkaline earth metals react in approximately constant quantities with the hydriodic acid in Karl Fischer reagent.



e.g. MgO, ZnO, Ag₂O, HgO, Cu₂O, LiOH, KOH, Ba(OH)₂, etc.

However, weakly acidic oxides react much less.

Substances that do not react at all include Al₂O₃, CuO, NiO and PbO.

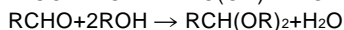
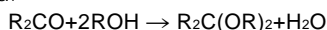
Oxides that react in constant amounts dissolve completely in the Karl Fischer at the titration end point, but Ni and Al compounds do not dissolve.

2. Other Substances that react with ingredients of Karl Fischer Reagents

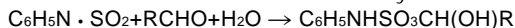
If methanol is used as the solvent for Karl Fischer reagent and the titration solvent, the following interference reactions will occur. In the case of aldehydes, there will be interference resulting from reactions with both sulfur dioxide and water.

(1) Carbonyl compounds

The following reactions with alcohol cause interference by producing water, leading to high analysis results. Frequently, the end point will never be reached.

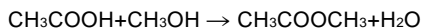


In addition to these reactions, aldehydes also capture water through the following interference reaction. This results in low analysis results.



(2) Lower carboxylic acids and their derivatives

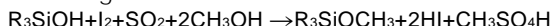
Formic acid, acetic acid, monochloroacetic acid and dichloroacetic acid trigger an esterification reaction with methanol at room temperature (20 °C) or higher. This reaction causes interference by gradually producing water.



Formic acid in particular is not suitable for Karl Fischer titration.

(3) Silanol and silanol derivatives

If methanol is present during Karl Fischer titration, the silanol in silicon oils will trigger the following interference reaction.



.....

Q10 | Please outline any methods that can be used to suppress interference reactions so that Karl Fischer titration can be employed.

The countermeasures used to suppress interference depend on the type of interference reaction.

- Basically, Karl Fischer titration cannot be used with substances that cause oxidation/reduction reactions. Special preliminary processes must therefore be used to convert these substances into other substances before titration.
- Where substances react with methanol, Karl Fischer titration is carried out under conditions that do not involve the use of methanol. With Karl Fischer Reagent SS-Z and SS, methanol is not used as the solvent, so it is possible to measure the water content in carbonyl compounds and other substances simply by using the reagent in conjunction with a dehydrated solvent formulated for use with ketones. These expanded range of uses greatly enhances the value of these products.
- In the case of interference substances that do not change when heated, it is possible to carry out Karl Fischer titration by using a water vaporization system.
- With substances that have strong basicity, such as amines, it is possible to use Karl Fischer titration if the substances are first neutralized by adding acid.

Specific examples are shown in the following tables. Individual researchers should optimize their approaches on the basis of these examples.

1. Substances requiring special treatment

| Compound | Treatment |
|-----------------------|---|
| Ammonia | Add acetic acid. |
| Ferric salts | Add 8-Hydroxyquinoline. |
| Hydrazine derivatives | Add acetic acid. |
| Hydroxylamine salts | Add sulfur dioxide:pyridine solution (1:1). |
| Thiol (mercaptan) | Prevent interference by adding olefins (octene, etc.). |
| Sulfuric acid | If the sulfuric acid is 92% pure or higher, add a large surplus of pyridine and titrate it as a salt. |
| Thio acid | Prevent interference by adding olefins (octene, etc.). |
| Thiourea | Prevent interference by adding olefins (octene, etc.). |

2. Using Karl Fischer reagents with interference substances

With ketones, aldehydes, lower carboxylic acid and amines with strong basicity, titration should be carried out using the Karl Fischer reagent in conjunction with the reagents shown below.

| Substance | Reagent Used | | |
|-------------------------------------|---------------------------|---|---|
| | Volumetric titration | | Coulometric titration |
| Ketones | Karl Fischer Reagent SS-Z | Dehydrated Solvent KTX | Aquamicon AKX |
| | Karl Fischer Reagent SS | Dehydrated Solvent CP | Aquamicon CXU |
| Aldehydes | Karl Fischer Reagent SS-Z | Dehydrated Solvent KTX | Aquamicon AKX |
| | Karl Fischer Reagent SS | Dehydrated Solvent CP | Aquamicon CXU (suitable only for certain aromatic aldehydes) |
| | | Dehydrated Solvent PP | |
| Low-grade carboxylic acid | Karl Fischer Reagent SS-Z | Dehydrated Solvent KTX | Aquamicon AKX |
| | Karl Fischer Reagent SS | Dehydrated Solvent CP | AquamiconCXU |
| Strong-base amines (pKa9 and above) | Karl Fischer Reagent SS-Z | Dehydrated Solvent GEX + salicylic acid | Aquamicon AX + salicylic acid |
| | Karl Fischer Reagent SS | Dehydrated Solvent MS + salicylic acid | Aquamicon CXU |

Note: Do not use Karl Fischer SS with Dehydrated Solvent KTX.

Measuring Moisture Content of Strong-Base Amines

Put 10g of salicylic acid into a titration flask (electrolysis cell). Add 50ml of Dehydrated Solvent GEX or MS (100ml in the case of Aquamicron AX) and mix together. Add the sample (amine) after dehydrating it with Karl Fischer reagent. Then initiate Karl Fischer titration. The amount of sample that can be measured will vary according to the type of amine.

.....

4. Procedures for Karl Fischer Titration

Q11 | How should we actually carry out volumetric titration?
Please describe the preparations and procedures involved.

To measure moisture content by means of volumetric titration, you will first need to prepare the following items.

- Titration agent: Karl Fischer Reagent SS-Z (or SS)
(It is necessary to assess the titer before use.)
- Titration solvent: Select the dehydrated solvent to suit the samples.
- A Karl Fischer volumetric titration system
(Reagents manufactured by Mitsubishi Chemical can be used with any commercially available system.)

Next, the amount of the sample is determined according to the anticipated moisture content.

In general, one of the following three methods of titration are used. The procedures for each are explained below.

- (1) Direct titration
- (2) Back titration
- (3) Water vaporization

1. Sample Size

It is important to determine the size of the sample according to the moisture content. If there is excessive moisture, Karl Fischer reagent will be wasted, and if there is too little, there will be significant effect on titration error and the results will lack precision. The following table can be used as a guide when determining the appropriate amount of sample in relation to anticipated moisture content. The figures shown here assume that the Karl Fischer reagent has a titer of 3mg/ml. If the titer is different, it will be necessary to adjust the figures accordingly.

| Anticipated moisture content (%) | Amount of Sample (g) |
|----------------------------------|----------------------|
| 0.1 or lower | 10-20 |
| 0.1-0.5 | 5 |
| 0.5-1 | 2 |
| 1-5 | 0.5 |
| 5-10 | 0.3 |
| 10-50 | 0.1 |
| 50 or higher | 0.03 |

2. Direct titration (standard method)

This is the standard and most commonly used method of volumetric titration. The sample is dissolved in a dehydrated solvent and titrated with Karl Fischer reagent. Titration is carried out in a sealed system isolated from the atmosphere.

[Procedures]

- Place 25-50ml of dehydrated solvent in a thoroughly dried flask.
- Titrate the Karl Fischer reagent SS-Z to the end point to remove all moisture. (This procedure is known as "pre-titration". It is not necessary to read the titration volume at this stage.)
- Measure out the sample (A, g) according to the anticipated moisture content and immediately place it in a titration flask.
- Titrate to the end point (B, ml) using Karl Fischer SS-Z for which the titer (F, mg/ml) is known, stirring continuously.
- Calculate the moisture content (W, %) according to the following formula.

$$W = \frac{B \times F}{A \times 1000} \times 100$$

3. Back Titration

In the case of solid samples that cannot readily be dissolved in dehydrated solvents, moisture is extracted by stirring for a specific period. An excess of Karl Fischer reagent is then added and the sample is left for a specific period to allow the moisture to react thoroughly with the reagent. The excess Karl Fischer reagent is then subjected to back titration using standard water/methanol solution.

[Procedures]

- a) All moisture is removed from the dehydrated solvent using the procedures described in the previous section.
- b) The sample (A', g) is immediately placed in a titration flask.
- c) A specific amount (C, ml) of excess Karl Fischer reagent SS-Z (titer F' mg/ml) is then added and the sample is stirred for the required period of time.
- d) The sample is then titrated to the end point (D, ml) using a standard water/methanol solution (titer f, mg/mg).
- e) Moisture content (W', %) is calculated according to the following formula.

$$W' = \frac{(C \times F') - (D \times f)}{A' \times 1000} \times 100$$

4. Moisture Vaporization Method

The moisture vaporization method is used with solid samples that do not readily dissolve in dehydrated solvents, or for samples that cause interference reactions. Moisture vaporization is carried out using a commercially available moisture vaporization system in combination with a volumetric titration system.

[Procedures]

- a) An oven is maintained at a temperature suitable for vaporizing the moisture content of the sample. Nitrogen gas, which has previously been passed through a drying tube, is passed through the moisture vaporization system at the rate of approximately 300ml/min.
- b) The titration system is dehydrated by means of pre-titration in the titration system in a flow of nitrogen gas.
- c) The sample is then quickly transferred to a sample boat and placed in an oven that has been maintained at the required temperature.
- d) The vaporized water is absorbed into a dehydrated solvent (GEX, MS or ME).
- e) Karl Fischer titration is then carried out according to the direct titration method.

Note: Dehydrated solvent GEX or MS should be used in a mixture consisting of one part of propylene glycol to three parts of dehydrated solvent by volume.

5. Determining Titer

The titer of the Karl Fischer reagent SS-Z (or SS) that is placed in the titration system must always be determined before use. Karl Fischer reagent SS-Z (or SS) is very stable and needs to be tested only once a week, provided that the bottle is kept airtight. Where particularly high accuracy is required, titer should be checked daily. Titer can be determined using one of the following four methods.

- Using pure water
- Using standard water solution
- Using standard water/methanol solution
- Using sodium tartrate dihydrate

The characteristics of these methods and the procedures for using them are described below.

(1) Using pure water

This method is the most accurate, since the standard for determining titer is water itself. The drawback with this method is the difficulty of measuring small amounts of water accurately. A microsyringe is used for conveying the water. It is convenient to use a commercially available dropping bottle with a small dripping pipette. Each drop from the pipette is 20-30mg.

[Procedures]

The amount of water obtained should be 10-30mg. The procedures are the same as for direct titration. The following calculation formula is used.

$$F = S/T$$

- Where
- F: Titer (mgH₂O/ml)
 - S: Amount of water obtained (mg)
 - T: Amount of Karl Fischer reagent required for titration (ml)

(2) Using standard water solution

With this method, a standard water solution with a guaranteed value is used in place of water. Where the value of the standard water solution is around 10mg/g, approximately 1g is obtained. The following calculation formula is used.

$$F = S \times K/T$$

- Where
- F: Titer (mgH₂O/ml)
 - S: Amount of standard water solution obtained (g)
 - K: Guaranteed value of standard water solution (mgH₂O/g)
 - T: Amount of Karl Fischer reagent required for titration (ml)

(3) Using standard water/methanol solution

Standard water/methanol solution is a standard water solution for which the moisture content has been accurately determined. It is especially suitable for determining the titer of Karl Fischer Reagent SS-Z (or SS). The moisture content is shown in the label (e.g. 2.02mgH₂O/ml).

[Procedures]

- a) 25-50ml of dehydrated solvent GEX (or MS) is placed in a titration flask.
- b) Karl Fischer Reagent SS-Z (or SS) is titrated to the end point to remove all moisture content. (It is not necessary to read the titration value at this stage.)
- c) 5-10ml of standard water/methanol solution is taken and added to the dehydrated solvent in the titration flask.
- d) The Karl Fischer Reagent SS-Z (or SS) that is to be assessed is titrated.
- e) Titer is calculated from the titration volume according to the following formula.

$$F = A \times f / B$$

Where F: Titer of Karl Fischer Reagent SS-Z (or SS) (mgH₂O/ml)
 A: Amount of standard water/methanol solution obtained (ml)
 f : Titer of standard water/methanol solution (mgH₂O/ml)
 B: Amount of Karl Fischer Reagent SS-Z (or SS) titrated (ml)

Note: Standard water/methanol solution has the same expansion coefficient as methanol. If it is used at a temperature that is significantly different from the assessment temperature shown on the label (20°C), it will be necessary to correct the volume (ml) of standard water/methanol solution used.

(4) Using sodium tartrate dihydrate

Sodium tartrate dihydrate is the most stable of the hydrate standard substances in relation to changes in atmospheric humidity. It has a theoretical moisture content of 15.66%. The low solubility of commercially available sodium tartrate dihydrate means that large amounts cannot be obtained. The amount for 50ml of methanol would be about 200mg or less. Users should be aware that the crystal size of commercially available products may vary. If the crystals are too small they may scatter when added, leading to errors.

[Procedures]

The amount of sodium tartrate dihydrate obtained should be around 150mg.

The procedures are the same as for direct titration.

The following calculation formula is used.

$$F = m \times 0.1566 / V$$

Where F: Titer (mgH₂O/ml)

m: Amount of sodium tartrate dihydrate obtained (mg)

V: Amount of Karl Fischer reagent required for titration (ml)

Helpful hint -6

Why does a solution that reached the titration end point change color if it is left standing?

If a solution is left standing for a period after it has reached the titration end point, it will turn yellow and will start to consume Karl Fischer reagent again. Conversely, it may turn the reddish brown color associated with over-titration.

This phenomenon results from contamination by external moisture, and from the free iodine from the iodide in the solution through the action of ultraviolet rays and oxygen.

Q12 | How can we actually measure moisture content using coulometric titration? Please describe the preparations and procedures involved.

To measure moisture content by means of coulometric titration, you will first need to prepare the following items.

- Electrolytes: Aquamicon series
To ensure proper functioning, it is essential to use the correct anolyte-catholyte combination.
- A Karl Fischer coulometric titration system
(Aquamicon series products manufactured by Mitsubishi Chemicals can be used with most commercially available systems.)

Next, the size of the sample is determined according to the anticipated moisture content.

There are actually two coulometric titration methods.

- (1) Direct titration (2) Moisture vaporization

1. Sampling amounts

Coulometric titration is suitable for the measurement of trace quantities of moisture. Sample size is an important consideration as excessive quantities will extend the time required for analysis.

Normally a sample containing 0.1-5mg of water is used. The guidelines in the following table assume that the appropriate moisture content range for coulometric titration is 1% or lower. This is not to say that coulometric titration cannot be used for samples with a moisture content above 1%. In such cases, however, the need to obtain samples in extremely small quantities will increase measurement errors, leading to problems with accuracy. If possible, volumetric titration should be used in such cases.

| Anticipated moisture content (%) | Sample quantity (g) |
|----------------------------------|---------------------|
| 0-0.05 | 5-10 |
| 0.05-0.1 | 2 |
| 0.1-0.2 | 1 |
| 0.2-0.5 | 0.5 |
| 0.5-2.0 | 0.1 |

2. Obtaining a Sample

A carefully dried syringe (1-10ml) should be used. First, flush the syringe 2-3 times with the sample substance. Next, the amount required for the sample should be taken. A piece of silicon rubber should be attached to the end of the syringe needle, and the syringe should then be weighed precisely.

The silicon rubber should then be removed, and the sample inserted into the

system. The rubber should then be replaced, and the syringe weighed again. The difference in weights should be equal to the weight of the sample.

3. Combination of Aquamicron Products

| | General use | With ketones |
|-----------|-----------------------------------|----------------|
| Anolyte | Aquamicron AX or Aquamicron AS | Aquamicron AKX |
| Catholyte | Aquamicron CXU | Aquamicron CXU |

4. Direct Titration

This method is suitable for liquid, solid or gaseous substance that can be dissolved in Aquamicron. Direct titration should not be used for insoluble solid samples since these may clog the membranes or affect the efficiency of the current.

[Procedures]

- a) Approximately 100ml of anolyte (Aquamicron AX, AS or AKX) is placed in an electrolyte cell (Figure 3) that has been carefully dried.
- b) The entire contents of a catholyte ampoule (Aquamicron CXU, 5ml) is placed in the catholyte chamber.
- c) An electrolytic current is applied to the anode-cathode while it is stirred to produce iodine and trigger the Karl Fischer reaction in order to remove all water from the electrolysis cell. (It is not necessary to read the moisture content at this stage.)
- d) The sample is introduced into the electrolysis cell and coulometric titration is then carried out until the end point.
- e) Moisture content is calculated according to the following formula.

$$W1 = M/S$$

or
$$W2 = M \times 100 / (S \times 10^6)$$

Where W1: Moisture content (ppm)

W2: Moisture content (%)

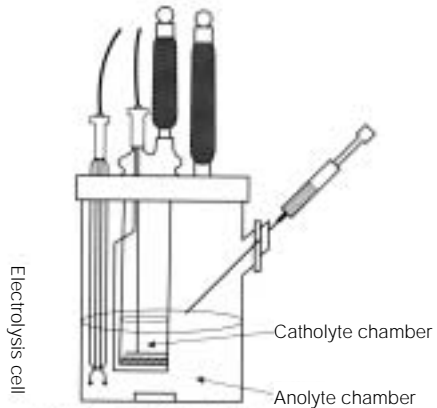
M: Measurement value ($\mu\text{gH}_2\text{O}$)

S: Amount of sample (g)



Silicon rubber

Figure 6: Sampling Syringe



Electrolysis cell

Catholyte chamber

Anolyte chamber

Figure 7: Sample Injection System

5. Moisture Vaporization

With this method, the coulometric titration system is used in conjunction with a moisture vaporization system. Approximately 150ml of anolyte (Aquamicron AX or AS) is placed in an electrolysis cell. Two ampoules (10ml) of catholyte (Aquamicron CXU) are used.

The condition for moisture vaporization should be optimized for the particular sample. Detailed instructions for various types of samples are provided later in this manual.

Q13 | Sampling procedures are one of the most important aspects of moisture content measurement. What are the specific methods and equipment involved?

At a room temperature of 25°C with 50% humidity, the moisture content of the atmosphere is 0.01mg per 1ml. Depending on the procedures used, moisture (humidity) may infiltrate the electrolysis cell (or titration flask), adhere to the equipment used to obtain samples, or adhere to or dissolve in the sample. It is important to be aware of this possibility as it can lead to error.

It is also essential to vary sample quantities in accordance with individual characteristics and moisture content. It is convenient to use commercially available sampling equipment of the types shown in Figures 9-17. These are designed to allow samples to be varied according to the particular circumstances. The procedures for using this equipment are described below.

1. Liquid Samples

Equipment used with liquid samples includes micro-syringes, syringes, pipettes and dropper bottles.

(1) Micro-syringes

Micro-syringes are used to obtain specific amounts of water, substances with a high moisture content, or check solutions for coulometric titration. Products are available commercially with capacities of 10, 25, 50 and 100ul. The needle should be as long as possible. Most commercial products have 50mm needles. The following precautions should be taken when using micro-syringes.

- a) Where possible, avoid using the full stroke of the micro-syringe when measuring the sample. We recommend using 2/3 or less of the stroke. (This is because the plunger could be contaminated by atmospheric moisture.)
- b) Dry the micro-syringe thoroughly. After the micro-syringe has been washed with an organic solvent (methanol, etc.) with a low boiling point, it should be thoroughly dried in a flow of dried nitrogen, etc., and then placed in a drier.
- c) Flush the micro-syringe 2-3 times with the sample.
- d) When adding the sample, push the plunger down quickly to ensure that no sample remains on the tip of the needle.

Sometimes samples are tested by weight using the same procedures as with syringes. The weight of the sample normally should be determined from measurements of volume and relative gravity (or density).

(2) Syringes

These are used for most liquid samples. Glass syringes are most commonly used, however plastic products (disposable) are also convenient. The most commonly used commercial products are 1, 2, 5 and 10ml syringes. General procedures for using syringes are described below.

- After carefully drying the syringe (figure 6), flush it two or three times with small amounts of the sample. Then draw in the required amount of the sample.
- Attach a piece of silicon rubber to the needle and weigh the syringe.
- Remove the silicon rubber and insert the syringe needle through the stopper attached to the side valve of the titration cell (Figure 8). Inject the sample.
- Pull out the syringe needle and weigh it accurately with the piece of silicon rubber attached to the needle.
- The difference between the two weights is the weight of the sample.

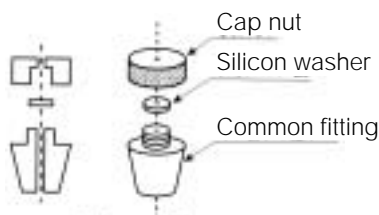


Figure 8: Stopper

(3) Pipettes

Because a stopper cannot be used with a pipette, the side stopper (or sample injection stopper) must be removed. With the stopper removed the experiment is exposed to the air and the results must be corrected for the infiltration by atmospheric moisture by conducting a blank test for the same period of time that the flask was open. The method is unsuitable, therefore, for the coulometric titration used to measure trace amounts of moisture.

The weight of the sample is determined by separate measurement of the relative gravity (or density). We recommend the use of syringes wherever possible.

(4) Dropper bottle

Dropper bottle (Figure 9) are used for water or for samples with a high moisture content. They are especially convenient for measuring water when determining the titer of Karl Fischer Reagent SS-Z (or SS) using water. With commercially available products, the pipettes produce droplets of about 30mg each.

[Procedures]

- After carefully drying the dropper bottle, introduce the sample. Attach the pipette and extract the sample.
- Accurately weigh all the equipment.
- Remove the pipette from the dropper bottle and titrate the titration solvent.
- Replace the pipette on the dropper bottle and weigh the equipment accurately.
- The difference between the two weights is the weight of the sample.

(5) Dropper bottle (for high-viscosity substances)

This equipment (Figure 10) is used for samples with the viscosity of treacle. Procedures are the same as in (4) above.

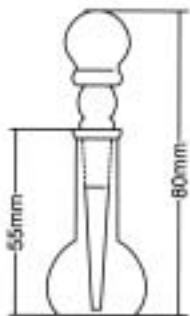


Figure 9: Dropper bottle



Figure 10: Dropper bottle
(for high-viscosity substances)

2. Solid Samples

The appropriate method must be selected with reference to the varying characteristics and forms of solid samples. There are commercial products that are suitable for each method and it is convenient to use these.

As the sample insertion aperture on the titration flask must be opened to insert the sample, a blank test must be carried out to adjust for the time while the flask is open. In general, the following procedures are used.

- Obtain the required amount of sample using a thoroughly dried sampling bottle.
- Accurately weigh the sampling bottle.
- Remove the stopper of the sample insertion aperture on the titration flask and quickly insert the sample.
- Close the stopper and record the time that stopper was open. (The lid should be opened for exactly the same period of time during the blank test.)
- Weigh the sampling bottle.

(1) Upright solid sampling bottle

An upright solid sampling bottle (Figure 11) is used for ordinary powdered, granular or lumpy samples. This type of sampling bottle is used frequently.

(2) Angled solid sampling bottle

A drawback with upright sampling bottles is that the sample must be shaken to some extent to make it drop to the bottom. The angled bottle solves this problem by means of a half-rotational bend that allows the sample to fall (Figures 12, 13). The angled-neck bottle is especially suitable for plastic pellets.

(3) Trace solid sampling bottle

This container (Figure 14) is used to obtain extremely small amounts of samples with a high moisture content. It is suitable for powdered samples.

(4) Syringe-type sampling bottle

The syringe-type sampling bottle (Figure 15) is used for consolidated powders and viscous solids. The sample is drawn into the syringe by pulling out the plunger, and then expelled the contents into the system by pushing in the plunger.

(5) Sampling bottle for semi-solids

This container (Figure 16) is used for high-viscosity samples, such as greases. The sample is first taken onto the sampling spoon (A), which is then weighed together with the bottle (B). Next, the sample is inserted into the titration flask together with the sampling spoon. The spoon is stirred for a period to allow the sample to dissolve. On completion of the measurement the sampling spoon is returned to the sampling bottle, which is then weighed. The difference between the two weights is the weight of the sample.

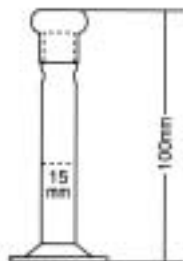


Figure 11:
Upright Sampling Bottle

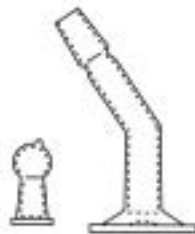


Figure 12:
Angled Sampling Bottle



Figure 13:
Angled-neck Sampling Bottle



Figure 14: Trace Sampling Bottle

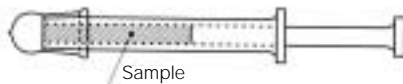
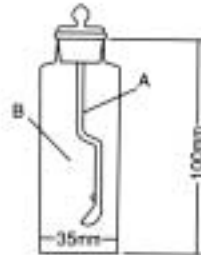


Figure 15: Syringe-Type Sampling Bottle



**Figure 16:
Semi-Solid Sampling Bottle**

3. Liquefied Gas Samples

A dual-aperture pressurized sampling bottle and stainless steel pipes are used. Commercial products are available to suit specific purposes and these are recommended.

The key requirement for sampling is to ensure that the liquid phase is introduced into the dehydrating solvent (or electrolyte). Errors may result if only the gaseous phase is introduced. Also, the entire amount of sample must be added. The general procedures are summarized below.

- Position the gas bottle upright or at an angle.
- Connect a pipe between the gas bottle and the sampling bottle.
- Introduce the liquid phase into the sampling bottle.
- Keep the amount of the sample to 80% or less of the vessel's capacity and determine the weight.

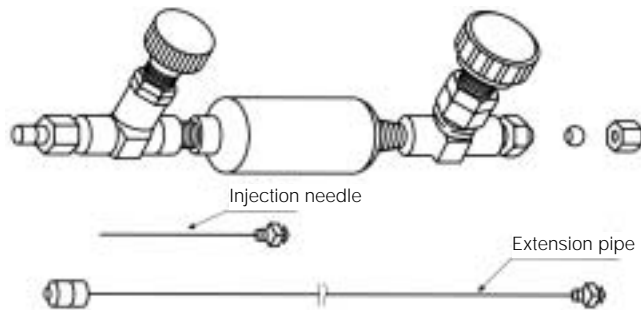
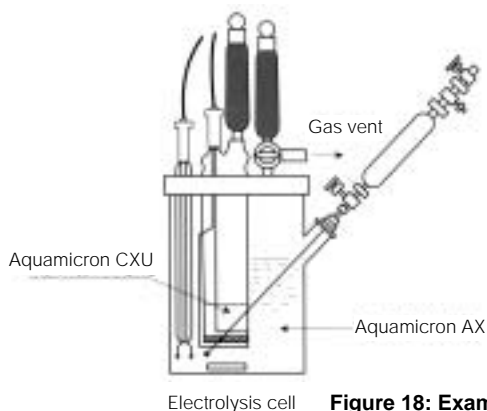


Figure 17: A Typical Sampling Bottle



Electrolysis cell **Figure 18: Example of an Injection Assembly**

5. Official Testing Methods and Documentation

Q14 | Karl Fischer titration is classed as an official testing method. What Japanese standards have been adopted?

Karl Fischer Reagent SS-Z (or SS), dehydrating solvent, and the Aquamicon series of products all conform with Japanese standards and can be used with confidence.

1. Japanese Industrial Standards (JIS)

| JIS | Name of Standard | Cited Standards |
|-------|---|-----------------|
| C2101 | Testing methods for electrical insulating oils. | |
| K0068 | Test methods for water content of chemical products | |
| K0113 | General rules for methods of potentiometric, amperometric, coulometric, and Karl-Fischer titrations | |
| K1422 | Carbon tetrachloride | K0068,K0113 |
| K1424 | Ammonium nitrate | K0068 |
| K1508 | Trichloroethylene | K0068,K0113 |

I-1. Questions & Answers about Karl Fischer Reagents

| | | |
|-------|---|-------------|
| K1521 | Perchloroethylene | K0068,K0113 |
| K1522 | Isopropyl alcohol | K4101 |
| K1527 | Ethylene glycol | K4101 |
| K1530 | Propylene glycol | K4101 |
| K1557 | Testing method of polyether for polyurethane | K0068 |
| K2211 | Refrigerating machine oils | K2275 |
| K2220 | Lubricating grease | K2275 |
| K2234 | Engine antifreeze coolants | K0068 |
| K2242 | Heat treating oils | K3362 |
| K2275 | Crude oil and petroleum products | |
| | - Determination of water content | K0113 |
| K2436 | Naphthalene, anthracene, carbazole | K0068,K0113 |
| K2437 | Phenols | K0068,K0113 |
| K2438 | Pyridine bases | K0068,K0113 |
| K3351 | Glycerines for industrial use | K0068 |
| K3362 | Testing methods for synthetic detergent | K0068 |
| K4101 | General testing methods for organic intermediates | K0113 |
| K4108 | Nitrobenzenes | K0113 |
| K4109 | Aminobenzenes | K0113 |
| K4112 | N-Substituted anilines | K0113 |
| K4127 | Benzoic acid | K0113 |
| K4129 | Naphthol | K0113 |
| K4132 | 1-Naphthylamine | K0113 |
| K4137 | Anisidine | K0113 |
| K4148 | Dinitrobenzenes | K0113 |
| K4153 | Diphenylamine | K0113 |
| K4156 | Nitrophenols | K0113 |
| K4809 | Analytical methods of explosives | |
| K6724 | Vinyl Acetate | |
| K6759 | Testing methods for acrylonitrile | |
| K6910 | Testing methods for phenolic resins | |
| M8001 | General testing methods for reagent chemicals | |
| M8211 | Iron ores — Method for determination of combined water content | K0113 |
| K8231 | Method for determination of combined water in manganese ores | |

2. Japan Pharmaceutical Codex (Revision 14)

General Test Method 27: Moisture Content Test (Karl Fischer Method)
The items listed in the Pharmaceutical Codex that stipulate the use of moisture content testing by means of Karl Fischer reagent are as follows.

| Item | Tolerance (sample amount) |
|--------------------------------------|-----------------------------------|
| Aspirin aluminum | 4.0% (0.15g) |
| Aminophylline | 7.9% (0.3g) |
| Isopropanol | 0.7%w/v (2ml) |
| Quinine ethylcarbonate | 3.0% (0.5g) |
| Ethosuximide | 0.5% (2g) |
| Suxamethonium chloride | 8.0-10.0% (0.4g) |
| Suxamethonium chloride for injection | 10.0% (0.4g) |
| Berberine chloride | 15.6% (0.3g) |
| Benzalkonium chloride | 15.0% |
| Thiamine hydrochloride | 5.0% (0.5g) |
| Anhydrous citric acid | 0.5% (2g) |
| Clofibrate | 0.2% (5g) |
| Cyclophosphamide | 5.5-7.0% (0.5g) |
| Distigumine bromide | 1.0% (1g) |
| Dextromethorphan hydrobromide | 4.0-5.5% (0.2g, back titration) |
| Isosorbide dinitrate | 1.5% (0.3g) |
| Hydroxyzine pamoate | 3.0% (1g) |
| Potassium guaiacolsulfonate | 3.0-4.5% (0.3g) |
| Metothrexate | 12.0% (0.2g, special method) |
| Mercaptopurin | 10.0-12.0% (0.2g, back titration) |
| Folic acid | 8.5% (0.2g, special method) |
| Riboflavin sodium phosphate | 10.0% (0.1g, back titration) |
| Protirelin tartrate | 4.5% (0.2g) |
| Terbutaline sulfate | 0.5% (1g) |
| Chlorobutanol | 6.0% (0.2g) |

I-1. Questions & Answers about Karl Fischer Reagents

| | |
|---------------------------|---------------------------|
| Sorbitan sesquioleate | 0.5% (1g) |
| Propylene glycol | 0.5% (2g) |
| Polysorbate 80 | 3.0% (1g, back titration) |
| Sodium lauryl sulfate | 5.0% (0.5g) |
| Polyvinyl pyrrolidone K25 | 5.0% (1.0g) |
| Polyvinyl pyrrolidone K30 | 5.0% (1.0g) |
| Polyvinyl pyrrolidone K90 | 5.0% (1.0g) |
| Macrogol 400 | 1.0% (2g) |
| Macrogol 1500 | 1.0% (2g) |
| Macrogol 4000 | 1.0% (2g) |
| Macrogol 6000 | 1.0% (2g) |
| Berberine tannate | 6.0% (0.7g) |

3. Notes to Official Food Additive List (7th ed., 1999)

General Test Method 17: Moisture Content Test (Karl Fischer Method)
The Karl Fischer method is stipulated for the following food additives.

| Item | Tolerance |
|------------------------------|---|
| 5'-Inosinic acid sodium salt | 29.0% or lower (0.15g, back titration) |
| 5'-Uridine acid sodium salt | 26.0% or lower (0.15g, back titration) |
| Citric acid (anhydrous) | 0.5% or lower (2g) |
| Disodium glycyrrhizate | 13.0% or lower (0.2g, back titration) |
| 5'-Cytidine acid sodium salt | 26.0% or lower (0.15g, back titration) |
| Sucrose fatty acid ester | 4.0% or lower (back titration) |
| Sodium dehydroacetate | 8.3-10.0% or lower (0.3g, back titration) |
| Folic acid | 8.5% or lower (0.2g, back titration) |
| 5'-Calcium ribonucleotide | 23.0% or lower (0.15g, back titration) |
| 5'-Sodium ribonucleotide | 27.0% or lower (0.15g, back titration) |

4. Japan Petroleum Institute Standards

Test for water in liquid petroleum products (Karl Fischer Method)

JPI-5S-14-76

5. Japan LPG Association Standards

Moisture Content Test Method in LPG: Karl Fischer Method

JLPGA-S-02-99

6. Japan Agricultural Standards (JAS)

Vegetable Oils (Karl Fischer Method, moisture content 0.2% or lower) (1969)

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Q15 | Please provide some examples of the international standards (ISO) and foreign standards that have been adopted for the Karl Fischer titration method.

Listed below are some examples of standards established by the International Organization for Standardization (ISO) and the American Society For Testing and Materials. The BS (U.K.) and DIN (Germany) systems are also based on these standards.

1. General Testing Methods

(1) Volumetric titration

ISO 760-1978

Determination of water - Karl Fischer method (General method)

ASTM E203-01

Water using Karl Fischer reagent

(2) Coulometric titration

ASTM E1064-92

Water in organic liquids by coulometric Karl Fischer titration

2. Individual Standards

ASTM D1364-95

Water in volatile solvents (Fischer reagent titration method)

ASTM D1533-96

Water in insulating liquids (Karl Fischer reaction method)

ASTM D1631-94

Water in phenol and related materials by the iodine reagent method

ASTM D1744-92

Water in liquid petroleum products by Karl Fischer reagent

ASTM D3277-95

Moisture content of oil-impregnated cellulosic insulation

ASTM D3466-85

Water content of trichlorotrifluoroethane

I-1. Questions & Answers about Karl Fischer Reagents

- ASTM D3621-84
Water in acetate esters
- ASTM D4017-96
Water in paint and paint materials by Karl Fischer method
- ASTM D4377-93
Water in crude oils (Karl Fischer) titration
- ASTM E700-79
Water in gases using Karl Fischer reagent
- ISO 2097: 1972
Glycerols for industrial use - Determination of water content - Karl Fischer method
- ISO 2514: 1974
Acetaldehyde for industrial use - Determination of water content - Karl Fischer method
- ISO 2596: 1994
Iron ores - Determination of hygroscopic moisture in analytical samples - Gravimetric and Karl Fischer methods
- ISO 2753: 1973
Urea for industrial use - Determination of water content - Karl Fischer method
- ISO 3699: 1976
Anhydrous hydrogen fluoride for industrial use - Determination of water content - Karl Fischer method
- ISO 4317: 1991
Surface-active agents and detergents - Determination of water content - Karl Fischer method
- ISO 5381: 1983
Starch hydrolysis products - Determination of water content - Karl Fischer method
- ISO 5791: 1978
Ammonium nitrate for industrial use - Determination of water content - Karl Fischer method
- ISO 6191: 1981
Light olefins for industrial use - Determination of traces of water - Karl Fischer method
- ISO 7105: 1985
Liquefied anhydrous ammonia for industrial use - Determination of water content - Karl Fischer method
- ISO 7335: 1987
Iron ores - Determination of combined water content - Karl Fischer method
- ISO 10101-1-3: 1993
Natural gas - Determination of water by the Karl Fischer method - Part 1: Introduction

- Part 2: Titration procedure
- Part 3: Coulometric titration
- ISO 10362-2: 1994
 - Cigarettes - Determination of water in smoke condensates - part 2: Karl Fischer method
- ISO 11817: 1994
 - Roasted ground coffee - Determination of moisture content - Karl Fischer method

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Q16 | What reference works are there concerning Karl Fischer measurement methods?

The following is a list of basic references concerning Karl Fischer titration. It consists mainly of works written by members of the Mitsubishi Chemical Corporation research team.

1. Mitchell & Smith: Aquametry, 2nd Edition, Part 3 (1980).
2. Funasaka, W., Muroi, M., Suibun no Teiryō [Measuring Moisture Content] II: Karl Fischer Method (out of print).
Bunseki Raiburari 14 [Analysis Library 14], published by Tokyo Kagaku Dojin(1969).
3. General Introductions
Muroi, K., "Karu Fisssha Ho ni Yoru Suibun no Sokuteiho" [Measuring Moisture Content Using the Karl Fischer Method] (in Keisoku Gijutsu [Measurement Technology], 3, 49, 1977).
Muroi, K., "Bunseki Kagaku ni Okeru Mizu" [Water in Chemical Analysis], (in Bunseki [Analysis] 2, 74, 1979).
4. Papers Concerning Pyridine-Free Types
Kato, H., Ono, M., Kuwata, S.:
 - (1) "New Karl Fischer Volumetric Reagent Composed of a Base" (in Bunseki Kagaku 35, 91, 1986).
 - (2) "Determination of Moisture by Karl Fischer Coulometric Reagent Composed of New Bases" (in Bunseki Kagaku 33, 638, 1984).
 - (3) "Determination of Moisture in Ketones and Lower Carboxylic Acids by New Karl Fischer Coulometric Reagent"(in Bunseki Kagaku 34, 147, 1985).

- (4) "Determination of Moisture in Amines by New Karl Fischer Coulometric Titration"
(in Bunseki Kagaku 34, 805, 1985).

Memo "Outline of official testing methods in other countries"

ISO: The International Organization for Standardization (ISO) was established to promote the discussion and adoption of global standards with a view to facilitating the international exchange of goods and services and to developing cooperation in the spheres of intellectual, scientific, technological and economic activity. Formally established in 1947, ISO has its headquarters in Geneva, Switzerland. JIS is currently reviewing its standards with the aim of making them compatible with these international standards.

ASTM: The American Society For Testing Materials (ASTM) is an American organization dedicated to science and technology. It was formed in 1898 to standardize specifications and test methods, etc., for industrial materials. It has published numerous ASTM standards which include testing methods.

BS: British Standards (BS) are standards established by the British Standards Institution, which was founded in 1901.

DIN: Industrie Normen (DIN) are standards established by the Deutsches Institut für Normung, which was renamed in 1975 to match the name of the standards.

6. Important Information about Handling and Using Karl Fischer Reagents

Q17 | Are there any safety requirements or other precautions that should be followed when using Karl Fischer reagents?

In addition to handling requirements related to the characteristics of Karl Fischer reagents, there are precautions to be taken in relation to safety and hygiene. It is important to fully understand both sets of requirements.

1. Safety and Hygiene Requirements

- 1) Never drink the reagent or inhale its vapor.
- 2) Avoid skin contact. If the reagent does come in contact with the skin, wash it off with soap, etc., and rinse well with water.
- 3) If reagent splashes into an eye, flush the eye immediately with water, for at least 15 minutes. The eye should be checked by an eye specialist.
- 4) Make sure that the room is adequately ventilated when handling Karl Fischer reagents.
- 5) Keep the reagents away from naked flames.
- 6) Observe general rules for handling reagents, including the following.
 - Organic Solvent Poisoning Prevention Regulations
 - Injury Prevention Rules For Specified Chemical Substances, etc.
 - Poisonous and Deleterious Substances Control Law
 - Fire Prevention Law (hazardous substances)

The regulations vary according to the specific type of reagent. For detailed information, contact the Mitsubishi Chemical Corporation.

2. Handling Requirements

(1) General Requirements

- a) Sampling bottles and other equipment must be dried thoroughly before use. During testing, take care to prevent contamination by atmospheric moisture. The following paper includes detailed information about the prevention of moisture contamination.

Muroi, M., "Measuring Trace Moisture Content Using the Karl Fischer Method - With Particular Emphasis on the Influence of Atmospheric Moisture and the Prevention Thereof" (in *Bunseki Kagaku* 12, 858, 1963)

- b) Check to find out if the sample will cause an interference reaction. If the sample is one where the interference reaction can be prevented, take the appropriate steps to do so.

- c) Store Karl Fischer reagents at or below room temperature and in a location that is not exposed to the light. Seal bottles to prevent the absorption of moisture.

(2) Volumetric Reagents

- a) Refer to the relevant sections for information about points that require particular care during volumetric titration, such as changes over time in the titer of Karl Fischer Reagent SS-Z (or SS), the titer of standard water-methanol and the evaluation procedures.
- b) Avoid the following combination when using volumetric reagents;
- Karl Fischer Reagent SS and Dehydrating Solvent KTX
 - Karl Fischer Reagent SS-Z and Dehydrating Solvent CP

(3) Coulometric Titration

- a) The analytical capability of Aquamicron AX and AS analytes is approximately 800-1,000mgH₂O per 100ml of anolyte. However, if a sample is added in stages so that the total amount exceeds 150ml, the sample will have an effect that causes a gradual decline in current efficiency. This may lead to inaccurate results. In such cases, discard all the reagent and begin again with fresh reagent.
- b) The analytical capability of Aquamicron CXU catholyte is approximately 130-150mgH₂O per 5ml of catholyte. With prolonged use, however, the reagent will gradually turn light brown and then dark brown. If the color begins to change, the reagent should be completely removed, with a pipette, etc., and replaced with fresh reagent. Do not add fresh reagent to discolored reagent.

Chapter II: Applications - 1

Chapter II: Applications - 1

This section is a summary of technical knowledge accumulated by Mitsubishi Chemical Corporation over many years. This information is included as a guide for those actually using Karl Fischer titration to measure the moisture content of individual compounds. There are specific examples for both organic and inorganic compounds.

II-1. Organic Compounds

Karl Fischer titration is the ideal method for measuring the moisture content of organic compounds. With very few exceptions, it is suitable for almost all compounds. Measurement is straightforward, as organic compounds can generally be dissolved in the solvents used with Karl Fischer reagents.

The section of Basic Knowledge gave an overview of the range of applications, grouped into those that can be measured directly, those that cause interference but which can be measured after modification, and those that cause interference. Refer to the relevant parts of the manual for essential information on the reactive functional groups that cause interference.

In the Section on Applications, we will describe specific Karl Fischer titration methods for individual compounds, together with examples that illustrate key factors to be taken into account when actually using these methods. Of course, it is impossible to cover every type of substance, so users should refer to the examples for similar compounds when establishing the conditions for moisture measurements.

Important!

Some of the examples refer to earlier reagent products. The latest products are those named as the "reagents to use". There may be exceptional cases in which measurements cannot be carried out as shown in the tables. Users should choose the most appropriate type of reagent and measurement method.

1. Hydrocarbons

Key Points

Hydrocarbons can be measured readily using standard procedures. Both volumetric and coulometric titration can be used. Moisture content tends to be very low, however, because of the low water solubility of hydrocarbons and because of their low water absorption capacity. For this reason, coulometric titration is suitable.

In the case of volumetric titration, standard dehydrated solvents are used. Solubility may be inadequate with long-chain hydrocarbons, but moisture content can be measured through dispersal extraction after sufficient stirring. Dehydrated solvents formulated for use with oils can be used to enhance solubility with good effect.

Substances with low moisture content can be measured accurately using Karl Fischer Reagent SS-Z (or SS) with a low titer.

With coulometric titration, the sample is added directly to the electrolyte solution (anolyte). Measurement is carried out after dissolution or dispersal.

In the case of olefins, double bonding may cause interference. Using the electrolyte solution (anolyte), the interference can be lowered.

Examples of substances that can be measured directly:

Ethylene, propylene, butadiene, propane, butane (see the discussion on industrial LPG in Chapter III: Applications 2, III-1).

Pentane, 2,4-dimethyl pentane, 2,2-methyl pentane, 2,2,4-trimethyl pentane, octane, 3-methylhexane, decane, octadecane, 2-pentene, dipentene, 1,3-pentadiene, isooctane, cyclopentane, methyl cyclopentane, cyclohexane, methyl cyclohexane, cyclohexene, benzene, toluene, xylene, ethyl benzene, mesitylene, styrene, naphthalene, diphenyl, decalin, hexamethyl benzene, anthracene, phenanthrene

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
 General-use Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (mg) | Moisture content (ppm) |
|-----------|--------------------|---------------------|------------------------|------------------------|
| n-Hexane | General-use | 6.5870 | 0.25 | 38 |
| Benzene | " | 8.7206 | 0.78 | 89 |
| Toluene | " | 8.5511 | 0.45 | 53 |
| Xylene | " | 4.3511 | 0.72 | 165 |

(2) Coulometric titration

Reagents used: Aquamicon AX (or AS) 100ml
 Aquamicon CXU 5ml

| Substance | Sample quantity (g) | Measurement value (μg) | Moisture content (ppm) |
|---------------|---------------------|------------------------|------------------------|
| n-Pentane | 2.5775 | 48 | 19 |
| n-Hexane | 1.8828 | 37 | 20 |
| Isooctane | 3.4600 | 89 | 26 |
| n-Decane | 2.0480 | 54 | 26 |
| n-Dodecane | 2.1048 | 63 | 30 |
| Ligroin | 2.1315 | 124 | 58 |
| Cyclohexene | 2.2335 | 69 | 31 |
| 1-Hexene | 0.7600 | 54 | 71 |
| 1-Decene | 0.7475 | 30 | 40 |
| 1-Tetradecene | 1.5460 | 21 | 14 |
| Benzene | 2.5297 | 334 | 132 |
| Toluene | 2.5151 | 380 | 151 |
| Xylene | 2.4930 | 174 | 70 |
| Naphthalene | 1.7755 | 129 | 73 |

All liquid samples can be measured continuously up to 20-50ml, using approximately the same amounts as shown in the table.

Note: It is convenient to use a syringe-type sampling bottle for naphthalene. Refer to JIS K2436 for details of the test method.

2. Halogenated Hydrocarbons

Key Points

The behavior of halogenated hydrocarbons is similar to that of hydrocarbons. Measurements can be carried out using standard procedures without problems.

Both volumetric and coulometric titration can be used, but coulometric titration is recommended because of the minute amounts of moisture included in these substances.

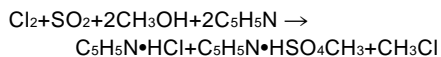
In the case of volumetric titration, standard dehydrated solvents are used. Halogenated hydrocarbons dissolve well in methanol, but solubility may become inadequate if the substance is added continuously. With sufficient stirring, however, it will be possible to extract and measure the moisture content. An effective way of enhancing solubility is to use dehydrated solvents formulated for use with oils.

Substances with low moisture content can be measured accurately using Karl Fischer Reagent SS-Z (or SS) with a low titer.

For coulometric titration, the sample is added directly to the electrolyte solution (anolyte). Measurement is carried out after dissolution or dispersal.

There is no interference, even in the case of substances such as vinyl chloride, with double bonding. Direct titration can be used in the same way.

Because of the processes used in their production, halogenated hydrocarbons sometimes contain trace amounts of free chlorine. This causes interference through the oxidation of iodide ions to produce free iodine. As a result, the moisture measured will be reduced in proportion to the amount of free iodine. This can be prevented by using Dehydrated Solvent MS as the titration solvent, and by agitating the solution thoroughly before the Karl Fischer titration, to render the free chlorine inactive. This is because of the reaction between amine and sulfur dioxide in the dehydrated solvent, as shown in the following formula.



Reference: Muroi, M., *Bunseki Kagaku* 16, 1061 (1967)
 "Determination of Water in Substances Containing Active Chlorine by Karl Fischer Titration"

Examples of substances that can be measured directly:

Methyl chloride, vinyl chloride, methylene chloride, methylene iodide, chloroform, carbon tetrachloride, iodoform, ethyl iodide, ethylene bromide, ethylidene bromide, 6-chloropropylene, 1,4-dichloro-2-butene, bromobenzene, iodobenzene, chloronaphthalene, bromonaphthalene

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
General-use Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (mg) | Moisture content (ppm) |
|-----------------------|--------------------|---------------------|------------------------|------------------------|
| Chloroform | General-use | 14.4999 | 1.60 | 110 |
| Carbon Tetrachloride | | 15.7825 | 0.49 | 31 |
| 1,2-Dichloroethane | " | 6.1605 | 1.48 | 240 |
| 1,1,2-Trichloroethane | " | 14.0776 | 0.74 | 53 |
| Chlorobenzene | " | 10.9400 | 0.71 | 65 |

(2) Coulometric titration

Reagents used: Aquamicon AX (or AS) 100ml
Aquamicon CXU 5ml

| Substance | Sample quantity (g) | Measurement value (µg) | Moisture content (ppm) |
|---------------------------|---------------------|------------------------|------------------------|
| Methylene chloride | 3.7445 | 62 | 17 |
| Ethylene chloride | 3.5193 | 244 | 70 |
| Chloroform | 4.1721 | 332 | 80 |
| 1,1,1-Trichloroethane | 3.7146 | 380 | 102 |
| 1,1,2,2-Tetrachloroethane | 7.9300 | 3553 | 430 |
| Carbon tetrachloride | 4.4559 | 101 | 22 |
| Chlorobenzene | 3.1038 | 207 | 67 |
| Methylene bromide | 2.4660 | 715 | 290 |
| Ethylene bromide | 2.2125 | 202 | 91 |
| Bromoform | 2.6518 | 1747 | 659 |
| 1-Bromotetradecane | 2.0400 | 168 | 75 |
| 1-Bromohexadecane | 1.0255 | 52 | 51 |
| Tetrabromoethane | 2.9079 | 478 | 164 |
| Methyl iodide | 2.3104 | 476 | 206 |
| Ethy iodide | 1.9392 | 337 | 174 |
| Hexadecyl bromide | 1.0067 | 50 | 50 |

3. Alcohols

Key Points

The moisture content of alcohols can be measured easily using direct titration. End-points are stable and highly accurate analytical results are attainable. Both volumetric and coulometric titration can be used.

In the case of volumetric titration, the sample is dissolved in a general-use dehydrated solvent and titrated. Alcohols dissolve very well in this type of solvent and there should not be any problems. Solubility may be inadequate with higher alcohols (such as stearyl alcohol). In such cases it is appropriate to use dehydrated solvents formulated for use with oils.

Propargyl alcohol interferes with the titration by reacting with the Karl Fischer reagent.

For coulometric titration, the sample is dissolved in the electrolyte solution (anolyte). Titration will be prolonged if samples have a high moisture content (2% or above). We recommend either the reduction of the sample quantity, or the use of volumetric titration.

Examples of substances that can be measured directly:

-Monohydric alcohols-

Methanol, ethanol, isopropanol, alkyl alcohol, n-, iso-, tert-butanol, isoamyl alcohol, 2-methyl-4-butanol, 2,4-dimethyl-3-pentanol, decanol, dodecanol, octadecanol, geraniol, citronellol, cyclohexanol, borneol, terpinenol, benzyl alcohol, cholesterol

-Polyhydric alcohols-

Ethylene glycol, 1,2-propanediol, 1,3-propanediol, glycerine, 1,4-butanediol, 1,4-butenediol, 2-methyl-1, 3-propanediol, diethylene glycol, pentaerythritol, D-mannitol, D-sorbitol

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS) 25-50ml
 General-use Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (mg) | Moisture content (ppm) |
|-------------------|--------------------|---------------------|------------------------|------------------------|
| Methanol | General-use | 3.8240 | 0.43 | 112 |
| Ethanol | " | 2.2102 | 3.33 | 1507 |
| n-Butanol | " | 3.9210 | 0.49 | 125 |
| Ethylene glycol | " | 5.5002 | 0.46 | 84 |
| Propylene glycol | " | 5.1726 | 0.78 | 151 |
| Diphenyl carbinol | " | 0.5953 | 0.33 | 554 |

Samples can be measured continuously up to 20-50ml using approximately the same quantities as those shown in the table.

(2) Coulometric titration

Reagents used: Aquamicon AX (or AS) 100ml
 Aquamicon CXU 5ml

| Substance | Sample quantity (g) | Measurement value (µg) | Moisture content (ppm) |
|---------------------------------|---------------------|------------------------|------------------------|
| Ethanol | 2.1936 | 3026 | 1379 |
| n-Propanol | 2.2488 | 1291 | 574 |
| i-Propanol | 2.2244 | 590 | 265 |
| i-Butanol | 2.2361 | 1043 | 467 |
| tert-Butanol | 2.1829 | 1315 | 602 |
| n-Amyl alcohol | 4.1200 | 3024 | 722 |
| Benzyl alcohol | 2.9511 | 280 | 95 |
| Ethylene glycol | 3.1536 | 539 | 171 |
| Propylene glycol | 2.9381 | 1212 | 412 |
| Ethylene glycol monoethyl ether | 2.6777 | 639 | 239 |
| 2-Ethyl hexanol | 0.8310 | 282 | 339 |
| Undecanol | 0.8240 | 63 | 76 |
| Glycerin | 0.7572 | 930 | 1228 |

Samples can be measured continuously up to 20-50ml using approximately the same quantities as those shown in the table.

4. Ethers

Key Points

The moisture content of ethers can be measured readily using direct titration. End-points are stable and highly accurate analytical results are obtainable. The behavior of ethers is similar to that of hydrocarbons. Both volumetric and coulometric titration can be used.

With volumetric titration, the sample is dissolved in a general-use dehydrated solvent and measured. Solubility may be inadequate with ethers that have a high carbon number. In such cases we recommend the use of dehydrated solvents formulated for use with oils.

In the ether group, the following compounds need special care:

Substances that have double bonding and cause interference - Vinyl ether (Note 1)

For coulometric titration, add the sample to the electrolyte solution (anolyte) and take the measurement. With most ethers, measurement can be carried out without difficulty. With propylene oxide, however, there is a limit to the quantity of sample that can be added (Note 2).

Examples of substances that can be measured directly:

Dimethyl ether, diethyl ether, isopropyl ether, ethylene oxide, tetramethylene oxide, methyl carbitol, diethylene glycol, ethylene glycol dimethyl ether, diphenyl ether, dioxane, tetrahydrofuran

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

General-use Dehydrated Solvent GEX (or MS) 25-50ml

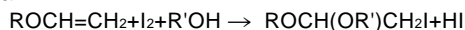
| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (mg) | Moisture content (ppm) |
|---------------------|--------------------|---------------------|------------------------|------------------------|
| γ-Butyrolactam | General-use | 5.6364 | 1.18 | 209 |
| Dioxane | " | 4.9618 | 1.13 | 228 |
| Tetrahydrofuran | " | 2.4548 | 2.96 | 1206 |
| Propylene oxide | " | 4.3472 | 3.09 | 711 |
| Ethyl vinyl ether | " | 0.1833 | 0.59 | 3200 |
| n-Butyl vinyl ether | " | 0.1657 | 0.10 | 600 |
| 2,3-Dihydrofuran | " | 0.2647 | 0.65 | 2400 |

(2) Coulometric titration

Reagents used: Aquamicon AX (or AS) 100ml
 Aquamicon CXU 5ml

| Substance | Sample quantity (g) | Measurement value (µg) | Moisture content (ppm) |
|-----------------------------------|---------------------|------------------------|------------------------|
| Isopropyl ether | 2.0613 | 430 | 208 |
| Ethylene glycol monoethyl ether | 2.7175 | 653 | 240 |
| Diethylene glycol Monoethyl ether | 2.8298 | 1094 | 387 |
| Diethylene glycol Ethyl ether | 4.5130 | 3961 | 878 |
| Dioxane | 2.9090 | 120 | 41 |
| Tetrahydrofuran | 0.8278 | 923 | 1115 |
| γ-Butyrolactam | 3.1256 | 507 | 162 |
| 2-Methyl tetrahydrofuran | 4.3290 | 944 | 218 |
| Propylene oxide | 1.7117 | 1217 | 711 |

Note 1: Vinyl ether causes interference by reacting with the Karl Fischer reagent to produce iodoacetal in accordance with the following formula.



The same type of interference occurs with 2,3-dihydrofuran and dihydropyran.

Corrected titration method:

Add a small amount of the sample (0.5g or less) to 50ml of Dehydrated Solvent CP and titrate this with Karl Fischer reagent. If the amount added is greater than 0.5g, an interference reaction will gradually occur.

Note 2: It proved possible to add propylene oxide in three amounts of 1.7g (total: 5.1g). Thereafter the analytical readings rose until finally, an end point was not reached.

With volumetric titration, it proved possible to add 50g and measure this directly without any problems.

5. Phenols

Key Points

With most phenols the moisture content can be measured directly. As a general rule there are no limitations with volumetric titration, but it is important to be aware that limitations do exist in the case of coulometric titration.

With volumetric titration, the sample is dissolved in a general-use dehydrated solvent in the same way as for alcohols, before undergoing Karl Fischer titration. Solubility is not a problem.

Aminophenols cannot be measured in methanol because of interference reactions. Measurements can be taken, however, by using a titration solvent prepared by adding salicylic acid to Dehydrated Solvent MS (see "12. Amines"). The size of the sample used in such cases should not exceed 2g.

In the case of coulometric titration, anodic oxidation produces a precipitate that adheres to the anode. The resulting contamination of the electrode precludes normal electrode performance and reduces the efficiency of the current. An end point cannot be reached with hydroquinone and aminophenols. This kind of interference is common with coulometric titration, and care should be taken when using the method. In tests carried out by Mitsubishi Chemical Corporation, however, measurements have proved possible under controlled conditions, as follows.

To 100ml of Aquamicron AX,

- a) approximately 1g of phenol is added to begin with.
- b) The total cumulative quantity added is approximately 5g. If there is too much phenol the efficiency of the current will decline and gradually lead to higher analytical values.

Examples of substances that can be measured directly:

Phenol, catechol, resorcinol, pyrogallol, guaiacol, picric acid, o-cresol, p-cresol, 5-methyl resorcinol, eugenol, p-tert-butyl catechol, α -naphthol, β -naphthol

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)

General-use Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|-----------|--------------------|---------------------|------------------------|----------------------|
| Phenol | General-use | 1.9139 | 1.94 | 0.101 |
| m-Cresol | " | 2.6048 | 1.92 | 0.074 |

(2) Coulometric titration

Reagents used: Aquamicon AX (or AS) 100ml

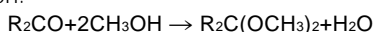
Aquamicon CXU 5ml

| Substance | Sample quantity (g) | Measurement value (μ g) | Moisture content |
|-------------|---------------------|------------------------------|------------------|
| Phenol | 1.8906 | 1241 | 656ppm |
| m-Cresol | 2.0319 | 242 | 119ppm |
| o-Cresol | 0.6042 | 3048 | 0.504% |
| 2,6-Xylenol | 1.4616 | 1737 | 0.119% |

6. Ketones

Key Points

If the Karl Fischer reagent and the titration solvent contain methanol, ketones react with the methanol (ketal bonding) as shown in the following formula. As it produces water this causes an interference reaction.



This may increase the time needed to reach the end point, or may mean that it is never reached. Excessively high moisture readings are among other phenomena that can adversely affect accuracy and precision. However, Karl Fischer titration can be carried out if the following counteracting steps are taken.

- Use a Karl Fischer reagent and titration solvent that do not contain methanol.
- The degree of interference varies according to the type of ketone compound. Determine the size of the sample to use with reference to the specific type of compound.

In general, acetone and cyclohexanone show the strongest reactivity among the aliphatic ketone compounds and reactivity decreases in proportion to the carbon number. Aromatic ketone compounds are reported to be less reactive than the aliphatics. Either volumetric or coulometric titration can be used with these ketones, but a reagent formulated for ketones should be chosen.

Karl Fischer Reagent SS-Z (or SS) is used for volumetric titration. It contains absolutely no methanol and can be used safely with ketones. Use Dehydrated Solvent KTX (or CP), which is formulated for ketones.

For coulometric titration, use a combination of Aquamicon AKX/CXU.

- Reference:** (1) Reference: Muroi, M, et al., J. Japan Petrol. Inst., 26, 97 (1983). "Determination of Water in Ketones and Silicone Oils by Karl Fischer Titration Method"
- (2) Kato, H.: "Determination of Moisture in Ketones and Lower Carboxylic Acids by New Karl Fischer Coulometric Reagent" (in Bunseki Kagaku 34, 147, 1984).

Examples of substances that can be measured directly:

The following inactive carbonyl compounds can be added to methanol (Dehydration Solvent GEX, MS) and measured directly.

Di-isopropyl ketone, camphor, benzophenone, deoxybenzoin, benzyl, benzoin, alizarin, quinalizarin, ninhydrin

For other substances, use a ketone-type reagent.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Ketone-type Dehydrated Solvent KTX (or CP, PP) 25-50ml

| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|------------------------|--------------------|---------------------|------------------------|----------------------|
| Acetone | Ketone-type | 1.4616 | 3.31 | 0.23 |
| Acetylacetone | " | 1.8327 | 1.46 | 0.080 |
| Methyl ethyl ketone | " | 2.2490 | 1.13 | 0.050 |
| Methyl isobutyl ketone | " | 2.2779 | 0.44 | 0.019 |
| Cyclohexanone | " | 0.8839 | 0.80 | 0.090 |
| Acetophenone | " | 2.0562 | 3.58 | 0.17 |
| Furfural | " | 0.5799 | 5.94 | 1.02 |
| Diacetone alcohol | " | 1.8455 | 3.33 | 0.18 |

Note: Dehydrated Solvent KTX should be used in combination with Karl Fischer Reagent SS-Z, and Dehydrated Solvents CP and PP with Karl Fischer Reagent SS.

A feature of Dehydrated Solvents KTX and CP is that they can be used to take measurements at normal temperatures. This is particularly convenient as interference can be suppressed and measurements made without regulating the reaction temperature.

Dehydrated Solvent KTX must always be used with a pyridine-free Karl Fischer Reagent SS-Z. A normal end point will not be achieved if Karl Fischer Reagent SS is used.

In general, the interference state of ketones is ascertained through the continuous addition of reagent. When the analytical reading begins to appear abnormally high, it should be assumed that interference has begun. Beyond that point, analytical readings must be discarded.

(2) Coulometric titration

Reagents used: Aquamicron AKX
 Aquamicron CXU

100ml
 5ml

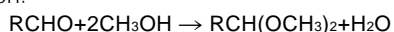
| Substance | Sample quantity (g) | Measurement value (µg) | MoistureContent (%) | Measurable amount (ml) |
|--------------------------------|---------------------|------------------------|---------------------|------------------------|
| Acetone | 0.3954 | 907 | 0.229 | 10 |
| Methyl ethyl ketone | 0.4141 | 464 | 0.112 | 15 |
| Methyl isobutyl ketone | 0.8010 | 102 | 127ppm | 15 |
| Acetylacetone | 0.9760 | 683 | 0.700 | 15 |
| Acetophenone | 0.5451 | 215 | 394ppm | 15 |
| Cyclopentanone | 0.4955 | 1090 | 0.220 | |
| Cyclohexanone | 0.3117 | 635 | 0.204 | 5 |
| Diacetone alcohol | 0.9602 | 217 | 226ppm | |
| 2-Methoxy-2-methyl-4-pentanone | 1.8963 | 81 | 43ppm | 2 |

It is important to be aware of patterns of blank current (also described as "background" or "drift" current) in the moisture meter. If a gradual rise in the blank current causes the end point to fluctuate, it will not be possible to obtain accurate analytical results. In such cases the electrolyte must be replaced.

7. Aldehydes

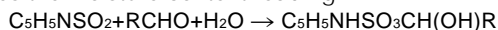
Key Points

If the Karl Fischer reagent and the titration solvent contain methanol, aldehydes react with the methanol (acetal bonding) as shown in the following formula. As it produces water, this causes an interference reaction.



This may cause end point fluctuation, or may mean that the end point is never reached. Other phenomena include excessively high moisture readings.

As shown in the following formula, aldehydes may also react with an ingredient in the Karl Fischer reagent (sulfur dioxide), causing an interference reaction that consumes water (bisulfite addition) and reduces the moisture content reading.



Furthermore, since aldehydes are more reactive than ketones, the reaction speed will vary considerably according to the specific aldehyde involved. Because of these complex problems it is very difficult to obtain accurate analytical readings for aldehydes.

In general, Karl Fischer titration can be carried out if the following counteracting steps are taken.

- a) Use a Karl Fischer reagent and titration solvent that do not contain methanol.
- b) Keep the size of the sample used for titration to a minimum to suppress the reaction that consumes water.
- c) Acetaldehydes are highly reactive and must be titrated under special conditions. These are described later in this manual.

With coulometric titration, sulfur dioxide in the electrolytic solution causes interference that leads to low moisture readings. Although an end point may be reached the analytical reading is unlikely to be accurate and using this method is difficult. In practice, this method should never be used with acetaldehydes.

Reference: Muroi, K, et al., Bull. Chem. Soc. Japan, 38,1176 (1965).
 "The Determination of the Water Content in Acetaldehyde by Means of Karl Fische Reagent"

Examples of substances that can be measured directly:

The following inactive carbonyl compounds can be dissolved in a general-use dehydrated solvent and measured directly.

Formaldehyde,
chloral

However, these substances tend to react with methanol at room temperature (above 25°C) and we recommend a titration method whereby the sample is dissolved in a ketone-type dehydrated solvent.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent KTX (or CP) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|------------------|---------------------|---------------------|------------------------|----------------------|
| n-Butyraldehyde | Ketone-type | 0.4020 | 3.56 | 0.886 |
| Isobutyraldehyde | " | 0.3952 | 0.96 | 0.243 |
| Crotonaldehyde | " | 0.4239 | 0.67 | 0.158 |
| Propionaldehyde | " | 0.2014 | 7.36 | 3.65 |
| Formalin | General-use | 0.0328 | 17.42 | 53.1 |
| Chloral hydrate | " | 0.1752 | 19.27 | 11.0 |

Note: Dehydrated Solvent KTX should be used in combination with Karl Fischer Reagent SS-Z, and Dehydrated Solvent CP with Karl Fischer Reagent SS.

Measuring moisture content in acetaldehydes

Given the intensity of the interference reaction that occurs with acetaldehydes, Dehydrated Solvent PP should be used as it contains no pyridine-sulfur dioxide. The following guidelines should apply.

If the acetaldehyde has a high moisture content, 0.2ml samples can be measured. If the moisture content is less than about 0.2%, however, the sample will be too small and this method cannot be used. Accordingly, when measuring trace amounts of moisture, 5-10ml of sample should be added to 5ml of Dehydrated Solvent PP in the apparatus shown in the diagram. The sample should be vaporized using dried nitrogen during the titration.

1) Sampling

Attach a piece of silicon rubber to the needle of a carefully dried syringe (capacity: 5-10ml, needle length: approx. 10cm). Place the syringe in a dry polyethylene bag and store it in a refrigerator. Remove the thoroughly chilled syringe from the refrigerator, together with a sample container (fitted with a metal sampling stopper) that has also been stored in the refrigerator. Insert the needle of the syringe into the metal stopper and extract some of the sample. Flush the syringe twice with the sample. On the third occasion, extract 5-10ml of sample.

2) Titration

Pour 5ml of Dehydrated Solvent PP into a titration flask (capacity: approx. 50ml), as shown in the diagram. Place the flask in a water bath at a temperature of 20-25 °C. Add dried nitrogen to the titration flask through a three-way cock (E) at a rate of approximately 0.9l/min. Titrate with Karl Fischer Reagent SS until the end point is reached. Stop the agitation of the Dehydrated Solvent PP and the nitrogen flow. Insert the syringe through one of the holes in the three-way valve (E) until the tip of the needle reaches the surface of the Dehydrated Solvent PP. Inject the sample immediately. Start the agitation of the Dehydrated Solvent PP and the nitrogen flow. At the same time, titrate to the end point, using Karl Fischer Reagent SS to drive off the vaporized acetaldehyde.

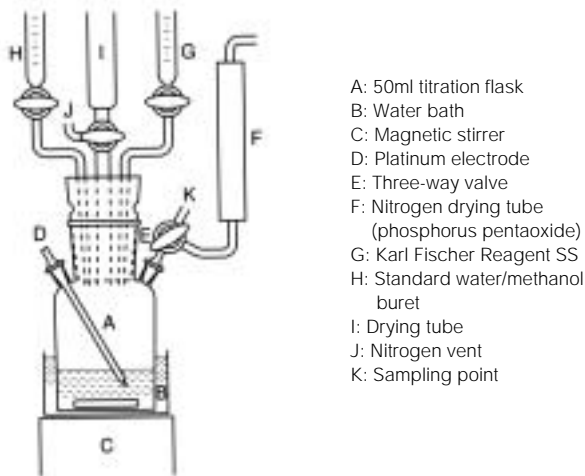


Figure 19: Acetaldehyde Moisture Titration System

Examples:

| No | Sample amount (ml) | Measurement (ml) | Measurement(mg) | |
|----|-----------------------|---------------------|-----------------|-------|
| | | | (mg) | (%) |
| 1 | 1 | 0.14 | 0.42 | 0.053 |
| 2 | 3 | 0.41 | 1.23 | 0.052 |
| 3 | 5 | 0.65 | 1.95 | 0.050 |
| 4 | 7 | 1.06 | 3.17 | 0.050 |
| 5 | 10 | 1.32 | 3.95 | 0.050 |

Note: Titer of Karl Fischer reagent: 3.00mg/ml

(2) Coulometric titration

Reagents used: Aquamicon AKX
Aquamicon CXU

100ml
5ml

| Substance | Sample quantity (g) | Measurement value (μ g) | Moisture Content (%) |
|-------------------------|------------------------|---------------------------------|-------------------------|
| Benzaldehyde | 0.5205 | 343 | 660ppm |
| Salicylaldehyde | 0.6257 | 751 | 0.120 |
| 3-Phenylpropionaldehyde | 0.5435 | 1467 | 0.270 |
| Chloral hydrate | 0.0441 | 4916 | 11.1 |

8. Organic Acids

Key Points

With most organic acids, moisture content can be measured directly and easily. If a dehydrated solvent with methanol as its main ingredient is used, however, interference will occur as the result of an esterification reaction between methanol and lower carboxylic acids such as formic acid, acetic acid and adipic acid. These reactions produce water and will be evidenced by a delayed end point or an unusually high analytical result.

Esterification reactions vary, depending on the individual acid. Formic acid shows a strong esterification reaction and will react very quickly with methanol. Reactivity lessens as the carbon number increases. Normally, during volumetric titration, propionic acid will not trigger interference attributable to an esterification reaction. Aromatic carboxylic acid is another substance that does not cause interference related to esterification.

Interference can also result from a reaction with iodine. Formic acid appears to be affected by the oxidation of iodine and L-ascorbic acid reacts quantitatively with Karl Fischer reagent.

For volumetric titration, a ketone-type dehydrated solvent is used with lower carboxylic acids. A general-use dehydrated solvent can be used with higher carboxylic acids and aromatic carboxylic acid. If problems are encountered with the methanol solubility of substances with high carbon numbers, a dehydrated solvent formulated for oils (such as stearic acid) should be used.

For measurements based on coulometric titration, a ketone-type of anolyte is used with the lower carboxylic acids. Coulometric titration cannot be used for formic acid, however, as an end point cannot be reached. A general-use electrolyte can be used with higher carboxylic acids and aromatic carboxylic acid.

Examples of substances that can be measured directly:

Acetic acid, mono-, di-, trichloroacetic acid, trifluoroacetic acid, propionic acid, acrylic acid, methacrylic acid, trimethylacetic acid, caproic acid, stearic acid, oleic acid, linolenic acid, cyclohexane carboxylic acid, cyclohexyl acetic acid, camphoric acid, abietic acid, 3,5-dinitrobenzoic acid, cinnamic acid, anisic acid, benzilic acid, 2,4-dichlorophenoxy acetic acid, benzoic acid

Polybasic acids

Oxalic acid, malonic acid, maleic acid, succinic acid, diglycolic acid, adipic acid, sebacic acid, nitrilotriacetic acid, phthalic acid, terephthalic acid

Sulfonic acids

Benzenesulfonic acid, toluenesulfonic acid, xylenesulfonic acid, naphthalenesulfonic acid, sulfanilic acid

Hydroxy acids

Glycolic acid, α -hydroxybutyric acid, citric acid, tartaric acid, δ -hydroxycaproic acid, α -hydroxyadipic acid, α,α -dihydroxyadipic acid, ricinoleic acid, salicylic acid

Amino acids

Glycine, leucine, sarcosine, valine, aspartic acid, iminodiacetic acid, creatine, asparagine, methionine, phenylalanine, glutamic acid

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)
 Dehydrated Solvent KTX (or CP) 25-50ml
 Dehydrated Solvent OL II (or CM)

| Substance | Dehydrated solvents | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|-----------------------|---------------------|---------------------|------------------------|----------------------|
| Acetic acid | Ketone-type | 4.8365 | 7.86 | 0.16 |
| Monochloroacetic acid | " | 1.0110 | 2.70 | 0.27 |
| Dichloroacetic acid | " | 0.7817 | 0.86 | 0.11 |
| Propionic acid | General-use | 4.9670 | 10.92 | 0.22 |
| Salicylic acid | " | 3.5186 | 0.85 | 0.024 |
| Oxalic acid | " | 0.1211 | 35.19 | 29.1 |
| Stearic acid | Oil-type | 2.4937 | 0.42 | 0.017 |

Note: Dehydrated Solvent KTX should be used in combination with Karl Fischer Reagent SS-Z, and Dehydrated Solvent CP with Karl Fischer Reagent SS.

(2) Coulometric titration

Reagents used: Aquamicon AKX (or AX) 100ml
 Aquamicon CXU 5ml

| Substance | Electrolyte | Sample quantity(g) | Measurement value (µg) | Moisture content (ppm) |
|---------------------|-------------|--------------------|------------------------|------------------------|
| Formic acid | Ketone-type | 1.220 | Not measurable | |
| Acetic acid | " | 1.050 | 687 | 655 |
| Propionic acid | " | 0.993 | 1321 | 1330 |
| Dichloroacetic acid | " | 1.563 | 1313 | 840 |
| Salicylic acid | General-use | 1.6222 | 341 | 210 |
| Stearic acid | " | 2.1418 | 130 | 61 |
| Oxalic acid | " | 0.0222 | 6645 | 29.9% |

9. Esters**Key Points**

Esters are substances for which moisture content can be measured very easily using standard Karl Fischer titration procedures. There are no significant interference reactions and behavior is similar to that of hydrocarbons. Both volumetric and coulometric titration can be used without any problem.

For volumetric titration, a general-use dehydrated solvent is used. Solubility will be a problem with long-chain aliphatic esters and a dehydrated solvent formulated for oils is recommended.

With coulometric titration, measurements are carried out by adding the sample directly to the electrolyte (anolyte).

Examples of substances that can be measured directly:**Esters**

Methyl formate, ethyl formate, methyl acetate, ethyl acetate, aryl formate, methyl acrylate, methyl methacrylate, ethyl malonate, methyl valerate, methyl adipate, methyl sebacate, methyl glycolate, 2,3-butylene di-acetate, ethyl citrate, cyclohexyl acetate, methyl benzoate, methyl salicylate, phenyl acetate

Inorganic esters

Ethyl carbonate, ethyl chlorocarbonate, butyl nitrite

Lactones

γ -butyrolactone

Carbamic acid esters

Methyl carbamate, ethyl carbamate

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS) 25-50ml
Dehydrated Solvent GEX (or MS)

| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (μg) | Moisture content (ppm) |
|------------------------|--------------------|---------------------|-------------------------------------|------------------------|
| Methyl acetate | General-use | 0.9467 | 2.15 | 2224 |
| Ethyl acetate | " | 4.3557 | 0.86 | 197 |
| Methyl acrylate | " | 2.8098 | 5.31 | 1890 |
| γ -Butyrolactam | " | 5.6364 | 1.18 | 210 |

(2) Coulometric titration

Reagents used: Aquamicron AX (or AS) 100ml
Aquamicron CXU 5ml

| Substance | Sample quantity (g) | Measurement value (μg) | Moisture content (ppm) |
|-----------------------|---------------------|-------------------------------------|------------------------|
| Methyl acetate | 2.5250 | 105 | 42 |
| Methyl isoamyl | 0.8548 | 1280 | 1494 |
| n-Butyl acetate | 2.4589 | 195 | 79 |
| Isopropyl isovalerate | 0.9186 | 1256 | 1367 |
| Di-isopropyl malonate | 1.0740 | 449 | 418 |
| Benzyl benzoate | 1.5825 | 319 | 202 |
| | 3.1695 | 512 | 162 |

10. Organic Acid Salts

Key Points

Since organic acid salts containing water of crystallization dissolve readily in methanol, their moisture content can be measured easily using a general-use dehydrated solvent. In the case of organic acid salts that do not contain water of crystallization, moisture content can be measured by dissolving or dispersing the substances in a general-use dehydrated solvent. As these substances are solids with a high moisture content, we recommend measurement using volumetric titration.

The organic salt sodium tartrate dihydrate was formerly used as a standard reagent for determining the titer of Karl Fischer reagents for use in volumetric titration.

Examples of substances that can be measured directly:

Organic acid salts containing water of crystallization

Barium acetate, cadmium acetate, cobalt acetate, lead acetate, magnesium acetate, nickel acetate, sodium acetate, zinc acetate, uranyl acetate, sodium citrate, lithium citrate, calcium lactate, calcium malonate, sodium naphthionate, ammonium oxalate, potassium oxalate, calcium propionate, sodium succinate, sodium benzoate, sodium tartrate

Organic acid salts without water of crystallization

Ammonium acetate, sodium adipate, potassium hydrogen tartrate, ammonium citrate, sodium formate, sodium phthalate, zinc stearate

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|--------------------|--------------------|---------------------|------------------------|----------------------|
| Sodium L-aspartate | General-use | 0.0841 | 4.32 | 5.14 |
| Lithium citrate | " | 0.0354 | 8.73 | 24.7 |
| Sodium citrate | " | 0.0812 | 10.08 | 12.4 |
| Ammonium acetate | " | 1.2884 | 6.44 | 0.500 |
| Cadmium acetate | " | 0.2750 | 37.07 | 13.5 |
| Magnesium acetate | " | 0.1918 | 64.27 | 33.5 |
| Lithium acetate | " | 0.1003 | 4.13 | 11.5 |
| Sodium acetate | " | 0.0678 | 10.75 | 15.8 |
| Sodium naphionate | " | 0.0731 | 5.85 | 22.8 |
| Calcium lactate | " | 0.2003 | 58.39 | 29.2 |
| Oxalic acid | " | 0.0825 | 23.58 | 28.6 |
| Manganese benzoate | " | 0.0862 | 9.45 | 11.0 |
| Calcium stearate | Oil-type | 0.2046 | 5.98 | 2.92 |

11. Organic Hydrates

Key Points

Since organic hydrates are solids, measurements can normally be carried out directly using volumetric titration. For measurements using volumetric titration, these substances can be dissolved or dispersed in a general-use dehydrated solvent. As with organic acid salts, volumetric titration is generally recommended for organic hydrates.

Water of crystallization is not always stable in organic hydrates and moisture content frequently varies with reference to temperature and humidity. Cyanuric acid, in particular, tends to lose most of its water of crystallization.

Examples of substances that can be measured directly:

Pyromellitic acid, L-asparagine, creatine, L-histidine, dextrose, L-rhamnose, raffinose, chloral hydrate, ninhydrin, alloxan, piperazine, o-phenantholine, brucine, brucine sulfate

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvents | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|-------------------|---------------------|---------------------|------------------------|----------------------|
| Chloral hydrate | General-use | 0.1752 | 19.27 | 11.0 |
| Hydrazine hydrate | " | 0.0732 | 25.68 | 35.1 |

12. Amines

Key Points

Some amines exhibit unusual behavior during Karl Fischer titration. That behavior falls into two categories; that caused by basicity and that caused by other chemical interference reactions. The titration conditions must be modified in accordance with the nature of the behavior that is involved.

In terms of basicity, substances can be divided into two groups using benzylamine with a pKa value of 9.4 ($K_a=2.4 \times 10^{-5}$) as the dividing line.

1) Amines below pKa9.4

Titration can be carried out without difficulty using standard procedures and behavior is comparable with hydrocarbons. In the case of volumetric titration, the substances are dissolved in a general-use dehydrated solvent and titrated directly. With coulometric titration, the sample is introduced into a general-use electrolyte (anolyte) and titrated directly.

2) Amines with strong-basicity (above pKa9.4)

Aside from the Karl Fischer reactions with water, interference reactions caused by the strong basicity of these substances gradually consume the Karl Fischer reagent and are known to cause the following phenomena.

- a. Poor end point stability
- b. Failure to reach end point
- c. Abnormally high analytical results

To suppress these interference reactions, the substances must be neutralized with acids before titration and the Karl Fischer titration system must be kept in a state that is close to neutrality. Salicylic acid is normally used for this purpose as it causes almost no esterification reaction with titration solvents which have methanol as their main ingredient. If acetic acid is used, the esterification reaction must be suppressed by chilling the system to 15 °C or below during the Karl Fischer titration.

For volumetric titration the titration solvent is prepared by dissolving 10g of salicylic acid in 50ml of Dehydrated Solvent GEX (or MS).

For coulometric titration the electrolyte is prepared by dissolving 10g of salicylic acid in 100ml of general-use electrolyte (anolyte).

Note:Up to 70mmol of amine can be neutralized with 10g of salicylic acid. This is why titration is normally carried out continuously with a quantity that corresponds to a sample of 70mmol.

Substances that react with electrodes or cause other interference reactions

Coulometric titration cannot be used for substances that react with electrodes, such as aniline, toluidine, diamines and aminophenol.

With substances such as aniline or toluidine, the end point will not be clear if methanol is used as the titration solvent for volumetric titration. Volumetric titration is possible, provided that Dehydrated Solvent CP is used. Diamines cause an interference reaction with iodine, with the result that the end point is never reached.

Reference:(1) Muroi, K. et al., "Measuring Trace Moisture Content in Amines Using the Karl Fischer Method" (in Bunseki Kiki [Analytical Equipment] 8, 374, 1969).

(2) Kato, H. et al., "Determination of Moisture in Amines by Karl Fischer Coulometric Titration" (in Bunseki Kagaku 34, 805 (1985)).

Examples of substances that can be measured directly using standard methods:

Pyridine, 2-aminopyridine, 2-picoline, quinoline, pyrrole, imidazole, triazine, triazole, indole, carbazole, benzothiazole, N,N-dimethylaniline, diphenylamine, 2-pyridyl ethanol, 4-pyridyl ethanol

Examples of substances that require neutralization with acid:

Trimethylamine, ethylamine, diethylamine, triethylamine, propylamine, isopropylamine, 3-methoxypropylamine, butylamine, di-isobutylamine, di-sec-butylamine, dipentylamine, hexylamine, N,N-dimethylcyclohexylamine, dicyclohexylamine, benzylamine, pyrrolidine, piperidine, piperazine, morpholine, ethanolamine, N,N-dimethylethanolamine, diethanolamine, triethanolamine, di-isopropanolamine, tri-isopropanolamine, Tris (hydroxymethyl) aminomethane

Examples of substances that require a methanol-free titration solvent:

Aniline, toluidine, anisidine, naphthylamine

[Examples of Measurement]**(1) Volumetric titration --neutralization using salicylic**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
 Dehydrated Solvent GEX (or MS) approx. 50ml
 Salicylic acid approx. 10g

| Substance | Dehydrated solvents | Sample quantity(g) | Measurement value (mg) | Moisture content (%) |
|--------------------------|----------------------------|--------------------|------------------------|----------------------|
| n-Butylamine | General-use+Salicylic acid | 0.7335 | 1.45 | 0.20 |
| Diethylamine | " | 0.7234 | 1.02 | 0.14 |
| Diethanolamine | " | 1.0240 | 2.62 | 0.26 |
| Piperidine | " | 0.9034 | 1.00 | 0.11 |
| Tri-n-butylamine | " | 1.6367 | 1.27 | 0.077 |
| Di-isopropyl amine | " | 1.5010 | 1.21 | 0.081 |
| 2-Methylaminopyridine | " | 1.052 | 0.47 | 0.12 |
| Triethanolamine | " | 1.124 | 0.70 | 0.17 |
| N-Ethyl morpholine | " | 0.905 | 0.88 | 0.26 |
| N,N-Dimethyl benzylamine | " | 0.900 | 1.55 | 0.17 |
| N-Ethyl aniline | " | 0.958 | 0.55 | 0.057 |
| Aniline | Ketone-type | 1.0185 | 1.49 | 0.15 |

Note:Salicylic acid crystals are bulky and difficult to handle. To overcome this problem, place 10g of salicylic acid in an empty titration flask and add Dehydrated Solvent GEX. The salicylic acid will dissolve readily and can be rendered moisture-free through a Karl Fischer titration that prepares for the main titration.

(2) Coulometric titration

Reagents used: Aquamicron AX (or AS) 100ml
 or with approx. 10g of Salicylic acid added
 Aquamicron CXU 5ml

| Substance | pKa | Sample quantity (g) | Measurement value (µg) | Moisture content (%) |
|-------------------------------|------|---------------------|------------------------|----------------------|
| i-Propylamine | 10.6 | 0.694 | 321 | 463ppm |
| n-Butylamine | 10.6 | 0.732 | 2440 | 0.333 |
| n-Hexylamine | 10.6 | 0.766 | 496 | 648ppm |
| Diethylamine | 11.0 | 0.707 | 989 | 0.140 |
| Di-i-propylamine | 11.1 | 0.722 | 931 | 0.129 |
| Di-n-butylamine | 11.3 | 0.760 | 3231 | 0.425 |
| Triethylamine | 10.7 | 0.726 | 5582 | 0.769 |
| Tri-n-propylamine | 10.7 | 0.753 | 1159 | 0.154 |
| Tri-n-butylamine | 10.9 | 0.778 | 626 | 805ppm |
| 3-Dimethylamino propionitrile | 6.9 | 0.870 | 2635 | 0.303 |
| Cyclohexylamine | 10.6 | 0.867 | 1741 | 0.201 |
| Monoethanolamine | 9.5 | 0.269 | 614 | 0.228 |
| Diethanolamine | 9.0 | 1.097 | 1199 | 0.109 |
| Triethanolamine | 7.8 | 1.124 | 1870 | 0.166 |
| 2-Diethylaminoethanol | 9.4 | 0.884 | 2757 | 0.312 |
| 1,3-Diaminopropane | | 0.218 | 1471 | 0.675 |
| 1,2-Propane diamine | | | Cannot be measured | |
| Pyrrolidine | 11.3 | | Cannot be measured | |
| Piperidine | 11.2 | 0.861 | 3971 | 0.461 |
| 4-Benzyl piperidine | 10.3 | 0.997 | 6314 | 0.633 |
| Piperazine | | 0.200 | 210 | 0.105 |
| Pyrrole | | 0.967 | 3104 | 0.321 |
| N-Methyl morpholine | 7.7 | 0.905 | 1907 | 0.211 |
| Benzylamine | 9.4 | 0.268 | 452 | 0.169 |
| N,N-Dimethyl benzylamine | 8.9 | 0.900 | 1042 | 0.116 |
| 2-Amino-3-picoline | 6.7 | 1.031 | 2621 | 0.254 |
| 2-Methyl aminopyridine | 6.7 | 1.052 | 1280 | 0.122 |
| o-Toluidine | 4.4 | | Cannot be measured | |
| m-Toluidine | 4.7 | | Cannot be measured | |
| p-Anisidine | 5.3 | | Cannot be measured | |
| m-Aminophenol | 4.2 | | Cannot be measured | |
| Dimethyl aminomethyl phenol | 7.9 | 0.986 | 1606 | 0.163 |
| N,N-Dimethyl-p-toluidine | 5.6 | 0.937 | 494 | 527ppm |
| Aniline | 4.6 | | Cannot be measured | |
| N,N-Diethyl aniline | 6.6 | 0.938 | 102 | 109ppm |
| o-Chloro-aniline | 2.6 | 1.213 | 361 | 298ppm |
| 2-Anilinoethanol | 4.0 | 1.085 | 2614 | 0.241 |

13. Amides, Anilides

Key Points

The moisture content of amides and anilides can be measured easily using standard methods. Amides behave in the same way as weak-basicity amines. Both volumetric and coulometric titration can be used. For volumetric titration, use either a general-use or an oil-type dehydrated solvent, depending on the solubility of the sample. In the case of coulometric titration, the sample is added directly to the electrolyte (anolyte).

Examples of substances that can be measured directly:

Formamide, acetamide, malonamide, dimethyl formamide, urea, ethylene urea, biuret, acetyl urea, alloxan, benzamide, salicylamide, acetanilide, propionanilide

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|------------------------|---------------------|---------------------|------------------------|----------------------|
| Formamide | General-use | 2.2307 | 1.71 | 0.077 |
| N,N-Dimethyl formamide | " | 2.6466 | 3.28 | 0.124 |
| Urea | " | 2.5000 | 1.40 | 0.056 |
| Acetanilide | " | 4.9110 | 10.35 | 0.211 |
| Stearamide | Oil-type | 3.6953 | 0.15 | 0.004 |

(2) Coulometric titration

Reagents used: Aquamicron AX (or AS) 100ml
 Aquamicron CXU 5ml

| Substance | Sample quantity (g) | Measurement value (µg) | Moisture Content (ppm) |
|------------------------|---------------------|------------------------|------------------------|
| Formamide | 2.1173 | 1510 | 713 |
| N,N-Dimethyl formamide | 2.6484 | 552 | 208 |
| Acetamide | 4.6866 | 314 | 67 |
| N,N-Dimethyl acetamide | 1.1590 | 707 | 612 |
| Oleylamide | 2.1790 | 78 | 36 |
| Erucamide | 3.8854 | 148 | 38 |

14. Nitriles, Cyanohydrins**Key Points**

Nitriles have weak basicity and can be measured easily using standard methods. Reliable moisture measurement is also possible with cyanohydrins. Both volumetric and coulometric titration can be used. For volumetric titration, a general-use dehydrated solvent is used. For coulometric titration, the sample is added directly to the electrolyte (anolyte).

Examples of substances that can be measured directly:

Acetonitrile, aminoacetonitrile, acrylonitrile, sebaconitrile, methylene aminoacetonitrile, adiponitrile, acetone cyanhydrin, formaldehyde cyanhydrin, acrolein cyanhydrin acetate

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
 Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|--------------|---------------------|---------------------|------------------------|----------------------|
| Acetonitrile | General-use | 2.1687 | 3.22 | 0.148 |

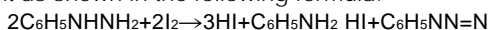
(2) Coulometric titration

Reagents used: Aquamicon AX (or AS) 100ml
 Aquamicon CXU 5ml

| Substance | Sample quantity (g) | Measurement value (µg) | Moisture Content (ppm) |
|---------------|---------------------|------------------------|------------------------|
| Acetonitrile | 0.7691 | 822 | 1070 |
| Acrylonitrile | 0.0800 | 295 | 3690 |

15. Hydrazines**Key Points**

Iodine oxidation causes hydrazine derivatives to react with Karl Fischer reagent as shown in the following formula.



Karl Fischer titration is possible also with acidic solvents. Moisture content can be measured without this reaction if the sample is first dissolved in an excess of acetic acid (approx. 2g of sample in 25ml of acetic acid).

The moisture content of dinitrophenyl hydrazine and benzoyl hydrazine can also be measured accurately if the sample is dissolved in acetic acid and then titrated. Hydrazine hydrochloride reacts with iodine on a mole-for-mole basis, but hydrazine sulfate does not react with Karl Fischer reagent and can be dissolved in methanol for titration.

In the case of hydrazine compounds, volumetric titration is the only method that can be used. Coulometric titration is not suitable.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
 Dehydrated Solvent GEX (or MS) approx. 50ml
 Titrate after cooling to 15°C or lower.

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-----------|---------------------|---------------------|------------------------|----------------------|
| Hydrazine | General-use | 0.0296 | 0.84 | 2.85 |

| Substance | Sample moisture (%) | content (%)Amount added | |
|-------------------------------|---------------------|-------------------------|-------------------|
| | | Added moisture | Measurement value |
| Semicarbazide hydrochloride | 0.39±0.00 | 2.52 | 2.50 |
| Phenylhydrazine hydrochloride | 0.37±0.01 | 2.50 | 2.53 |

16. Other Nitrogenous Compounds

Key Points

Both volumetric and coulometric titration can be used directly for other nitrogenous compounds. For volumetric titration, the substance is dissolved in a general-use dehydrated solvent and titrated. If a substance is difficult to dissolve its solubility can be improved with the addition of another solvent.

Coulometric titration is carried out using a general-purpose electrolyte and in accordance with standard procedures.

Examples of substances that can be titrated directly:

Lactam, Imines

ε -Caprolactam, benzal-n-butylimine

Cyanohydrine

Formaldehyde cyanohydrin, acetone cyanhydrin, acrolein cyanohydrines

Azo-, azole compounds

p-Aminoazobenzene, diazoaminobenzene, benzotriazole

Isocynates, nitroso compounds

1-Naphthyl isocyanate, phenyl isocyanate, N-nitrosodiphenylamine

Nitro compounds

Nitromethane, nitroglycerine, 2-nitropropane, m-dinitrobenzene, 3,5-dinitrobenzoic acid

Oximes, hydroxamic acids

Acetone oxime, dimethylglyoxime, butylaloxime, hepta-aldoxime, cyclohexanone oxime

Cyanic acid derivatives

Cyanamides, dicyanamides, cyanuric acid, melamine

Amidines

Guanidine nitrate

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-------------------------|---------------------|---------------------|------------------------|----------------------|
| Nitromethane | General-use | 5.6235 | 0.99 | 0.018 |
| Nitroethane | " | 2.0672 | 4.63 | 0.22 |
| 1-Nitropropane | " | 1.8575 | 2.75 | 0.15 |
| m-Nitroaniline | " | 2.3233 | 1.26 | 0.054 |
| p-Nitrophenol | " | 0.9844 | 11.30 | 1.15 |
| o-Nitro-p-chloroaniline | " | 0.9209 | 0.30 | 0.033 |
| m-Dinitrobenzene | " | 1.0835 | 0.15 | 0.014 |
| 2,4-Dinitrotoluene | " | 1.9935 | 0.06 | 0.003 |
| ε-Caprolactam | " | 1.5336 | 3.22 | 0.21 |
| N-Methyl pyrrolidine | " | 3.1519 | 2.14 | 0.068 |
| m-Nitro-p-toluidine | *1 | 2.1785 | 0.45 | 0.021 |
| p-Dichloro nitrobenzene | *2 | 10.1400 | 0.78 | 0.008 |

*1: Dehydrated Solvent MS 25ml + dinitromethane 10ml

*2: Dehydrated Solvent MS 25ml + dichloromethane 10ml

(2) Coulometric titration

Reagents used: Aquamicron AX (or AS) 100ml
Aquamicron CXU 5ml

| Substance | Sample quantity (g) | Measurement value (μg) | Moisture Content (ppm) |
|-------------------------|---------------------|------------------------|------------------------|
| Nitromethane | 1.1312 | 993 | 879 |
| Nitroethane | 10237 | 2224 | 0.217% |
| 1-Nitropropane | 0.9757 | 1324 | 0.136% |
| 2-Nitropropane | 1.0338 | 816 | 789 |
| p-Nitrophenol | 0.5196 | 5507 | 1.06% |
| m-Nitroaniline | 1.5120 | 875 | 579 |
| m-Nitro-p-toluidine | 2.0193 | 404 | 200 |
| o-Nitro-p-chloroaniline | 1.0060 | 295 | 293 |
| N-Vinyl pyrrolidone | 1.0675 | 340 | 319 |
| ε-Caprolactam | 0.6448 | 1290 | 0.200% |
| Isocyanate | 3.3597 | 95 | 28 |

In all cases, samples can be measured up to a volume of 20-50ml, as shown in the table.

17. Acid Anhydrides

Key Points

Acid anhydrides and acylates can be measured directly using volumetric titration. The sample is subjected to Karl Fischer titration after it has been dissolved in either a general-use dehydrated solvent or a compound solvent made up of one part pyridine to four parts methanol by volume.

Examples of substances that can be titrated directly:

Acid Anhydrides

Acetic anhydride, propionic anhydride, butyric anhydride, n-valeric anhydride, succinic anhydride, benzoic anhydride, phthalic anhydride

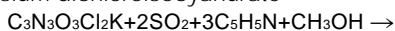
18. Acid Chlorides

Key Points

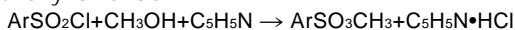
The following acid chlorides cause interference through oxidation of the hydriodic acid in Karl Fischer reagent and the release of free iodine. For this reason, water content is measured using volumetric titration as follows.

To suppress the interference, neutralize the sample by adding 1-3g of the sample to a methanol solvent that includes 20% pyridine/sulfur dioxide (SO₂ 32g/pyridine 100ml). Then carry out the Karl Fischer titration.

1) Potassium dichloroisocyanurate



2) Aryl sulfonyl chloride



Coulometric titration cannot be used because of the interference.

Examples of substances that can be titrated directly:

Acid Chlorides

Propionyl chloride, butyryl chloride, valeryl chloride, caproyl chloride, capryl chloride, stearoyl chloride, benzoyl chloride

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS

Dehydrated Solvent MS + SO₂/pyridine solvent 25-50ml

| Substance | Sample quantity (g) | Measurement value (mg) | Moisture Content (%) |
|-----------------------------------|---------------------|------------------------|----------------------|
| Potassium dichloroisocyanurate | 1.0228 | 2.45 | 0.24* |
| p-Toluene sulfonyl chloride | 1.0541 | 0.82 | 0.078 |
| p-Chlorobenzene sulfonyl chloride | 1.0059 | 1.20 | 0.12** |
| Toluene 2,4-disulfonyl chloride | 0.8721 | 2.18 | 0.25 |
| p-Ethylbenzene sulfonyl chloride | 1.6708 | 0.54 | 0.032 |
| Methanesulfonyl chloride | 2.9444 | 2.10 | 0.071 |

*: Drying method 0.23%

**: Infrared method 0.14%

19. Quinones**Key Points**

Quinones interfere with the titration through the oxidation of hydriodic acid, which is produced from a reaction between water and Karl Fischer reagent, to produce free iodine. For this reason, direct titration is impossible. Instead, an indirect method based on water vaporization is used.

Either volumetric or coulometric Karl Fischer titration can be used. Refer to the section on Basic Knowledge for information on the water vaporization method.

[Examples of Measurement]**(1) Water vaporization - Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)

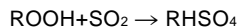
Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating temperature (°C) | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|----------------------|--------------------------|---------------------|------------------------|----------------------|
| Naphthoquinone (wet) | 160 | 0.1185 | 7.62 | 6.43 |
| Naphthoquinone (dry) | 160 | 2.2096 | 0.82 | 0.037 |
| p-Quinone | 130 | 3.5710 | 0.15 | 0.0042 |

20. Peroxides

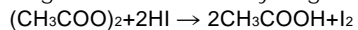
Key Points

As shown in the following formula, peroxides react with the sulfur dioxide in Karl Fischer reagent. In general, however, there is no interference.

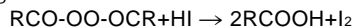


It is important to ensure that there is always an adequate excess of sulfur dioxide.

Acetyl peroxide is highly reactive and causes interference by releasing iodine through the oxidation of hydrogen iodide.



Other substances may also cause interference if there is insufficient sulfur dioxide. Dialkyl peroxides (R-OO-R) are not reactive and have no effect on Karl Fischer titration. Diacyl peroxides (RCO-OO-OCR) cause interference through the oxidation of hydrogen iodide as shown in the following formula.



Examples of substances that can be measured directly:

Di-tert-butyl peroxide (this substance causes an exothermic reaction when titrated with Karl Fischer reagent, but moisture content can be measured accurately), diethyl peroxide, lauryl peroxide, triacetone peroxide

21. Sulfur Compounds

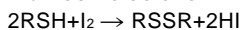
Key Points

The moisture content of most sulfur compounds, including sulfides, disulfides, thiocyanic acid and sulfonic acid, can be measured by means of direct titration using standard procedures. As with hydrocarbons, these compounds have a tendency to slow the rate of the reaction between water and Karl Fischer reagent, so they should always be measured in excess methanol.

For volumetric titration, the substances are measured after they have been dissolved in a general-use dehydrated solvent.

For coulometric titration, the sample is added directly to a general-use electrolyte (anolyte).

The only substances that cause interference are mercaptan, thiourea, thioacetic acid and dithio acid. These consume Karl Fischer reagent by reacting with iodine as shown in the following formulae.



Before these substances can be titrated, they must be neutralized using special procedures.

Dimethyl sulfoxide (DMSO) exhibits unusual behavior. Karl Fischer titration appears to move toward a stable end point without any difficulty, but with sequential addition of the sample the moisture content declines with each analysis. It is important to note that the presence of DMSO reduces the percentage of water recovered.

Examples of substances that can be measured directly:

Sulfides

Carbon disulfide, allyl sulfide, n-butyl sulfide, n-butyl disulfide, thiophene, benzothiophene

Thiocyanates, etc.

Ethyl thiocyanate, ethylene thiocyanate, n-butyl thiocyanate, ethyl isothiocyanate, 1-naphthyl isothiocyanate, ethyl thioacetate, benzothiazole, 1-acetyl-2-thiourea, methyl isothiurea

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (mg) | Moisture content (ppm) |
|--------------------|--------------------|---------------------|------------------------|------------------------|
| Carbon disulfide | General-use | 6.3050 | 0.62 | 98 |
| Dimethyl sulfoxide | " | 3.0721 | 0.92 | 298 |

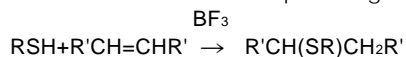
(2) Coulometric titration

Reagents used: Aquamicon AX (or AS) 100ml
Aquamicon CXU 5ml

| Substance | Sample quantity (g) | Measurement value (µg) | Moisture Content (ppm) |
|--------------------|---------------------|------------------------|------------------------|
| Dimethyl sulfoxide | 1.0773 | 784 | 728 |
| Benzothiophene | 1.1633 | 158 | 136 |

Measuring the Moisture Content of Mercaptan

Interference caused by mercaptan can be eliminated by reacting an active olefin such as octene with the sample using boron trifluoride as the catalyst.



- a) Reagent Solution of boron trifluoride and ethyl ether (BF₃ 45%)
or Solution of boron trifluoride and acetic acid (100gBF₃/l)
Isooctene, glacial acetic acid, pyridine

b) Measurement method

Put 5-10ml of glacial acetic acid into a 250ml measuring flask. Add the sample making sure that the amount of mercaptan does not exceed 15 millimoles. Next, add 3ml of boron trifluoride/ethyl ether solution or 10ml of boron trifluoride/acetic acid solution and 6ml of isooctene. Mix well and leave for about 30 minutes at room temperature. Carefully add 5ml of pyridine and then titrate the solution with Karl Fischer reagent. Using the same procedures, obtain a dummy test result for the reagent. Subtract this from the titration value to determine the moisture content. However, the reagent used should always be thoroughly dehydrated.

(JACS., 62, 1 (1940))

Note:An error will occur at the rate of 0.3ppm of water for every 1ppm of sulfur in the mercaptan. If the mercaptan content is low, an accurate measurement of the moisture content can be obtained by adjusting the measurement value.

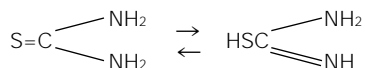
Reference:JISK2275 Crude oil and petroleum products - Determination of water content

Test Examples

| Sample | Moisture (%) | content (%) | |
|---------------------|--------------|----------------|----------------------|
| | | Added moisture | Observed moisture(%) |
| Ethyl mercaptan | 0.70 | 6.30 | 6.35 |
| Isopropyl mercaptan | 0.90 | 6.30 | 6.25 |
| Butyl mercaptan | 0.85 | 3.05 | 3.05 |
| Isoamyl mercaptan | 0.40 | 2.85 | 2.90 |
| Hexyl mercaptan | 0.15 | 1.85 | 1.85 |
| Heptyl mercaptan | 0.70 | 4.60 | 4.60 |
| Benzyl mercaptan | 0.25 | 2.80 | 2.80 |
| Thiophenol | 0.25 | - | - |
| 2-Thionaphthol | 0.05 | 1.35 | 1.35 |
| Thioglycollic acid | 3.85 | 6.95 | 7.00 |

Other Substances that Cause Interference

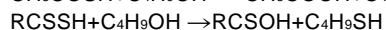
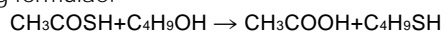
It may not be possible to obtain a clear end point with thiourea as it reacts with iodine. This is because thiourea triggers tautomerism and interconverts to isothiurea, which causes the same reaction as mercaptan.



1-Phenyl-2-thiourea, 1, 3-diphenyl thiourea and thiobenzamide also react in the same way as thiourea. However, N-methyl thiourea and 1-acetyl-2-thiourea can be titrated directly without causing a reaction.

When thioacetic acid is titrated directly, it reacts quantitatively with Karl Fischer reagent and consumes 1 mole of iodine per mole. Dithio acid causes a similar quantitative reaction. This interference can be prevented by taking the following preliminary steps.

First, add an equivalent amount of n-butanol to the sample and treat it with olefin using boron trifluoride as the catalyst. It appears that the butyl mercaptan produced in this way combines with the olefin as shown in the following formulae.



If excess butanol is used it will react with the acid during titration and produce ester and water. The results must be corrected to allow for this.

II-2. Inorganic Compounds

Interference reactions are more common with inorganic compounds than with organic compounds. Refer to the comments on interference in Q9 of the section on Basic Knowledge. Also, the moisture vaporization method is used more often because there are a number of substances that cannot be dissolved in the titration solvents. For each substance, it is essential to consider whether or not to use the moisture vaporization method (heat vaporization system). In addition, when taking measurements careful consideration must be given to the way in which moisture is present (adhesion water or compounded water).

1. Metals and Simple Substances

Key Points

Since these substances are solids and cannot be dissolved in methanol, they are normally measured using the moisture vaporization method. The sample is powdered in preparation for the measurement. During this preliminary process it is important to prevent absorption of humidity or dissipation of the moisture content.

For volumetric titration, it is possible to disperse the sample in dehydrated solvent and carry out Karl Fischer titration directly. However, the moisture vaporization method is normally used.

With coulometric titration the presence of insoluble substances, such as powdered metal, interferes with the electrode reaction. Other causes of interference include membrane blockage. For these reasons, coulometric titration cannot be used directly.

In most cases the moisture vaporization method is effective with these samples. Because moisture content is commonly low, Karl Fischer titration is carried out using the coulometric method. The heating temperature for moisture vaporization is 100-250°C. If necessary, the process can be carried out at temperatures of 600-700°C.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|-------------------------|--------------------|---------------------|------------------------|----------------------|
| Aluminum paste | General-use | 0.2524 | 0.83 | 0.329 |
| Powdered aluminum + oil | " | 0.5968 | 0.15 | 0.075 |
| Powdered tungsten | " | 4.2880 | 0.71 | 0.017 |
| Titanium | " | 0.4541 | 10.97 | 2.42 |
| Sulfur | " | 1.1710 | 0.47 | 0.042 |
| Ferrite | " | 0.3121 | 11.11 | 3.56 |

(2) Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample quantity (g) | Measurement value (µg) | Moisture content (%) |
|-----------------------|--------------------------|---------------------|------------------------|----------------------|
| Aluminum paste | 110 | 0.2646 | 3831 | 1.45 |
| Powdered aluminum | 600 | 3.3284 | 524 | 157ppm |
| Powdered metal (Cd) | 110 | 0.2572 | 354 | 0.138 |
| " | 250 | 0.1494 | 787 | 0.527 |
| Powdered metal (zinc) | 250 | 3.8345 | 35 | 9ppm |
| Powdered silicon | 700 | 0.0537 | 1252 | 2.33 |
| Powdered cobalt alloy | 200 | 2.3461 | 563 | 240ppm |
| Powdered brass | 250 | 1.5277 | 1951 | 0.128 |
| Copper wire | 200 | 2.4454 | 332 | 136ppm |
| Powdered lead tin | 400 | 9.9006 | 531 | 54ppm |
| Nickel | 250 | 1.0724 | 316 | 295ppm |
| Powdered sulfur | 100 | 2.3143 | 151 | 65ppm |
| Red phosphorus | 180 | 0.2036 | 1470 | 0.722 |
| Ferrite | 700 | 0.0774 | 3034 | 3.92 |

2. Inorganic Acids

Key Points

The following problems arise when methanol is used as the titration solvent for inorganic acids.

- 1) The pH of the Karl Fischer titration system is shifted to the acid side.
This lowers the reaction rate.
- 2) An esterification reaction occurs with acids at high temperatures.
This produces water, raising the measurement value.

To suppress these interference reactions the sample should be neutralized with an amine, such as pyridine, before Karl Fischer titration.

Since these substances commonly have a high moisture content, volumetric titration is used. It is convenient to use Dehydrated Solvent MS (manufactured by Mitsubishi Chemical). As this product contains a relatively high percentage of pyridine as a reaction accelerant, it is not necessary to add more pyridine.

In the case of hydrogen chloride gas, moisture is condensed in special apparatus at -78°C . The main constituent, hydrogen chloride, is then separated so that the condensed water can be dissolved in pyridine-methanol and titrated.

Reference: Muroi, Ono: *Microchem.J.*, 18,234 (1973)

"Determination of Trace Moisture in Hydrogen Chloride Gas by Karl Fischer Titration."

Examples of test methods

1) Sulfuric acid

Concentrated sulfuric acid (95% or higher) causes an esterification reaction in methanol and produces water. By adding 50ml of Dehydrated Solvent MS and using a small sample (approx. 0.5g or less), it is possible to carry out direct titration without any interference reaction.

2) Nitric acid

The reagent nitric acid can be titrated directly by adding about 0.3g of sample to 50ml of Dehydrated Solvent MS. In the case of fuming nitric acid, the sample will have to be neutralized with pyridine.

3) Hydrochloric acid

The reagent hydrochloric acid can be titrated directly by adding about 0.03g of sample to 50ml of Dehydrated Solvent MS.

4) Hydrofluoric acid

The reagent hydrofluoric acid can be titrated directly by adding about 0.03g of sample to 50ml of Dehydrated Solvent MS.

However, as hydrofluoric acid erodes glass parts of the titration cell and the electrodes, teflon-coated parts should be used.

5) Hydrocyanic acid

The reagent hydrocyanic acid can be dissolved in Dehydrated Solvent MS for direct titration.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|-------------------------|--------------------|---------------------|------------------------|----------------------|
| 97% Sulfuric acid | General-use | 0.2423 | 7.69 | 3.17 |
| 92% Sulfuric acid | " | 0.1145 | 8.74 | 7.63 |
| Nitric acid | " | 0.0360 | 35.04 | 97.3 |
| Nitric acid (85%) | " | 0.1155 | 16.87 | 14.6 |
| Hydrochloric acid (38%) | " | 0.0379 | 23.67 | 62.5 |
| Hydrofluoric acid (48%) | " | 0.0368 | 18.96 | 51.5 |
| Hydrocyanic acid | " | 0.3888 | 5.56 | 1.43 |
| Phosphoric acid (85%) | " | 0.0533 | 7.85 | 14.7 |

Hydrogen chloride gas

Hydrogen chloride gas reacts with Karl Fischer reagent and cannot be titrated directly. The moisture content is titrated after condensation in a trap at -78°C, using the following procedures.

- a) To ensure that the system is free of moisture, nitrogen gas that has first been dried with silica gel and phosphorus pentoxide is passed inside titration flask D in the direction L → M → y at a rate of approximately 0.5l/min. (The moisture content of the nitrogen that passed through the system is titrated.)

- b) Titration flask D is cooled to -78°C in a methanol dry ice cooling bath.
- c) Immediately after the nitrogen flow has been stopped, the sample gas is passed into titration flask D in the direction $A \rightarrow M \rightarrow y$ at a rate of approximately 0.5 l/min .
- d) When 5–20 l of gas has passed through the system, the three-way cock is switched to allow nitrogen to flow into titration flask D in the direction $L \rightarrow M \rightarrow y$ for about one minute to drive out all of the sample gas.
- e) The flow of nitrogen is then stopped and 20 ml of a 1:1 pyridine/methanol solution is introduced from B to flush out the water that has condensed in E.
- f) Titration flask D is removed from the methanol dry ice cooling bath. When the flask has returned to room temperature, the water captured in the pyridine/methanol solution is titrated.
- g) A dummy value is established from 20 ml of pyridine/methanol solution using the same procedures. Moisture content is determined by subtracting this value from the titration result.

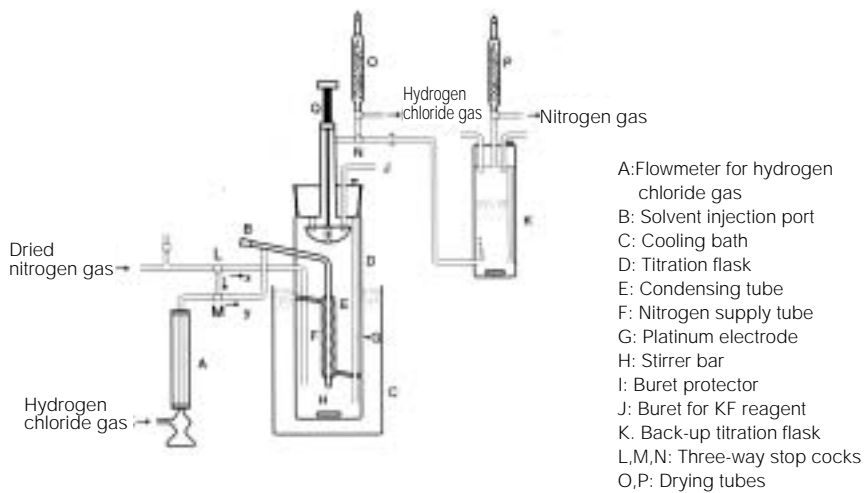


Figure 20: Titration Apparatus for Hydrogen Chloride Gas

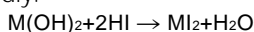
Test Examples

| Gas flow rate (l/min.) | Volume (l) | Measurement value (mg) | Moisture content (ppm) |
|---------------------------|---------------|---------------------------|---------------------------|
| 0.3 | 20 | 0.44 | 12.6 |
| 0.4 | 20 | 0.43 | 12.4 |
| 0.5 | 20 | 0.45 | 12.8 |
| 0.6 | 20 | 0.40 | 11.5 |
| 0.7 | 20 | 0.38 | 10.4 |
| 0.8 | 20 | 0.33 | 9.4 |

Note:Karl Fischer Reagent SS with a titer of 0.35mg/ml was used.
(At present there is no reagent with this titer.)

3. Hydroxides**Key Points**

Metallic hydroxides generally react with the iodine in Karl Fischer reagent in accordance with the following formula. In particular, alkaline metal and alkaline earth hydroxides (strong basicity) react quantitatively and rapidly.



For example, lithium hydroxide, sodium hydroxide, potassium hydroxide and barium hydroxide all produce water and react immediately with Karl Fischer reagent. For this reason, direct titration cannot be used. Moisture content is measured using the moisture vaporization method.

[Examples of Measurement]**(1) Moisture vaporization - Coulometric titration**

Reagents used: Aquamicon AX (or AS) 150ml
Aquamicon CXU 10ml

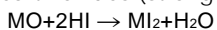
| Substance | Heating temperature(°C) | Sample quantity (g) | Measurement value (µg) | Moisture content (%) |
|---------------------|-------------------------|---------------------|------------------------|----------------------|
| Calcium hydroxide | 110 | 0.6375 | 2953 | 0.463* |
| " | 900 | 0.0289 | 6708 | 23.2** |
| Magnesium hydroxide | 150 | 0.4956 | 670 | 0.135* |
| Nickel hydroxide | 150 | 0.1222 | 1797 | 1.47* |
| " | 600 | 0.1092 | 22098 | 20.2** |

Note:*Adhesion water, ** bonded water

4. Oxides

Key Points

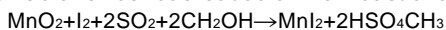
Metallic oxides generally react with the iodine in Karl Fischer reagent in accordance with the following formula. In particular, alkaline metal and alkaline earth oxides (strong basicity) react quantitatively and rapidly.



A number of substances, such as magnesium oxide, zinc oxide, silver (I)oxide, mercury (I) oxide and copper (I) oxide, react with Karl Fischer reagent in accordance with the formula below.



Manganese dioxide reacts with Karl Fischer reagent as shown below. Lead dioxide and red lead cause similar reactions.



As a result, direct titration is not possible and moisture content is measured using the moisture vaporization method. For measurement using moisture vaporization, the heating temperature for normal adhesion water is set at 100~200°C.

[Examples of Measurement]**(1) Moisture vaporization - Coulometric titration**

Reagents used: Aquamicron AX (or AS) 150ml
 Aquamicron CXU 10ml

| Substance | Heating temperature(°C) | Sample quantity (g) | Measurement value (µg) | Moisture content (%) |
|-------------------|-------------------------|---------------------|------------------------|----------------------|
| Zinc oxide | 200 | 2.1892 | 1715 | 783ppm |
| Aluminum oxide | 200 | 1.4522 | 1801 | 0.124 |
| " | 700 | 0.7433 | 1581 | 0.213 |
| Antimony oxide | 150 | 1.9930 | 211 | 106ppm |
| Cadmium oxide | 250 | 0.7301 | 228 | 312ppm |
| Gadolinium oxide | 800 | 0.1192 | 977 | 0.820 |
| Calcium oxide | 100 | 1.3610 | 261 | 192ppm |
| " | 800 | 0.2526 | 1862 | 0.737 |
| Silicon oxide | 250 | 0.1295 | 1313 | 1.01 |
| Copper (I) oxide | 110 | 0.4958 | 654 | 0.132 |
| " | 700 | 0.3140 | 4734 | 1.51 |
| Copper (II) oxide | 700 | 0.6090 | 2366 | 0.389 |
| Titanium oxide | 300 | 0.3858 | 3691 | 0.957 |
| Nickel oxide | 250 | 0.9014 | 1135 | 0.126 |
| Bismuth oxide | 100 | 2.5479 | 182 | 71ppm |
| Magnesium oxide | 130 | 0.2773 | 906 | 0.327 |
| Manganese oxide | 750 | 0.1382 | 6650 | 4.81 |
| Iron (III) oxide | 200 | 0.5168 | 1460 | 0.283 |
| " | 500 | 0.5353 | 1729 | 0.323 |
| Red iron oxide | 200 | 0.4209 | 1751 | 0.416 |
| " | 700 | 0.4079 | 2076 | 0.509 |

5. Halides (halogenides)

Key Points

As a general rule, halides do not cause interference and can be measured directly. Also, some halides can be dissolved in titration solvents and titrated with either volumetric or coulometric titration.

Volumetric titration is carried out using a general-purpose dehydrated solvent. If a substance cannot be dissolved or causes interference, the moisture vaporization method is used. Care needs to be taken when taking samples as many of these substances absorb humidity very readily.

Some substances, such as ammonium chloride, sodium chloride, potassium chloride, potassium iodide and cerium iodide, occlude their moisture content during crystallization. The extent of this effect is reported to be 0.1~0.3%. Since these salts generally dissolve readily in formamide, moisture content can be measured using a dehydrated solvent formulated for sugars as the titration solvent.

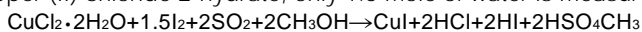
Reference: Solubility of salts in formamide (g/100g)

| | | | |
|--------------------|-------|-----|------|
| NaCl | 9.33 | NaI | 62.7 |
| KCl | 6.31 | KI | 62.5 |
| NH ₄ Cl | 11.05 | | |

Alkaline earth halides crystallize as hydrates. Substances that can be measured without major problems include magnesium chloride 6-hydrate, calcium chloride 2-hydrate, strontium chloride 6-hydrate, and barium chloride 2-hydrate. The same is true of bromides and iodides. Potassium fluoride (anhydride and 2-hydrate) is soluble and can be measured without any difficulty. Calcium fluoride is insoluble and its moisture content cannot be measured through direct titration.

Similar measurement procedures can be used for substances such as aluminum chloride 6-hydrate, manganese (II) chloride 4-hydrate, cobalt chloride 6-hydrate, cadmium chloride 2.5-hydrate and tin (IV) chloride 5-hydrate. However, care is needed with the following salts as their water does not react with iodine on a mole-for-mole basis.

With copper (II) chloride 2-hydrate, only 1.5 mole of water is measured.



With iron (III) chloride 6-hydrate, only 5.5 mole of water can be measured.



Tin (II) chloride 2-hydrate is a powerful reducing agent. Direct measurement is not possible as it reduces the iodine in Karl Fischer reagent.



[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvents | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|------------------------------|---------------------|---------------------|------------------------|----------------------|
| Aluminum chloride 6-hydrate | General-use | 0.0331 | 15.17 | 45.8 |
| Potassium chloride | " | 0.5178 | 1.37 | 0.26 |
| Magnesium chloride 6-hydrate | " | 0.0554 | 30.04 | 54.2 |
| Magnesium chloride anhydride | " | 0.6703 | 3.01 | 0.45 |
| Lithium chloride | " | 0.1004 | 5.11 | 5.09 |
| Manganese chloride | " | 0.0759 | 27.94 | 36.8 |
| Strontium chloride | " | 0.0412 | 16.75 | 40.6 |
| Vanadium chloride | " | 0.0766 | 18.10 | 23.6 |
| Barium chloride | " | 0.5933 | 86.92 | 14.7 |
| Lithium chlorate | " | 0.1053 | 13.77 | 13.1 |
| Dried lithium chlorate | " | 0.0783 | 2.13 | 2.72 |
| Sodium iodide | " | 3.3707 | 1.63 | 0.048 |

(2) Coulometric titration

Reagents used: Aquamicron AX (or AS) 100ml
Aquamicron CXU 5ml

| Sample | Sample quantity (g) | Measurement value (μg) | Moisture content (%) |
|-----------------------------|---------------------|------------------------|----------------------|
| Aluminum chloride 6-hydrate | 0.0166 | 7490 | 45.1 |
| Manganese chloride | 0.1607 | 700 | 0.436 |
| Lithium chloride | 0.0932 | 4780 | 5.13 |
| Sulfur hexafluoride | 10.29 | 230 | 22ppm |

(3) Moisture vaporization - Coulometric titration

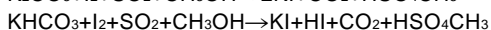
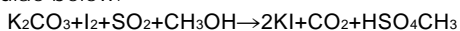
Reagents used: Aquamicron AX (or AS) 150ml
Aquamicron CXU 10ml

| Substance | Heating temperature(°C) | Sample quantity (g) | Measurement value (µg) | Moisture content (%) |
|--------------------|-------------------------|---------------------|------------------------|----------------------|
| Potassium chloride | 100 | 0.9903 | 1056 | 0.107 |
| " | 750 | 1.0021 | 3044 | 0.304 |
| Lithium chloride | 200 | 0.1035 | 5117 | 4.94 |
| Cesium iodide | 200 | 9.5975 | 18 | 2ppm |
| Sodium iodide | 400 | 2.9079 | 1510 | 519ppm |
| Barium fluoride | 800 | 0.5323 | 291 | 547ppm |
| Aluminum fluoride | 800 | 0.6244 | 55 | 88ppm |
| Zinc fluoride | 500 | 0.8577 | 596 | 695ppm |

6. Carbonates, Bicarbonates

Key Points

Direct measurement is not possible with carbonates and bicarbonates as they react with Karl Fischer reagent and cause interference. The degree of interference depends on the solubility of each substance. For example, alkaline metal carbonates and bicarbonates react as shown in the formulae below.



Direct measurement is possible with calcium carbonate. Since it does not dissolve in dehydrated solvent it is dispersed and the moisture content extracted. This is only possible with volumetric titration.

Direct measurement is not possible with sodium bicarbonate and the moisture vaporization method is also unsuitable as the substance releases water when heated. In general, for carbonates that are stable when heated, the moisture content is measured using the moisture vaporization method.

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, OL II (or MS, CM) 25-50ml

| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|-------------------|--------------------|---------------------|------------------------|----------------------|
| Calcium carbonate | General-use | 1.0272 | 1.86 | 0.181 |
| Calcium carbonate | Oil-type | 1.0053 | 1.63 | 0.162 |

Note:The end point was more stable with an oil-type dehydrated solvent.

(2) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
Aquamicon CXU 10ml

| Substance | Heating temperature(°C) | Sample quantity (g) | Measurement value (µg) | Moisture content (%) |
|---------------------------|-------------------------|---------------------|------------------------|----------------------|
| Calcium carbonate | 100 | 0.1223 | 623 | 0.509 |
| " | 600 | 0.0975 | 1554 | 1.58 |
| Potassium carbonate | 200 | 0.6278 | 1712 | 0.273 |
| Sodium carbonate | 180 | 0.2004 | 4099 | 2.05 |
| Barium carbonate | 300 | 0.6761 | 805 | 0.119 |
| " | 700 | 0.8437 | 1103 | 0.131 |
| Basic magnesium carbonate | 250 | 0.0249 | 3605 | 14.5 |
| Manganese carbonate | 110 | 0.0334 | 1723 | 5.16 |
| " | 600 | 0.0466 | 3699 | 7.94 |

Measuring the moisture content of sodium bicarbonate

Sodium bicarbonate is used in fire extinguishers and various other applications. Even trace amounts of moisture can lead to problems during storage or use. It is difficult to measure moisture content accurately using the conventional sulfuric acid desiccator method, so the Karl Fischer titration method is used together with a moisture extraction-correction technique as described below.

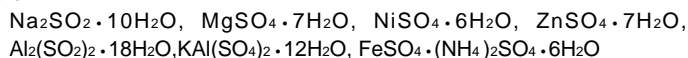
Approximately 100g of sample is taken in a 500ml separating funnel. To this, 130ml of dehydrated methanol is added. The mixture is stirred well and then left to stand. When the sample and methanol have separated, 50ml of liquid is extracted and placed in the titration flask of a Karl Fischer titration system, and titrated. The small quantity of sample dissolved in the extracted liquid is titrated by neutralization titration, and the moisture content is determined by correcting the Karl Fischer titration result.

Reference:N.G. Leavitt, C.B. Robert: Anal.Chem., 26,1367 (1954).

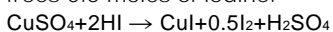
7. Sulfates, Sulfites

Key Points

Differences in reactivity to Karl Fischer reagent mean that the choice of direct titration method must be made with reference to the individual substance. In most cases we recommend the measurement of moisture content using the moisture vaporization method. Sulfates crystallize as hydrates. In general, hydrates with six or more molecules of water of crystallization dissolve in methanol and remain in solution during titration. This means that they can be measured directly using a general-purpose solvent. Some examples of this type of substance are listed below.

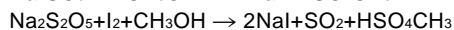
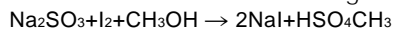


Water is strongly bonded in zinc sulfate 1-hydrate and manganese sulfate 1-hydrate and cannot be measured. Karl Fischer titration cannot be used for calcium sulfate 2-hydrate at normal room temperatures as the water is released very slowly. Total moisture content can be measured by using the moisture vaporization method at a temperature above 200°C. Copper sulfate causes interference by oxidizing hydrogen iodide, the reactive substance in Karl Fischer reagent. This reaction frees 0.5 moles of iodine.



As the resulting free iodine acts as a reagent, the measurement results will be low. In general, the weakly acidic salts of alkaline metals react in the same way as oxides.

Sulfites and pyrosulfites react quantitatively. Sodium sulfite and sodium pyrosulfite react as shown in the following formulae.



Accordingly, the moisture vaporization method is used with these salts.

[Examples of Measurement]**(1) Moisture vaporization - Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) 50-100ml

| Substance | Heating temperature(°C) | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|-------------------------|-------------------------|---------------------|------------------------|----------------------|
| Sodium metabisulfite | 150 | 0.1926 | 11.39 | 5.91 |
| Potassium metabisulfite | 150 | 0.2215 | 3.85 | 1.74 |
| Gypsum | 250 | 0.2060 | 14.76 | 7.17 |

(2) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
Aquamicon CXU 10ml

| Substance | Heating temperature(°C) | Sample quantity (g) | Measurement value (µg) | Moisture content (%) |
|--|-------------------------|---------------------|------------------------|----------------------|
| Sodium dithionite (Sodium hydrosulfite) | 200 | 0.4796 | 2671 | 0.557 |
| Sodium sulfite | 250 | 4.0301 | 247 | 61ppm |
| Aluminum sulfate | | | | |
| 100°C dried | 700 | 0.0229 | 8787 | 38.4 |
| 200°C dried | 700 | 0.0515 | 8139 | 15.8 |
| Sodium sulfate | 250 | 3.1305 | 375 | 120ppm |
| Calcium sulfate | 200 | 0.0521 | 3310 | 6.35 |
| " | 600 | 0.0684 | 4337 | 6.34 |
| " | 900 | 0.0612 | 3868 | 6.32 |

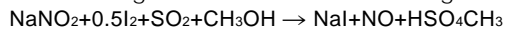
8. Other Salts

Key Points

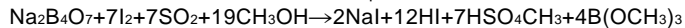
Some salts react with Karl Fischer reagent and others do not. Direct measurement is possible with salts that do not react with Karl Fischer reagent and that can be dissolved or dispersed in a titration solvent. As a general rule, moisture content can be determined easily by using the moisture vaporization method. First, however, it is necessary to take the heating temperature into consideration because of the need to check for such factors as intramolecular dehydration. Procedures for the various types of salts are described below.

Nitrates can be measured directly using volumetric titration. A general-purpose dehydrated solvent is used. Depending on the solubility of the substance, a solvent formulated for sugars may be used. Examples of substances for which this method is suitable include ammonium nitrate, sodium nitrate, potassium nitrate, chromium nitrate, cobalt nitrate and mercury (I) nitrate.

Sodium nitrite cannot be measured directly as it reacts quantitatively with Karl Fischer reagent as shown in the following formula.



Chromates and bichromates also react with Karl Fischer reagent, but the reactions are not quantitative. Potassium permanganate is insoluble and will not react. Sodium tetraborate produces a similar reaction with boric acid, and direct measurement is not possible.



Sodium arsenite reacts in the same way with oxides (anhydrous arsenites.)



Primary phosphates can be measured directly using volumetric titration. The behavior of secondary phosphates reflects their weak basicity, but they do not cause any significant interference. Tertiary phosphates cause interference because of their strong basicity and they must be neutralized with acid before Karl Fischer titration.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvent | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|--------------------------------|--------------------|---------------------|------------------------|----------------------|
| Di-ammonium hydrogen phosphate | General-use | 0.1511 | 3.94 | 2.61 |
| Sodium nitrate | " | 2.1116 | 2.46 | 0.116* |
| Sodium nitrate | Sugar-type | 2.2079 | 2.73 | 0.124** |

Note:* Partially insoluble. ** Soluble

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) 50-100ml

| Substance | Heating temperature(°C) | Sample quantity (g) | Measurement value (mg) | Moisture content (%) |
|---------------------|-------------------------|---------------------|------------------------|----------------------|
| Sodium metasilicate | 200 | 0.1039 | 41.52 | 40.0 |

(3) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
Aquamicon CXU 10ml

| Substance | Heating temperature(°C) | Sample quantity (g) | Measurement value (µg) | Moisture content (%) |
|--------------------------------|-------------------------|---------------------|------------------------|----------------------|
| Aluminum nitrate | 700 | 0.0200 | 8853 | 44.3 |
| Sodium nitrate | 130 | 2.0903 | 721 | 345ppm |
| " | 400 | 0.4948 | 1501 | 0.303 |
| Sodium tripolyphosphate | 100 | 1.1821 | 1555 | 0.132 |
| " | 150 | 1.1219 | 6044 | 0.539 |
| " | 250 | 1.1523 | End point | not reached |
| Di-ammonium hydrogen phosphate | 110 | 0.0960 | 2568 | 2.68 |
| Tri-sodium phosphate | 150 | 0.0342 | 18449 | 53.9 |
| Magnesium hypophosphite | 180 | 0.0338 | 13640 | 40.4 |

9. Inorganic Gases

Key Points

The moisture content of non-condensing gases, such as nitrogen, oxygen and hydrogen, is captured by passing the sample gas through a titration solvent or electrolyte.

Karl Fischer titration is then carried out. It is necessary, therefore, to obtain and assemble equipment which includes pipes for the sample gases and gas meters. Metal pipes should be used at the injection ports. Pipes made of vinyl chloride or other plastics should be avoided as these absorb atmospheric moisture.

For volumetric titration, an absorption solution is prepared by mixing a general-use dehydrated solvent with propylene glycol in a ratio of 3:1. For short periods, general-use dehydrated solvent can be used alone. In such cases, changes in the quantity of the titration solvent, caused by volatilization, must be monitored carefully.

For substances with low moisture content, accurate measurements can be obtained by using a low-titer Karl Fischer reagent.

Because of the minute amounts of moisture in inorganic gases, we recommend coulometric titration.

[Examples of Measurement]

(1) Volumetric titration

Place 150ml of dehydrated solvent in a titration flask. Titrate the Karl Fischer reagent to the end point to remove all moisture. Next pass the sample gas through the dehydrated solvent in the titration flask at a rate of 0.2-0.5l/min. The flow of gas should be measured using a gas meter. Stop the flow of gas (A) after the amount of water absorbed into the dehydrated solvent has reached 5-50mg. Titrate (Bml) immediately using a Karl Fischer reagent with a known titer (FmgH₂O/ml). Calculate the moisture content (W%) according to the following formulae.

$$W (\text{Vol}\%) = \frac{B \times F \times 1.244 \times \frac{760}{P} \times \frac{(273+t)}{273}}{A \times 100} \times 100$$

$$W (\text{Wt}\%) = \frac{B \times F}{A \times \frac{P}{760} \times \frac{273}{273+t} \times \frac{M}{22.4} \times 1000} \times 100$$

Here, P: Atmospheric pressure (mmHg) at time of measurement
 t: Temperature of gas at time of measurement (°C)
 M: Molecular weight of sample gas

| Sample gas | Sample quantity (l) | Titration quantity (ml) | Moisture content (v/v%) |
|------------|---------------------|-------------------------|-------------------------|
| Hydrogen | 10.0 | 2.21 | 0.030 |
| Nitrogen | 30.0 | 0.38 | 0.0017 |
| Oxygen | 30.0 | 3.09 | 0.014 |

Note:Using Karl Fischer Reagent SS (titer: 1mg/ml)

Reference:Muroi, K., Bunseki Kagaku [Analytical Chemistry] 10, 847 (1961).

"Determination of a Micro-quality of Water in Gaseous Sample by the Karl Fischer Method"

(2) Coulometric titration

Inject 150ml of Aquamicron AX into the anode chamber of an electrolytic cell fitted with a gas adapter. Inject 10ml of Aquamicron CXU into the cathode chamber. Apply an electrolytic current to the Aquamicron AX while stirring, and use coulometric titration to remove all water from the system. Next, pass the sample gas into the electrolytic cell via the gas adapter at a rate of 0.3-0.5l/min. Use a gas meter to measure the volume of the gas flow. Stop the flow of gas after the amount of water absorbed into the Aquamicron AX has reached 0.1-5mg. Immediately, carry out coulometric titration to the end point and calculate the moisture content.

| Sample gas | Sample quantity (l) | Titration quantity (µg) | Moisture content (v/vppm) |
|------------|---------------------|-------------------------|---------------------------|
| Nitrogen | 20 | 475 | 31.6 |
| Oxygen | 20 | 171 | 11.4 |
| Hydrogen | 20 | 99 | 6.8 |
| Argon | 20 | 28 | 1.9 |

Chapter III: Applications - 2

Chapter III: Applications - 2

In this section we provide some actual examples of the use of Karl Fischer titration with chemical products, other industrial products, foodstuffs, pharmaceuticals and other substances.

III-1. Industrial Products

Most general chemical and industrial products consist of organic or inorganic compounds, either singly or as mixtures. This means that for many products moisture content can be determined using Karl Fischer titration. Because of the wide variety of substance characteristics and forms, however, it is important to choose the most appropriate measurement method with reference to the substances that make up each product. In this chapter we give actual examples of moisture measurement for as many products as possible.

1. Fertilizers

Key Points

Single-salt fertilizers, such as ammonium sulfate, ammonium chloride, ammonium nitrate, urea and potassium chloride, can be either dissolved or dispersed in a general-use dehydrated solvent for Karl Fischer titration. Other substances, such as synthetic fertilizers containing urea, should be dispersed in a general-use dehydrated solvent in preparation for Karl Fischer titration. The moisture content of synthetic fertilizers that do not contain urea can be measured using the moisture vaporization method.

Coulometric titration can be used only in conjunction with moisture vaporization.

Moisture vaporization is sometimes effective with fertilizers, but account must be taken of the fact that some ingredients in compound fertilizers, such as urea, ammonium phosphate and single superphosphate, break down when heated to certain temperatures.

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) 25-50ml

III-1. Industrial Products

| Substance | Sample quantity (g) | Measurement value (mg) | Moisture Content (%) | Heating loss method (%) |
|--|---------------------|------------------------|----------------------|-------------------------|
| Ammonium sulfate | 5.1321 | 0.70 | 136ppm | 0.016 |
| Ammonium chloride | 5.0541 | 1.80 | 356ppm | 0.044 |
| Sodium nitrate | 2.5784 | 15.60 | 0.605 | 0.59 |
| Ammonium nitrate | 5.0635 | 5.01 | 0.099 | 0.080 |
| Urea | 2.5089 | 1.40 | 558ppm | 0.060 |
| Potassium chloride | 2.5113 | 8.80 | 0.350 | 0.36 |
| Urea+ammonium nitrate | 2.5213 | 23.75 | 0.942 | 0.94 |
| Urea+ammonium sulfate +ammonium phosphate | 2.5055 | 33.75 | 1.35 | 1.30 |
| Chemical fertilizer | 0.4920 | 14.63 | 2.97 | 2.23 |
| High-grade chemical fertilizer | 0.1500 | 5.34 | 3.56 | 3.30 |

(2) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml

Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|--------------------------------|--------------------------|---------------------|------------------------|----------------------|
| Ammonium sulfate | 100 | 0.6294 | 2827 | 0.449 |
| Chemical fertilizer | 100 | 0.0998 | 2000 | 2.00 |
| High-grade chemical fertilizer | 100 | 0.0929 | 3539 | 3.81 |

2. Agricultural Chemicals

Key Points

Direct Karl Fischer titration is possible for substances that can be dissolved in dehydrated solvent. Samples of main ingredients and other products can be dissolved in a general-use dehydrated solvent and titrated directly. Powders that include fillers and other substances should be stirred for a while in a general-use dehydrated solvent. The moisture content can then be fully extracted and titrated.

Alternatively, the moisture vaporization method can be used.

However, chloropicrin is oxidative and causes interference by freeing iodine.

Substances that may react with Karl Fischer reagent include copper powders, mercury powders, copper-mercury powders, zineb granules and arsenate-lime powders. The normal moisture vaporization method is suitable for agricultural chemicals in solid form. Adhesion water can be measured at 100-150°C. The heating temperature should be determined in accordance with the individual substance.

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Sample Quantity (g) | Measurement value (mg) | Moisture Content (%) | Remarks |
|-----------------|---------------------|------------------------|----------------------|---|
| Chloropicrin | 3.3387 | 0.31 | 0.0093 | Turns brown immediately after end point |
| Kitazine-P | 1.0875 | 2.27 | 0.209 | |
| Insecticide | 5.1263 | 3.51 | 685ppm | Insoluble |
| Captan | 0.2394 | 6.64 | 2.77 | |
| Namekat | 0.1437 | 5.69 | 3.96 | |
| Powdered sulfur | 1.0222 | 5.93 | 0.580 | |

(2) Coulometric titration

Reagents used: Aquamicon AX (or AS) 100ml
Aquamicon CXU 5ml

| Substance | Sample quantity (g) | Measurement value (µg) | Moisture content (%) |
|-----------|---------------------|------------------------|----------------------|
| IBP* | 1.0260 | 2210 | 0.215 |

*:O,O-Diisopropyl-S-benzylthiophosphate

(3) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|-----------------|--------------------------|---------------------|------------------------|----------------------|
| TPN (Daconil) | 100 | 0.4867 | 241 | 495ppm |
| Zineb (Diefar) | 110 | 0.1021 | 1459 | 1.43 |
| Namekat | 110 | 0.1314 | 6606 | 5.03 |
| Captan | 110 | 0.0679 | 1914 | 2.82 |
| Bryeslin powder | 150 | 0.1109 | 4822 | 4.35 |

Captan: N-Trichloromethylthio-4-cyclohexene-1,2-dicarboximide

TPN: Tetrachloroisophthalonitrile

Zineb: Zinc ethylenebisdithiocarbamate

3. Glass/Ceramics

Key Points

Because glass, ceramics and similar substances do not dissolve in organic solvents, both volumetric titration and coulometric titration are used in combination with moisture vaporization.

The heating temperature and other conditions for moisture vaporization must be determined with reference to the type of sample. Particular care is required with glass as it will melt at certain temperatures and adhere to the sample boat used in the moisture vaporization method. Up to about 600°C, adhesion can be stopped if the boat is covered with aluminum foil.

Direct titration is not possible with cement. The moisture content of cement is chemically bonded, while the oxides in cement cause interference by reacting with Karl Fischer reagent to produce water. The usual method is to carry out moisture vaporization at 800-1,000°C, followed by Karl Fischer titration.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Sample quantity (g) | Measurement Value (mg) | Moisture Content (%) | Vaporization method (%) |
|---------------------|---------------------|------------------------|----------------------|-------------------------|
| Porous glass powder | 0.1589 | 2.50 | 1.56 | 1.55 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating temperature (°C) | Sample quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-----------------|--------------------------|---------------------|------------------------|----------------------|
| Hydrated cement | 700 | 0.1291 | 19.85 | 15.3 |

(3) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
Aquamicon CXU 10ml

| Substance | Heating temperature (°C) | Sample quantity (g) | Measurement Value (µg) | Moisture Content (ppm) |
|-----------------------|--------------------------|---------------------|------------------------|------------------------|
| Glass wool | 200 | 0.5127 | 196 | 382 |
| Lead glass (powder) | 400 | 0.7471 | 811 | 0.109% |
| Fluorine glass | 700 | 0.9856 | 79 | 80 |
| Phosphate glass | 800 | 0.2757 | 285 | 0.103% |
| Porous glass (powder) | 300 | 0.2062 | 3199 | 0.155% |
| Sealer | 800 | 2.2730 | 339 | 149 |
| Glass | 600 | 1.0121 | 34 | 34 |
| Ceramics (powder) | 130 | 2.5429 | 2974 | 0.117% |
| IC ceramics | 800 | 6.7010 | 222 | 33 |
| Cement | 800 | 0.3102 | 2219 | 0.715% |
| Cellite (dried) | 180 | 0.1721 | 128 | 743 |

4. Liquefied Petroleum Gases

Key Points

Liquefied petroleum gases, such as propane and butane, can be added directly to dehydrated solvents or electrolytes and subjected to Karl Fischer titration, using either the volumetric or coulometric methods. Coulometric titration is most suitable, since liquefied petroleum gases usually contain only trace amounts of moisture.

To obtain accurate measurements of moisture content, it is important to add the sample in the liquid phase. In particular, allowance must be made for a marked tendency for fluctuations in the moisture content of samples at around the 50ppm level. Be sure to inject the entire sample into the sampling bottle. For details of the methods used, refer to the LPG Testing Method Standards of the Japan LPG Association.

Reference: Muroi, K. et al., "Rapid Determination of Water in LPG by Karl Fischer Method" J. Japan Petroleum Institute 11, 440 (1968).

Sampling Method

Liquid-phase samples are obtained as follows.

- (1) Place the canister containing the gas upside-down or on an angle. Connect a high-pressure sampling bottle to the canister outlet using a hose designed for this purpose (Figure 22).
- (2) Open valves A and B of the sampling bottle. Next, gradually open the valve on the canister, allowing a small amount of the gas to vaporize. Release the gas through the sampling bottle.
- (3) Close valve B, and open the valve on the canister to release the sample into the sampling bottle.

Note: The sample can be moved into the sampling bottle by opening and closing valve B, repeatedly. Do not fill the bottle completely with liquid sample. Always keep the sample below 80% of the volume and leave some vapor space.

- (4) Close valve A and the valve on the canister. Remove the hose. Weigh the sampling bottle, and then attach a syringe needle to valve B (Figure 21).

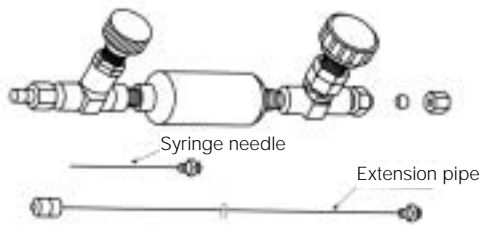


Figure 21: Sampling bottle and hose

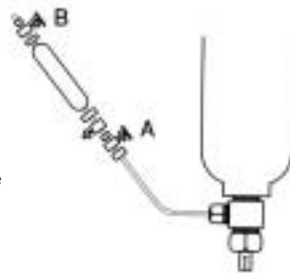


Figure 22: Obtaining a sample from a gas canister

Titration Method

Coulometric titration (or volumetric titration) is carried out as follows.

- (1) First place 150ml of analyte (or 100ml of general-use dehydrated solvent) in an electrolytic cell and use coulometric titration (or Karl Fischer Reagent SS-X) to remove all moisture.
- (2) Introduce the syringe needle through the side port of the electrolytic cell (or titration flask) until it reaches the bottom of the cell (or titration flask), as shown in Figure 23.

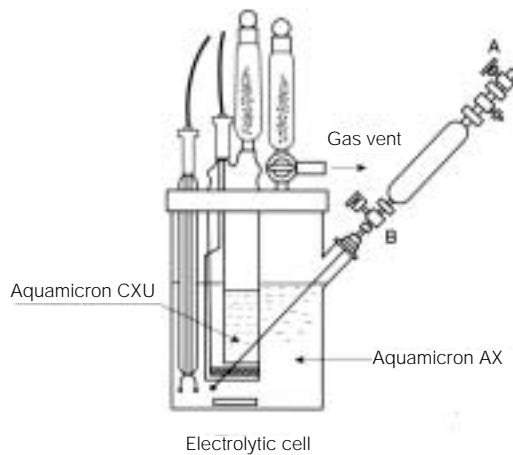


Figure 23: Injecting the sample (coulometric titration)

- (3) Gradually open valve B while stirring the anolyte (or general-use dehydrated solvent). Inject the sample for 10-15 minutes (at a rate of about 1g/min.).

Note:The sample will gasify as it is injected and it will escape through the upper vent valve into a draft chamber, or to the outside air.

- (4) Withdraw the syringe from the sampling bottle.
 (5) Weigh the sampling bottle. Subtract this weight from the weight before the injection of the sample to determine the weight of the sample.
 (6) Titrate the moisture absorbed into the anolyte (or general-use dehydrated solvent) to the end point, using coulometric titration (volumetric titration).
 (7) Calculate the moisture content using the following formulae.

For coulometric titration:

$$\text{Moisture content (ppm)} = \frac{\text{measurement value } (\mu\text{g})}{\text{sample quantity (g)}}$$

For volumetric titration

$$\text{Moisture content (ppm)} = \frac{\text{Titration volume(ml)} \times \text{Titer(mgH}_2\text{O/ml)}}{\text{sample quantity (g)} \times 1000} \times 100$$

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS) 100ml
 Dehydrated Solvent GEX (or MS) 100ml

| Substance | Sample quantity (g) | Titration quantity (mg) | Moisture content (ppm) |
|-----------------|---------------------|-------------------------|------------------------|
| LPG | 25.1 | 1.40 | 56 |
| Propane | 29.0 | 1.11 | 38 |
| Methyl chloride | 18.3 | 4.95 | 271 |
| Vinyl chloride | 15.7 | 7.41 | 475 |
| Sulfur dioxide | 53.1 | 17.6 | 331 |
| Aerosol | 27.4 | 1.18 | 35 |

(2) Coulometric titration

Reagents used: Aquamicron AX (or AS) 150ml
 Aquamicron CXU 10ml

| Substance | Sample quantity (g) | Titration quantity (μg) | Moisture content (ppm) |
|---------------|---------------------|--------------------------------------|------------------------|
| LPG | 23.24 | 253 | 11 |
| Ethylene | 40.06 L | 55 | 1.7 |
| Propane | 6.50 | 280 | 43 |
| Butadiene | 16.63 | 120 | 7.2 |
| Flon gas R113 | 7.97 | 234 | 29 |
| Spray cans | 6.26 | 1008 | 161 |

5. Coals, Tars

Key Points

The moisture content of coals is normally measured using a moisture vaporization system. Measurements can be obtained using either volumetric or coulometric titration.

Tars are subjected to Karl Fischer titration using the moisture vaporization system designed for oils.

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX, OL II (or MS, CM) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|------------|---------------------|---------------------|------------------------|----------------------|
| Brown coal | General-use | 0.0389 | 4.38 | 11.3 |
| Coal tar | Oil-type | 0.1619 | 7.30 | 4.5 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-X (or SS)
Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature ($^{\circ}\text{C}$) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|---------------|--|---------------------|------------------------|----------------------|
| Powdered coal | 150 | 0.1262 | 5.76 | 4.56 |

(3) Moisture vaporization - Coulometric titration

Reagents used: Aquamicron AX (or AS) 150ml
Aquamicron CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|---------------|--------------------------|---------------------|------------------------|----------------------|
| Brown coal | 110 | 0.0497 | 5456 | 11.0 |
| Powdered coal | 130 | 0.2509 | 1188 | 0.473 |
| Coal tar | 150 | 0.1114 | 4718 | 4.24 |
| Coke | 500 | 0.0448 | 1813 | 4.05 |
| Pitch tar | 180 | 0.4892 | 335 | 685ppm |

6. Petroleum Products

Key Points

Karl Fischer titration is an excellent method for the measurement of trace moisture in petroleum products. Karl Fischer titration has been the standard test method for the Petroleum Society since 1976, and it became a Japan Industrial Standard in 1982.

As moisture is generally present only in trace quantities in petroleum products, coulometric titration is presently in widespread use.

Coulometric titration is carried out by adding a sample, such as insulating oil, refrigerating machine oil, transformer oil, kerosene or diesel oil, to an electrolyte.

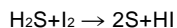
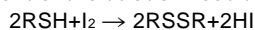
The sample is added 5-10ml at a time. Though some substances fail to dissolve and may cloud the solution, their moisture content can be measured once they are thoroughly dispersed.

For volumetric titration, the substance is dissolved in a dehydrated solvent formulated for oils. Karl Fischer titration can then be carried out directly. Silicon oils can be titrated directly by adding samples to a ketone-type dehydrated solvent.

Some additives, such as antioxidants, cause interference reactions with Karl Fischer reagent. If lubricants (e.g. gasoline engine oils and diesel engine oils) and other products contain such substances, Karl Fischer titration must be carried out using an oil-type moisture vaporization system.

Dissolve greases that do not contain interference substances in oil-type dehydrated solvent and titrate directly. For those that do contain interference substances, Karl Fischer titration should be carried out indirectly using a moisture vaporization system.

Petroleum products occasionally contain trace amounts of mercaptan or hydrogen sulfide. These react with Karl Fischer reagent. They react quantitatively with iodine on a mole for mole basis, however, so provided that the amount of mercaptan or the hydrogen sulfide content is known, moisture content can be determined accurately through adjustment of the titration result.



As shown in the above formulae, 1ppm of sulfur in mercaptan or hydrogen sulfide is equivalent to 0.28ppm and 0.56ppm of moisture content, respectively.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, OL II (or MS, CM) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (ppm) |
|---------------------------|---------------------|---------------------|------------------------|------------------------|
| Industrial gasoline | Oil-type | 20.0 | 0.42 | 21 |
| Aviation gasoline | " | 20.0 | 0.30 | 15 |
| Kerosene | " | 20.0 | 1.22 | 61 |
| Diesel oil | " | 20.0 | 1.66 | 83 |
| Heavy oil | " | 1.0805 | 27.88 | 2.58% |
| Crude oil | " | 1.5023 | 5.41 | 0.360% |
| Transformer oil | " | 20.0 | 0.52 | 26 |
| Refrigerating machine oil | " | 20.0 | 1.24 | 62 |
| Rust preventive oil | " | 20.0 | 1.80 | 90 |
| Compressor oil | " | 15.0 | 3.60 | 240 |
| Air filter oil | " | 20.0 | 1.96 | 98 |
| Heat treatment oil | " | 20.0 | 1.10 | 55 |
| Hydraulic oil | " | 20.0 | 0.30 | 15 |
| Rolling oil | " | 20.0 | 1.08 | 54 |
| Hydraulic actuation oil | " | 20.0 | 0.84 | 42 |
| Rotary pump oil | " | 30.0 | 0.30 | 10 |
| Aviation oil | " | 15.0 | 1.50 | 100 |
| Fluoride oil | " | 20.0 | 0.34 | 17 |
| Liquid paraffin | " | 30.0 | 0.45 | 15 |
| Asphalt | " | 5.0 | 0.95 | 190 |
| Cutting oil | " | 15.0 | 1.58 | 105 |
| Grinding oil | " | 15.0 | 2.01 | 134 |
| Wax | " | 0.1001 | 4.72 | 4.72% |
| Brake oil | General-use | 1.0555 | 1.27 | 0.120% |

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (ppm) |
|-----------------------|---------------------|---------------------|------------------------|------------------------|
| [Insulating oil] | | | | |
| Mineral oil | Oil-type | 8.8431 | 0.20 | 23 |
| Alkylbenzene 2-1 | " | 8.5784 | 0.17 | 20 |
| Alkylbenzene 2-2 | " | 8.7058 | 0.55 | 63 |
| Alkylbenzene 2-3 | " | 8.3116 | 0.23 | 28 |
| Polybutene 3-1 | " | 8.1933 | 0.14 | 17 |
| Polybutene 3-2 | " | 6.8850 | 0.19 | 28 |
| Polybutene 3-3 | " | 5.9730 | 0.11 | 18 |
| Alkyl naphthalene 4-1 | " | 9.2462 | 0.15 | 16 |
| Alkyl naphthalene 4-2 | " | 9.3594 | 0.14 | 15 |
| Alkyl diphenyl ethane | " | 9.4135 | 0.38 | 40 |
| Silicon oil | Ketone-type | 9.6343 | 0.37 | 38 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) | |
|---------------------|--------------------------|---------------------|------------------------|----------------------|-------|
| Gasoline engine oil | 150 | 4.3793 | 0.66 | 0.015 | |
| Diesel engine oil | 150 | 5.5145 | 0.94 | 0.017 | |
| Marine engine oil | 150 | 5.4998 | 1.04 | 0.019 | |
| Marine cylinder oil | 150 | 5.4565 | 1.91 | 0.035 | |
| Cap grease | JIS 1-1 | 120 | 1.0865 | 2.39 | 0.220 |
| | JIS 2-2 | 140 | 1.0776 | 4.20 | 0.390 |
| Fiber greases | JIS 2-3 | 140 | 1.0112 | 0.39 | 0.039 |
| | JIS 2-4 | 140 | 1.0523 | 0.43 | 0.041 |
| Graphite greases | JIS 1-1 | 140 | 1.0519 | 1.89 | 0.180 |
| | JIS 2-1 | 120 | 1.0219 | 1.11 | 0.109 |

(3) Coulometric titration

Reagents used: Aquamicon AX (or AS) 100ml

Aquamicon CXU 5ml

III-1. Industrial Products

| Substance | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (ppm) |
|---------------------------|---------------------|------------------------|------------------------|
| Gasoline | 3.9353 | 351 | 89 |
| Naphtha | 0.7280 | 117 | 161 |
| Kerosene | 0.7940 | 27 | 34 |
| Heavy oil | 4.4103 | 286 | 65 |
| Rolling oil | 4.3029 | 233 | 54 |
| Aviation oil | 2.5869 | 270 | 104 |
| Refrigerating machine oil | 2.4350 | 101 | 42 |
| Actuation oil | 4.2943 | 387 | 90 |
| Brake oil | 2.9758 | 904 | 304 |
| Liquid paraffin | 8.6600 | 130 | 15 |
| Electric insulating oils | 4.1460 | 77 | 19 |
| Alkylbenzene | 4.3132 | 73 | 17 |

(4) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
 Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (ppm) |
|-------------------------|--------------------------|---------------------|------------------------|------------------------|
| Diesel oil | 130 | 4.0973 | 241 | 59 |
| Heavy oil | 110 | 4.4278 | 290 | 66 |
| C heavy oil | 150 | 0.3820 | 2188 | 0.573% |
| Mineral oil | 130 | 4.5434 | 273 | 60 |
| Turbine oil | 130 | 8.4001 | 296 | 35 |
| Rolling oil | 110 | 4.3029 | 233 | 54 |
| Aviation oil | 130 | 3.3879 | 328 | 97 |
| Engine oil | 130 | 0.9133 | 908 | 994 |
| Gasoline engine oil | 180 | 4.6133 | 168 | 36 |
| Diesel engine oil | 130 | 4.3132 | 1298 | 301 |
| Gear oil | 130 | 2.6322 | 244 | 93 |
| Cutting oil | 150 | 1.7824 | 134 | 75 |
| Actuation oil | 130 | 4.2394 | 98 | 23 |
| Grinding oil | 150 | 1.7166 | 186 | 108 |
| Turbine oil | 130 | 4.4632 | 149 | 33 |
| Brake fluid | 150 | 2.9758 | 904 | 304 |
| Hydraulic oil | 130 | 4.3793 | 392 | 90 |
| Rust preventive oil | 130 | 1.7590 | 532 | 303 |
| Machine oil (paraffin) | 130 | 4.3941 | 263 | 60 |
| Machine oil (naphthene) | 130 | 4.5122 | 274 | 61 |
| Crude oil | 130 | 0.4156 | 1506 | 0.362% |
| Wax | 150 | 0.7235 | 8 | 11 |

7. Plastics

Key Points

Plastics reach high temperatures during the molding process and trace amounts of moisture can cause bubbling or seriously affect the performance of a plastic by reducing its molecular weight through pyrolysis. This means that moisture management is a very important aspect of the drying processes for plastics. Karl Fischer titration is the ideal method for measuring trace moisture content in plastics. The moisture vaporization method permits accurate and relatively fast (10-30 minutes) determination of moisture content.

When using the moisture vaporization method, it is important to set the heating temperature with reference to the type of plastic. The optimal temperature range must be determined for each plastic. The generally accepted view is that plastics should be heated to around melting point. Figure 24 provides guidelines on the appropriate heating temperatures

[If the analytical result is low]

If the heating temperature is too low, moisture vaporization will be delayed and the analytical time will be longer. The measurement process may end before the moisture has been vaporized, leading to a low analytical result. The result may also be low if vaporized moisture is absorbed by additives or degraded plastic constituents that have condensed in the tubes of the moisture vaporization system.

[If the analytical result is high]

Plastics that contain OH bases, such as polyvinyl alcohol, phenol resin and polyvinyl acetate, may produce high readings if the heating temperature is too high. It may be impossible to complete titration in some cases. Such phenomena appear to be caused by the formation of water through heating. Moisture content of urea resin cannot be measured normally at temperatures above 120°C because ammonia produced through the breakdown of urea resins reacts with iodine. Melamine resins appear to cause interference in the same way.

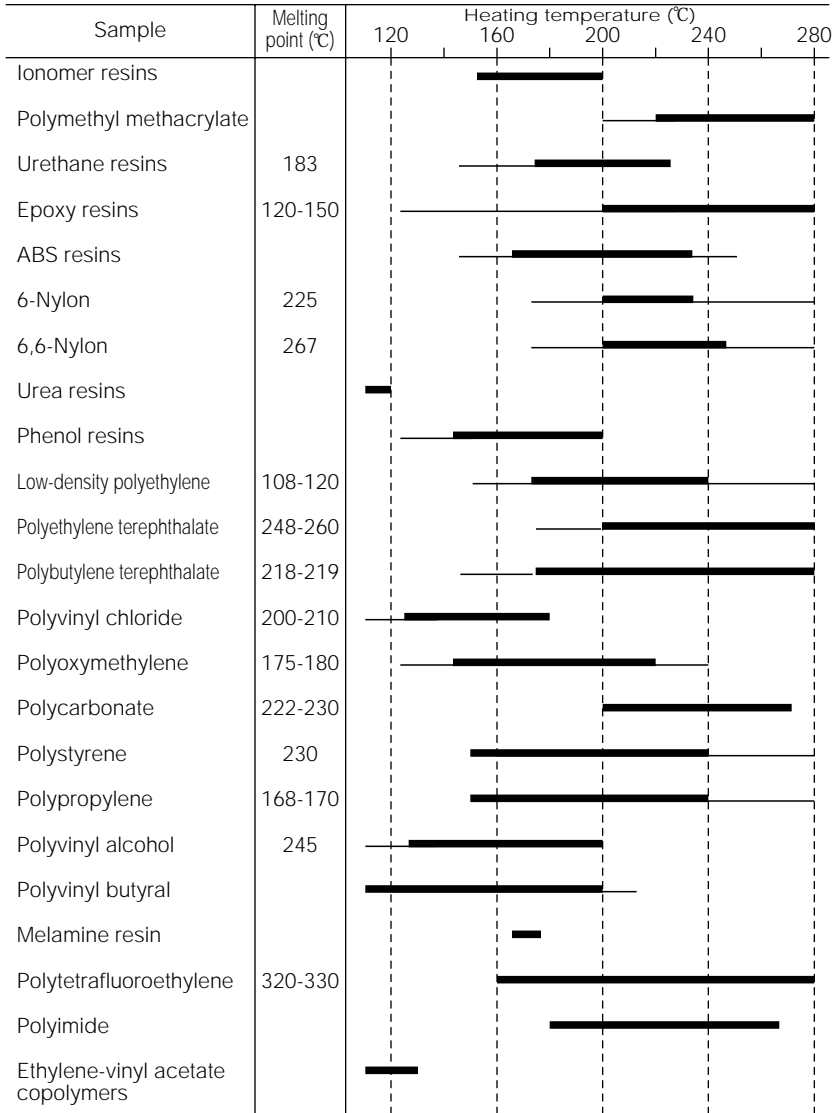


Figure 24: Optimal Moisture Vaporization Temperature Ranges for Plastics

Reference: Kato, H. et al.: *Kobunshi Kako*, 35, 584 (1986).
 Muroi, K. et al.: *Bunseki Kagaku*, 11, 351 (1962).

[Examples of Measurement]**(1) Moisture vaporization - Coulometric titration**

Reagents used: Aquamicron AX (or AS) 150ml
 Aquamicron CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (ppm) |
|----------------------------------|--------------------------|---------------------|------------------------|------------------------|
| Polyethylene | 180 | 3.7702 | 67 | 18 |
| Cross-linked polyethylene | 180 | 1.2786 | 145 | 113 |
| Polypropylene | 160 | 2.3185 | 97 | 42 |
| Vinyl chloride | 130 | 0.9815 | 412 | 420 |
| Vinyl acetate | 130 | 1.5925 | 1549 | 973 |
| Ethylene vinyl acetate copolymer | 180 | 0.4743 | 1005 | 0.212% |
| Polyvinyl alcohol | 150 | 0.1392 | 3739 | 269 |
| Polyvinyl butyral | 180 | 0.5641 | 1486 | 0.263% |
| Polystyrene | 180 | 2.7896 | 965 | 345 |
| Styrol foam | 130 | 0.2892 | 218 | 753 |
| Polyester | 230 | 2.4615 | 512 | 208 |
| PET | 230 | 4.6003 | 171 | 37 |
| PBT | 250 | 1.2020 | 223 | 186 |
| Polycarbonate | 250 | 1.0830 | 972 | 898 |
| Polyacetal | 200 | 1.5227 | 2181 | 0.143% |
| Phenol resins | 200 | 0.1142 | 5227 | 4.58% |
| 6-Nylon | 230 | 0.2211 | 3007 | 1.36% |
| 6,6-Nylon | 250 | 0.0492 | 1200 | 2.44% |
| Metacrylic resins | 250 | 1.6017 | 1337 | 835 |
| ABS resins | 200 | 0.8455 | 2073 | 0.245% |
| Urea resins | 110 | 0.4898 | 3587 | 0.732% |
| Fluorine resins | 160 | 2.4470 | 18 | 7 |
| Epoxy resins | 120 | 0.4142 | 2360 | 0.570% |
| Polyol | 150 | 1.0286 | 1258 | 0.122% |
| Urethane | 180 | 1.4886 | 3136 | 0.211% |

8. Rubber, Rubber Products, Compounding Agents

Key Points

The qualities of rubber are adversely affected by the presence of moisture in raw materials or in compounding agents. Moisture content can be measured accurately, quickly (10-20 minutes) and conveniently by combining moisture vaporization with coulometric titration.

Hints:

1. The sample should weigh between 0.5g and 1g.
2. The heating temperature for moisture vaporization should be 130-200°C. Direct titration is not possible with vulcanization accelerators and antioxidants as these react with Karl Fischer reagent to release iodine. The moisture content of carbon black cannot be measured through direct titration as the end point cannot be determined.

Reference: Muroi, K. et al.: Journal of Japan Rubber Institute, 52, 61 (1979).

[Examples of Measurement]

(1) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|---------------------------------|--------------------------|---------------------|------------------------|----------------------|
| [Rubber] | | | | |
| NBR (nitrile-butadiene rubber) | 150 | 0.8001 | 2554 | 0.319 |
| SBR (styrene-butadiene rubber) | 150 | 1.2264 | 475 | 387ppm |
| CR (chloroprene rubber) | 130 | 1.4352 | 1148 | 800ppm |
| Butyl rubber | 150 | 1.9435 | 894 | 460ppm |
| Silicon rubber | 200 | 0.1657 | 2081 | 1.25 |
| EPR (ethylene propylene rubber) | 180 | 3.4106 | 1001 | 293ppm |
| Natural rubber | 150 | 0.6374 | 1734 | 0.272 |
| [Rubber products] | | | | |
| Rubber caps | 150 | 0.6121 | 3158 | 0.516 |
| Power cable rubber | 130 | 0.0977 | 871 | 0.892 |
| Oil seal rubber | 150 | 0.3228 | 1661 | 0.515 |
| Tire rubber | 200 | 0.5031 | 2635 | 0.524 |
| Silicon rubber | 200 | 0.4937 | 1199 | 0.243 |

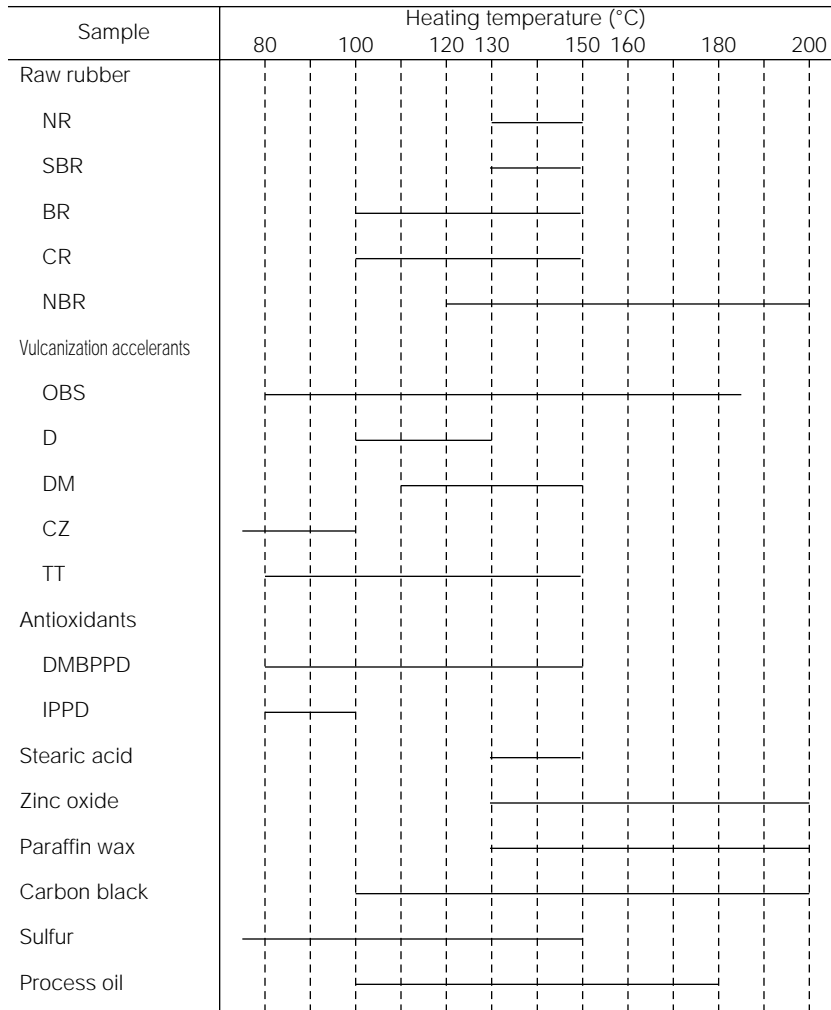


Figure 25: Optimal Heating Temperature Range for Raw Rubber and Compounding Agents

Reference: Muroi, K. et al.: Journal of Japan Rubber Institute, 52, 61 (1979).

9. Fibers, Papers

Key Points

Because samples of fibers and paper do not dissolve in dehydrated solvent, moisture content is measured using moisture vaporization followed by Karl Fischer titration (volumetric or coulometric).

A heating temperature of 130-150°C is appropriate for moisture vaporization. Moisture content in samples of these substances typically reaches several per cent. The following guidelines are suggested for sample quantities.

- 1) Volumetric titration: 0.5g
- 2) Coulometric titration: 0.05-0.1g

Reference: Muroi, K. et al., "Determination of Water Content in Electric Insulating Papers by the Karl Fischer Method" in *Bunseki Kagaku* 30, 624 (1981).

[Examples of Measurement]

(1) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|---------------------|--------------------------|---------------------|------------------------|----------------------|
| Bakelite paper | 150 | 0.5111 | 34.70 | 6.80 |
| Condenser paper | 150 | 0.4955 | 36.74 | 7.42 |
| Pressed board paper | 150 | 0.6646 | 49.29 | 7.42 |
| Filter paper | 230 | 0.1700 | 8.82 | 5.19 |

(2) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|--------------------|--------------------------|---------------------|------------------------|----------------------|
| Kraft paper | 150 | 0.0663 | 3840 | 5.79 |
| Synthetic paper | 150 | 0.0563 | 2910 | 5.17 |
| Woodfree paper | 150 | 0.0201 | 722 | 3.59 |
| Machine-made paper | 150 | 0.0948 | 4793 | 5.06 |
| Photocopy paper | 150 | 0.0665 | 3099 | 4.66 |
| Oil paper | 180 | 0.0526 | 3160 | 6.01 |
| Paper tape | 150 | 0.2057 | 4892 | 2.38 |
| Cellotape | 150 | 0.0741 | 6975 | 9.41 |
| Copy paper | 150 | 0.8160 | 2553 | 0.313 |
| Cellulose (paper) | 150 | 0.0500 | 3057 | 6.11 |
| Acrylic fibers | 110 | 0.2396 | 2653 | 1.07 |
| Polyester | 180 | 0.2177 | 430 | 0.198 |
| Chemical fibers | 180 | 0.0497 | 2596 | 5.22 |
| Wool | 150 | 0.0838 | 7225 | 8.62 |
| Absorbent cotton | 150 | 0.0631 | 4379 | 6.94 |

10. Dyestuff Intermediates

Key Points

Many dyestuff intermediates are solids and must be dissolved in solvents. Most Japanese Industrial Standards stipulate volumetric titration. These standards should be taken into account when setting conditions for the moisture content test methods that should be used with individual compounds.

To raise the solubility of specific substances in the dehydrated solvent used for the volumetric titration, it may be necessary to add other solvents, such as those listed below, to the methanol. It should also be noted that special solvents are sometimes used with amines.

Volumetric titration solvents and the main compounds for which they are used

- 1) Dehydrated Solvent MS (or GEX)
- 2) Dehydrated Solvent CP : anilines, o-anisidines, p-cresidines, p-chloroanilines
CP+acetic acid : p-anisidines, p-phenetidines, m-aminophenols
- 3) Dehydrated Solvent PE : Peri acid

- 4) Dehydrated Solvent MS+pyridine : metanilic acid,
o-toluenesulfonamide, C-acids
- 5) Dehydrated Solvent MS+dichloromethane : nitro compounds,
some chloro compounds

Coulometric titration can be used. However, interference reactions make it unsuitable for some substances (* e.g. anilines and other electrode-reactive substances).

Substances for which coulometric titration cannot be used

Anilines, p-anisidines, m-aminophenols, p-chloroanilines, p-toluidines, metanilic acid

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, KT (or MS, CP) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (ppm) |
|----------------------------|----------------------|---------------------|------------------------|------------------------|
| p-Toluidines | CP+acetic acid (2:1) | 2.9253 | 0.89 | 304 |
| p-Anisidines | " | 2.0115 | 0.46 | 229 |
| p-Phenetidines | " | 1.1072 | 1.68 | 0.152% |
| m-Aminophenols | " | 1.0152 | 0.29 | 286 |
| Anthranilic acid | General-use | 1.0164 | 0.11 | 108 |
| Diphenyl amine | " | 8.3429 | 0.25 | 30 |
| 2-Aminonaphthalene | " | 0.5290 | 1.62 | 0.306% |
| -1-sulfonic acid | " | " | " | " |
| Sodium naphthionate | " | 0.0593 | 13.45 | 22.7 |
| J-acid | " | 0.1051 | 5.88 | 5.60% |
| Carbonyl J-acid | " | 0.2062 | 6.15 | 2.98% |
| m-Nitroaniline | " | 1.5089 | 0.95 | 630 |
| p-Nitrophenol | " | 0.9844 | 11.30 | 1.15% |
| 1-Hydroxy-2-naphthoic acid | " | 2.0959 | 0.54 | 258 |
| Anilines | Ketone-type | 2.1601 | 1.92 | 889 |
| 5-Amino-2-chlorotoluene | MS+pyridine (5:1) | 1.9911 | 0.09 | 45 |
| -4-sulfonate(C-acid) | " | " | " | " |

(2) Coulometric titration

Reagents used: Aquamicron AX (or AS) 100ml
 Aquamicron CXU 5ml

| Substance | Electrolyte | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (ppm) |
|---|-------------|---------------------|------------------------|------------------------|
| Anthranilic acid | General-use | 1.1934 | 370 | 310 |
| Diphenyl amine | " | 4.0630 | 104 | 26 |
| 2-Aminonaphthalene-1-sulfonic acid(Tobias acid) | " | 0.5500 | 1721 | 0.313% |
| Sodium naphthionate | " | 0.0514 | 11653 | 22.7% |
| 8-Amino-2-naphthalene sulfonic acid(Peri acid) | " | 0.0561 | 4260 | 7.59% |
| m-Aminophenol | Ketone-type | 0.4592 | 117 | 255 |

11. Pigments**Key Points**

Most pigments are insoluble in titration solvents and cannot be titrated directly. In particular, direct titration should be avoided with inorganic pigments which react with Karl Fischer reagent.

The moisture content of any pigment can be measured quickly (10-30 minutes) and accurately using the conventional drying method based on moisture vaporization. Either volumetric or coulometric titration can be used, depending on the moisture content.

(1) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)
 Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-------------------|--------------------------|---------------------|------------------------|----------------------|
| Zinc white | 300 | 3.1135 | 3.73 | 0.120 |
| Titanium oxide | 200 | 1.0405 | 4.16 | 0.400 |
| Prussian blue | 200 | 0.4002 | 22.17 | 5.540 |
| Red iron oxide | 300 | 3.0021 | 10.21 | 0.340 |
| Chrome yellow | 300 | 2.9988 | 8.40 | 0.280 |
| Aluminum powder | 400 | 5.0211 | 1.00 | 199ppm |
| Antimony oxide | 300 | 3.5011 | 3.85 | 0.110 |
| Calcium carbonate | 100 | 2.1111 | 10.77 | 0.510 |
| " | 600 | 1.0050 | 16.18 | 1.610 |
| Barium carbonate | 500 | 3.1009 | 4.03 | 0.130 |

(2) Moisture vaporization - Coulometric titration

Reagents used: Aquamicron AX (or AS) 150ml
 Aquamicron CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|------------------|--------------------------|---------------------|------------------------|----------------------|
| Cuprous oxide | 230 | 0.3651 | 2959 | 0.810 |
| " | 700 | 0.1497 | 1953 | 1.30 |
| Titanium oxide | 200 | 1.0378 | 3631 | 0.350 |
| Yellow pigment | 230 | 0.1949 | 2028 | 1.04 |
| Red pigment | 200 | 0.0415 | 2370 | 5.71 |
| Barium carbonate | 500 | 3.1009 | 4.30 | 0.130 |

12. Paints**Key Points**

Moisture content in paints causes bubbling, condensation and lumps in painted surfaces. Moisture measurement is, therefore, very important for quality management.

Drying methods cannot be used as there is a risk that other constituents will vaporize with the water. Distillation is also unsuitable because it takes too long, and because many paints include hydrophilic substances that are difficult to separate. As a result, Karl Fischer titration has been chosen as the moisture measurement method for paints and it is stipulated as a Japanese industrial Standard (K5407). Paints include a variety of film-forming substances as well as various other ingredients such as enamels with pigments and varnishes, some of which may react with Karl Fischer reagent.

The possibility that some of these substances will cause an interference reaction is something that must be checked in advance.

JIS K5407 (testing method for paint constituents) stipulates both volumetric and coulometric titration. The level of moisture content in paints is generally within the range for either method. If a product contains a number of substances that will not dissolve in solvents, volumetric titration should be used in preference to coulometric titration.

For volumetric titration, the sample must be dissolved or dispersed in a suitable solvent in preparation for Karl Fischer titration. A ketone-type dehydrated solvent is excellent for samples that contain ketones. If a sample contains other substances that cause interference reactions, Karl Fischer titration should be used in combination with moisture vaporization. Either volumetric or coulometric titration can be used in

such cases.

Because of the high viscosity of most paints, it is difficult to obtain a sample and inject it into a titration cell. Select equipment that matches the characteristics of the sample, such as a thick needle (2mm diameter), a sampling spoon or a glass rod.
(now, JIS K5407 is abolished.)

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent OL II, KT (or CM, CP) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-----------------------------|---------------------|---------------------|------------------------|----------------------|
| Epoxy resin paints | Oil-type | 0.6645 | 0.43 | 647ppm |
| Fluoroethylene resin paints | " | 1.0017 | 1.11 | 0.111 |
| Paints | " | 0.9953 | 4.97 | 0.499 |
| Paint thinners (incl.MEK) | Ketone-type | 4.8894 | 4.33 | 886ppm |
| Melamine varnish | " | 0.1504 | 1.09 | 0.725 |

(2) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|----------------------------|--------------------------|---------------------|------------------------|----------------------|
| Enamel | 150 | 0.1388 | 1902 | 1.37 |
| Paints | 130 | 1.3175 | 742 | 563ppm |
| Lacquer paint | 200 | 0.0650 | 2798 | 4.30 |
| Powder paint | 180 | 0.4513 | 1395 | 0.309 |
| Epoxy resin paint | 150 | 2.2101 | 1454 | 658ppm |
| Fluoroethylene resin paint | 180 | 1.0507 | 1170 | 0.111 |
| Polyester paint | 150 | 0.1931 | 978 | 0.506 |
| Liquid varnish | 300 | 0.1122 | 1934 | 1.73 |
| Melamine varnish | 110 | 0.1894 | 1324 | 0.699 |

13. Printing Inks and Imaging Materials

Key Points

Volumetric titration is used for printing inks and imaging materials. Inks in particular may have a high moisture content. Samples can be obtained in small quantities and directly dissolved or dispersed in dehydrated solvent for Karl Fischer titration. Coulometric titration is commonly used in conjunction with moisture vaporization for samples that cannot be dissolved in solvent or that contain interference substances.

Because of the high viscosity of many inks, it may be difficult to obtain a sample and inject it into a titration cell. Select equipment that matches the characteristics of the sample, such as a thick needle (2mm diameter), a sampling spoon or a glass rod.

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, KTX, OL II (or MS, CP, CM) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|------------------------------|---------------------|---------------------|------------------------|----------------------|
| Printing ink | General-use | 0.4511 | 5.85 | 1.30 |
| Offset ink | Oil-type | 1.0834 | 4.33 | 0.400 |
| Metallic ink | " | 0.3172 | 1.66 | 0.523 |
| Oil-based ink | " | 0.1768 | 22.83 | 12.9 |
| Water-based ink | " | 0.0209 | 17.51 | 83.8 |
| Emulsion ink | " | 0.0561 | 31.75 | 56.6 |
| Inkjet ink | " | 0.0372 | 27.34 | 73.5 |
| Gravure ink | Ketone-type | 0.4125 | 1.38 | 0.335 |
| [Printing ink pigment] | | | | |
| Carmin 6B | Oil-type | 0.4606 | 3.28 | 0.712 |
| Lake red | " | 0.4174 | 0.71 | 0.170 |
| Copper phthalophenone yellow | " | 0.5640 | 0.74 | 0.131 |
| Benzidine yellow | " | 0.6273 | 0.74 | 0.118 |
| [Ink raw materials] | | | | |
| Acrylates | General-use | 0.6104 | 1.54 | 0.252 |
| Epoxy resins | Oil-type | 0.8443 | 4.80 | 0.569 |
| Phenolic novolak | " | 0.7655 | 3.87 | 0.506 |
| Photosensitive resins | " | 0.0315 | 6.90 | 21.9 |
| Toners | Ketone-type | 0.1374 | 1.02 | 0.742 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|---------------------------|--------------------------|---------------------|------------------------|----------------------|
| Emulsion inks | 200 | 0.0626 | 34.78 | 55.7 |
| Water-based ball-pen inks | 200 | 0.0338 | 18.68 | 55.3 |

14. Adhesives**Key Points**

The moisture content of adhesives ranges from minute to high, so both volumetric and coulometric titration are used. For volumetric titration, the sample is dissolved or dispersed in a suitable solvent. Moisture vaporization is used for substances that are totally insoluble.

Coulometric titration can be carried out directly in the case of substances that dissolve in electrolytes. Moisture vaporization is used for samples that are even slightly insoluble.

Adhesives are very viscous and instant adhesives solidify quickly when exposed to air. Because of these and other characteristics, a number of samples are very difficult to handle and sampling equipment must be selected with reference to the attributes of each sample. If the viscosity of the product allows it to be sampled in a syringe, use a thick needle (2mm diameter). For substances with higher viscosity, use a sampling spoon or glass rod. Special procedures are needed for instant adhesives.

Refer to the following document.

Reference: Muroi, K. et al., "Determination of Minute Traces of Water in Cyanoacrylate Adhesive Compositions by the Coulometric Karl Fischer Titration Method Using the Anodic Electrolytic for Ketones" in *Journal of the Japan Adhesive Society* 21, 186 (1985).

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent OL II, KTX (or CM, CP) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|------------------------|---------------------|---------------------|------------------------|----------------------|
| Porcelain adhesives | Oil-type | 1.5001 | 1.65 | 0.110 |
| Aluminum adhesives | " | 0.5508 | 3.75 | 0.681 |
| Woodworking bonds | " | 0.0785 | 46.70 | 59.5 |
| Construction putties | " | 0.2324 | 1.78 | 0.766 |
| Rubber-metal adhesives | Ketone-type | 0.6883 | 3.14 | 0.456 |
| Adhesives | " | 4.4427 | 0.79 | 178ppm |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)
Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|----------------------|--------------------------|---------------------|------------------------|----------------------|
| Pastes | 150 | 0.4960 | 1.59 | 0.321 |
| Woodworking bonds | 200 | 0.0546 | 32.24 | 59.1 |
| Construction putties | 250 | 0.8479 | 2.33 | 0.275 |

(3) Coulometric titration

Reagents used: Aquamicon AX (or AS), AKX 100ml
Aquamicon CXU 5ml

| Substance | Electrolyte | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (ppm) |
|----------------------|-------------|---------------------|------------------------|------------------------|
| Epoxy resins | General-use | 0.5112 | 1507 | 295 |
| Isocyanate hardeners | " | 1.5368 | 98 | 64 |
| Bonds | " | 0.9403 | 524 | 557 |
| Cyanoacrylates | ketone-type | 1.9786 | 430 | 217 |
| Adhesives | " | 2.3736 | 430 | 181 |

(4) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|-------------------------|--------------------------|---------------------|------------------------|----------------------|
| Epoxy resins (powder) | 250 | 0.7074 | 1080 | 0.153 |
| Isocyanates (principal) | 180 | 0.3079 | 941 | 0.306 |
| Silicon bonds | 210 | 0.4800 | 909 | 0.189 |
| Aluminum adhesives | 200 | 0.2670 | 1180 | 0.442 |
| Pastes | 150 | 0.3230 | 954 | 0.295 |
| Porcelain adhesives | 180 | 0.9336 | 964 | 0.103 |
| Sealing compounds | 230 | 0.4367 | 1218 | 0.279 |

15. Soaps and Detergents

Key Points

Because soaps and detergents generally have a high moisture content, volumetric titration is used. The moisture vaporization method is used for metallic soaps, some of which cause interference.

Direct coulometric titration can be used for samples that will dissolve in electrolyte.

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, OL II(or MS,CM) 30-50ml

III-1. Industrial Products

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-------------------------------|---------------------|---------------------|------------------------|----------------------|
| Cosmetic soap | Oil-type | 0.0863 | 9.61 | 11.5 |
| Soft soap | General-use | 0.2133 | 41.59 | 19.5 |
| Facial soap | " | 0.0549 | 10.84 | 19.8 |
| Cleansers | " | 0.0391 | 21.36 | 54.6 |
| Shampoo | " | 0.0353 | 27.68 | 78.4 |
| Alkyl benzene sulfonate | " | 0.2551 | 2.29 | 0.897 |
| ABS detergents | " | 0.0345 | 26.23 | 76.0 |
| Laundry detergents | " | 0.0707 | 6.03 | 8.60 |
| High-grade alcohol detergents | " | 0.1366 | 81.41 | 59.9 |
| Liquid detergent | " | 0.0453 | 20.54 | 45.4 |
| Anionic surfactants | " | 0.5323 | 10.86 | 2.04 |
| Cationic surfactants | " | 3.0084 | 1.84 | 612ppm |
| Nonionic surfactants | " | 3.0155 | 1.48 | 491ppm |
| Amphoteric surfactants | " | 1.0295 | 11.43 | 1.11 |
| Polyglycerine | " | 1.5572 | 5.45 | 0.350 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-------------------------|--------------------------|---------------------|------------------------|----------------------|
| Cosmetic soaps | 200 | 0.0739 | 7.65 | 10.4 |
| Facial soaps | 180 | 0.0998 | 19.76 | 19.8 |
| Alkyl benzene sulfonate | 150 | 0.1870 | 1.69 | 0.904 |
| ABS detergents | 130 | 0.0303 | 22.80 | 76.0 |
| Laundry detergents | 180 | 0.0690 | 5.84 | 8.46 |
| Cleansers | 200 | 0.0503 | 27.47 | 54.6 |

(3) Coulometric titration

Reagents used: Aquamicon AX (or AS) 100ml

Aquamicon CXU 5ml

| Substance | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|-----------|---------------------|------------------------|----------------------|
| Soaps | 0.2934 | 1314 | 0.448 |
| Shampoos | 0.0209 | 16073 | 76.9 |

(4) Moisture vaporization - Coulometric titration

Reagents used: Aquamicron AX (or AS) 150ml
 Aquamicron CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|------------|--------------------------|---------------------|------------------------|----------------------|
| Detergents | 180 | 0.0324 | 5084 | 15.7 |
| Soaps | 150 | 0.4901 | 1517 | 0.310 |
| Cleansers | 600 | 0.0330 | 2475 | 7.50 |

16. Cosmetics**Key Points**

Creams, emulsions, rinses, hair tonics, lotions and other cosmetics have high moisture content. Accordingly, volumetric titration is the main method used with these items. When carrying out the volumetric titration it is convenient to use a high-titer Karl Fischer reagent. An oil-type dehydrated solvent is used for products with a high oil content, such as creams. A general-purpose dehydrated solvent is used for hair tonics and lotions.

Coulometric titration can also be used. However, the high moisture content of these products means that titration will be prolonged, even with small samples. For this reason, volumetric titration should be used whenever possible.

Sampling devices should be selected carefully. Viscous products such as creams should be sampled with a sampling spoon and dissolved directly in the dehydrated solvent. For lotions and similar products, a sampling flask with pipette is convenient. For cosmetics that will not dissolve in dehydrated solvent, volumetric or coulometric titration should be used in combination with moisture vaporization.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
 Dehydrated Solvent GEX, OL II (or MS, CM) 25-50ml

III-1. Industrial Products

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|------------------|---------------------|---------------------|------------------------|----------------------|
| Cream | Oil-type | 0.1072 | 61.21 | 57.1 |
| Emulsion | " | 0.1011 | 74.61 | 73.8 |
| Rinse | " | 0.1151 | 88.39 | 76.8 |
| Nourishing cream | " | 0.0281 | 12.72 | 45.3 |
| Cleansing cream | " | 0.0454 | 15.00 | 33.0 |
| Cold cream | " | 0.0556 | 14.09 | 25.3 |
| Hair tonic | General-use | 0.0409 | 17.33 | 42.4 |
| Hair treatments | " | 0.0328 | 16.92 | 51.6 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-----------|--------------------------|---------------------|------------------------|----------------------|
| Mascara | 150 | 0.0262 | 13.53 | 51.6 |
| Essence | 150 | 0.0660 | 43.42 | 65.8 |

(3) Coulometric titration

Reagents used: Aquamicon AX (or AS)

100ml

Aquamicon CXU

5ml

| Substance | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|-----------------|---------------------|------------------------|----------------------|
| Cream | 0.0364 | 23089 | 63.4 |
| Cleansing cream | 0.0416 | 11188 | 26.9 |
| Emulsion | 0.0330 | 28611 | 86.7 |
| Cream lotion | 0.0153 | 11580 | 75.7 |

(4) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS)

150ml

Aquamicon CXU

10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|--------------|--------------------------|---------------------|------------------------|----------------------|
| Lip cream | 180 | 0.0722 | 4871 | 6.75 |
| Cream lotion | 180 | 0.0180 | 13600 | 75.6 |

17. Chemicals & Materials for Electronic Equipment and Electrical Parts

Key Points

Materials for electronic equipment and electrical parts are made of mixed or composite materials. They vary widely in terms of both the raw materials and their form. The methods used to measure moisture content must be selected with reference to the characteristics of each item. These items generally have a low moisture content and many are insoluble in solvents. For this reason, moisture content is measured using moisture vaporization and coulometric titration.

Chemical products such as liquid crystals, photoresists and capacitor electrolytes can be dissolved in dehydrated solvents or electrolytes. This means that they can be titrated directly using volumetric or coulometric titration.

Chemical substances may be either liquid or solid. For viscous liquids, a syringe with a 2mm diameter needle should be used.

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, OL II (or MS, CM) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-----------------------|---------------------|---------------------|------------------------|----------------------|
| Capacitor electrolyte | General-use | 0.0454 | 3.67 | 8.08 |
| Liquid crystal | " | 1.0998 | 0.23 | 209ppm |
| Photoresist | Oil-type | 1.0823 | 3.23 | 0.298 |

(2) Coulometric titration

Reagents used: Aquamicron AX (or AS) 100ml

Aquamicron CXU 5ml

| Substance | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|----------------|---------------------|------------------------|----------------------|
| Liquid crystal | 1.0504 | 196 | 187ppm |
| Photoresist | 0.5578 | 998 | 0.179 |

(3) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
 Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|-----------------------|--------------------------|---------------------|------------------------|----------------------|
| Liquid crystal | 180 | 2.2303 | 248 | 111ppm |
| Photoresist | 180 | 1.7653 | 334 | 189ppm |
| Capacitor | 260 | 0.1194 | 217 | 0.182 |
| IC chip | 250 | 0.6872 | 1709 | 0.249 |
| Silicon wafer | 700 | 4.1167 | 29 | 7ppm |
| Printed circuit board | 200 | 0.0976 | 1303 | 1.34 |
| Polycarbonate disk | 230 | 0.4430 | 678 | 0.153 |

III-2. Foodstuffs

The food category encompasses a wide range of substances with varying properties.

It includes agricultural, livestock and marine products and processed products, as well as food additives. The moisture content of these items also varies widely. It is necessary, therefore, to select the most appropriate sample handling procedures and measurement method for each individual product.

Test methods for foodstuffs are mostly stipulated in the JAS standards. In most cases moisture content is measured using heating and drying methods, but Karl Fischer titration is specified for some items. In the case of chemically defined foodstuffs, such as sugars and additives, Karl Fischer titration can be applied using the same methods as for normal chemicals.

Food items with complex structures, such as cereals and meats, contain not only adhesion moisture but also moisture incorporated within cells. Measurement results for these items are provided for your information.

Because many food items do not dissolve in organic solvents, the moisture vaporization method is used extensively. However, foodstuffs commonly become unstable when heated, and water may be formed as substances break down. Care must be taken, therefore, when setting analytical conditions.

1. Food Additives and Flavorings

Key Points

Food additives are substances used in the manufacture, processing and preservation of foodstuffs. There are many types with varying attributes. Most are solid, but those that dissolve in dehydrated solvents or electrolytes can be titrated directly using Karl Fischer titration. However, it is necessary first to determine whether or not interference substances are present. Direct titration should be avoided in the case of insoluble substances, and the moisture vaporization method is recommended. As the moisture content of these substances is generally high, volumetric titration is used.

However, coulometric titration can also be used if the sample quantity is kept small.

When using moisture vaporization, it is necessary to set the measurement conditions after determination of the heating temperature. Official specifications for food additives commonly stipulate the loss-on-drying method, so conformance with that method should be checked.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, SU (or MS, FM) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|--|---------------------|---------------------|------------------------|----------------------|
| [Flavorings] | | | | |
| Flavor | General-use | 0.0228 | 10.93 | 48.0 |
| Orange powder | " | 0.2623 | 5.01 | 1.91 |
| Palm lemon | Sugar-type | 0.0765 | 7.08 | 9.25 |
| Strawberry powder | " | 0.2789 | 3.69 | 1.33 |
| [Condiments] | | | | |
| Sodium citrate | General-use | 0.1711 | 20.97 | 12.3 |
| Sodium 5'-inosinate | Sugar-type | 0.0802 | 20.65 | 25.7 |
| Sodium glutamate | " | 0.1303 | 13.38 | 10.3 |
| Yeast extract | " | 0.0810 | 2.84 | 3.65 |
| [Emulsifiers] | | | | |
| Sorbitan fatty acid ester | General-use | 2.0962 | 2.95 | 0.141 |
| [Sweeteners] | | | | |
| Potassium glycyI rhizinate | General-use | 0.1652 | 12.45 | 7.54 |
| Maltitol | Sugar-type | 0.1891 | 25.77 | 13.6 |
| Sorbit | " | 0.4317 | 2.71 | 0.628 |
| Aspartame | " | 0.0535 | 1.33 | 2.49 |
| [Preservatives] | | | | |
| Sorbic acid | General-use | 1.0059 | 1.14 | 0.113 |
| Potassium sorbate | " | 1.0489 | 0.53 | 505ppm |
| Sodium benzoate | " | 1.0787 | 6.89 | 0.639 |
| [Strengtheners] | | | | |
| Thiamine hydrochloride | General-use | 0.2321 | 9.89 | 4.26 |
| Calcium lactate | Sugar-type | 0.0475 | 13.75 | 28.9 |
| [Acidulants] | | | | |
| Malic acid | General-use | 1.0382 | 2.52 | 0.243 |
| Citric acid | " | 0.1044 | 9.23 | 8.84 |
| [Water-retaining emulsifying stabilizer] | | | | |
| Sodium chondroitin sulfate | Sugar-type | 0.0483 | 4.49 | 9.30 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Aquamicron SS-Z (or SS) 150ml

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-------------------|--------------------------|---------------------|------------------------|----------------------|
| [Flavorings] | | | | |
| Cheese powder | 130 | 0.1915 | 12.34 | 6.44 |
| Vanilla powder | 130 | 0.1161 | 4.70 | 4.05 |
| Yoghurt powder | 130 | 0.0984 | 8.47 | 8.61 |
| Strawberry powder | 50 | 0.3188 | 4.25 | 1.33 |
| Orange powder | 150 | 0.2943 | 6.01 | 2.04 |
| Palm lemon | 180 | 0.0630 | 5.68 | 9.02 |
| [Strengtheners] | | | | |
| Calcium lactate | 200 | 0.0513 | 14.50 | 28.3 |

(3) Coulometric titration

Reagents used: Aquamicron AX (or AS) 100ml

Aquamicron CXU 5ml

| Substance | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|---------------------|---------------------|------------------------|----------------------|
| Sodium 5'-inosinate | 0.0524 | 13467 | 25.7 |
| Sodium citrate | 0.0785 | 9649 | 12.3 |
| Sorbic acid | 0.9221 | 1048 | 0.114 |
| Potassium sorbate | 1.0728 | 411 | 383ppm |
| Sodium benzoate | 1.0179 | 6463 | 0.635 |
| Malic acid | 1.0728 | 2471 | 0.230 |
| Saccharin | 0.0921 | 12813 | 13.9 |

(4) Moisture vaporization - Coulometric titration

Reagents used: Aquamicron AX (or AS) 150ml

Aquamicron CXU 10ml

III-2. Foodstuffs

| Substance | Heating temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|--|--------------------------|---------------------|------------------------|----------------------|
| [Condiments] | | | | |
| Sodium glutamate | 80 | 1.1071 | 358 | 323ppm |
| Sodium glutamate | 180 | 0.0484 | 4739 | 9.79 |
| Disodium succinate | 120 | 0.0536 | 21575 | 40.3 |
| Trisodium citrate | 200 | 0.1071 | 13056 | 12.2 |
| Yeast extract | 80 | 0.0391 | 1446 | 3.70 |
| Sodium 5'-guanylate | 200 | 0.0249 | 4744 | 19.1 |
| Sodium 5'-inosinate | 200 | 0.0165 | 4256 | 25.8 |
| [Sweeteners] | | | | |
| Saccharin | 150 | 0.0648 | 8869 | 13.7 |
| Aspartame | 150 | 0.0426 | 1001 | 2.35 |
| [Preservatives] | | | | |
| Sorbic acid | 160 | 1.0252 | 3495 | 0.341 |
| Potassium sorbate | 160 | 1.0139 | 341 | 336ppm |
| Sodium benzoate | 160 | 1.0259 | 6456 | 0.629 |
| [Strengtheners] | | | | |
| Calcium citrate | 150 | 0.0940 | 12257 | 13.0 |
| [Acidulants] | | | | |
| Malic acid | 105 | 1.0389 | 2132 | 0.205 |
| [Quality enhancers] | | | | |
| Sodium polyphosphate | 130 | 2.0194 | 4988 | 0.247 |
| [Water-retaining emulsifying stabilizer] | | | | |
| Sodium chondroitin sulfate | 150 | 0.0440 | 4182 | 9.50 |

2. Cereals and Dried Vegetables

Key Points

Volumetric titration is suitable for cereals and starches which have a high moisture content (approximately 10%). If the sample is in powder form it can be dispersed in dehydrated solvent, allowing the moisture content to be extracted for direct Karl Fischer titration. When using a dehydrated solvent with sugars, solubility is sometimes enhanced if the temperature is raised to 40-45°C before titration. The moisture vaporization method is suitable for the many items that do not dissolve in solvents. Care needs to be taken with the heating temperature for moisture vaporization. Temperatures in the 130-180°C range are commonly used. High temperatures may cause various phenomena, including discoloration, abnormal results or failure to reach an end point. In such cases the measurement must be repeated at a lower temperature.

Moisture vaporization should be used with coulometric titration. Cereals cannot be titrated directly as they do not dissolve in electrolytes.

Cereals are sometimes sampled after preliminary processing (e.g. pulverization).

Care is needed to avoid moisture vaporization or absorption during these processes.

Volumetric titration is the principal method used for dried vegetables. The sample is added to the dehydrated solvent and stirred well for a period of 5-10 minutes before direct titration. Moisture vaporization is used when the moisture content cannot be fully extracted from samples in this way. Karl Fischer titration can be carried out using either the volumetric or coulometric methods. As moisture content tends to be high, however, volumetric titration is usually preferable.

The precautions stipulated for moisture vaporization in connection with cereals also apply to dried vegetables.

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, SU (or MS, FM) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|---------------------|---------------------|---------------------|------------------------|----------------------|
| Apple powder | General-use | 0.0989 | 2.16 | 2.19 |
| Dried carrot powder | " | 0.1231 | 3.74 | 3.04 |
| Dried onions | " | 0.0366 | 2.81 | 7.68 |
| Dried tomato powder | " | 0.1309 | 3.07 | 2.35 |
| Sweet potato starch | " | 0.1885 | 31.10 | 16.5 |
| Corn flour | " | 0.0627 | 6.06 | 9.67 |
| Soy protein | " | 0.0574 | 4.09 | 7.13 |
| Corn starch | Sugar-type | 0.1612 | 21.15 | 13.1 |
| Wheat | " | 0.0635 | 9.05 | 14.3 |
| Soy protein | " | 0.0756 | 5.43 | 7.18 |
| Soy flour | " | 0.0692 | 5.26 | 7.60 |
| Potato powder | Sugar-type (45°C) | 0.0721 | 5.80 | 8.04 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|----------------------|--------------------------|---------------------|------------------------|----------------------|
| Corn starch | 150 | 0.1103 | 13.77 | 12.5 |
| Maize | 130 | 0.0529 | 6.34 | 12.0 |
| Wheat flour | 180 | 0.0826 | 13.10 | 15.9 |
| Corn flour | 180 | 0.1421 | 53.65 | 37.8 |
| Devil's-tongue flour | 130 | 0.1270 | 11.30 | 8.90 |
| Apple powder | 110 | 0.1647 | 3.60 | 2.19 |
| Dried onions | 70 | 0.0457 | 3.44 | 7.53 |
| Soy flour | 150 | 0.0719 | 5.33 | 7.41 |

(3) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml

Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|---------------|--------------------------|---------------------|------------------------|----------------------|
| Corn starch | 150 | 0.0490 | 6409 | 13.1 |
| Wheat | 150 | 0.0524 | 7498 | 14.3 |
| Malt | 110 | 0.0764 | 4530 | 5.93 |
| Maize | 150 | 0.0482 | 7009 | 14.5 |
| Wheat flour | 130 | 0.0659 | 6382 | 9.68 |
| Soy protein | 150 | 0.0463 | 3337 | 7.21 |
| Potato powder | 110 | 0.0602 | 4876 | 8.10 |

3. Sugars and Condiments

Key Points

Sugars are dissolved in a sugar-type dehydrated solvent and titrated. Volumetric titration is used. If a substance is slow or difficult to dissolve the solvent can be heated (up to 50°C) and titrated. (If the temperature exceeds 50°C the formamide in the sugar-type dehydrated solvent will gradually break down. The Karl Fischer reagent will be consumed in small amounts leading to uncertainty about the end point.)

Condiments are normally dispersed in general-use dehydrated solvent. This is followed by extraction and titration. If the ingredients of a particular item give it a high sugar content, a sugar-type dehydrated solvent is used. An oil-type dehydrated solvent is used for products with a high fat content.

Moisture vaporization should generally be avoided for sugars as these tend to break down when heated. Moisture vaporization is unnecessary for condiments, since in almost all cases moisture content can be measured using direct titration. When using the moisture vaporization method the optimal heating temperature must be determined first. Changes in the sample could lead to errors.

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, SU, OL II (or MS, FM) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|------------------|---------------------|---------------------|------------------------|----------------------|
| Wasabi paste | General-use | 0.0465 | 10.23 | 22.0 |
| Roast meat gravy | " | 0.0187 | 10.66 | 57.0 |
| Soy sauce | " | 0.0265 | 17.55 | 66.2 |
| Soup powder | " | 0.0754 | 2.89 | 3.83 |
| Bonito stock | " | 0.1475 | 7.48 | 5.07 |
| Sugar syrup | " | 0.0691 | 40.56 | 58.7 |
| Powdered miso | " | 0.1228 | 3.79 | 3.09 |
| Glucose | Sugar-type | 1.1052 | 1.64 | 0.148 |
| White sugar | " | 0.2550 | 3.51 | 1.38 |
| Maltose | " | 0.0695 | 3.56 | 5.12 |
| Malt syrup | " | 0.0505 | 12.49 | 24.9 |
| Soup | " | 0.0322 | 19.87 | 61.7 |
| Refined sugar | Sugar-type (40°C) | 0.4729 | 4.04 | 0.854 |
| Soup stock | Sugar-type (40°C) | 0.4363 | 5.66 | 4.22 |
| Granulated sugar | Sugar-type (45°C) | 2.8133 | 0.71 | 252ppm |
| Mayonnaise | Oil-type | 0.1425 | 28.93 | 20.3 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|--------------|--------------------------|---------------------|------------------------|----------------------|
| Soup powder | 90 | 0.0824 | 3.70 | 4.49 |
| Wasabi paste | 110 | 0.0522 | 11.68 | 22.4 |
| Soy sauce | 200 | 0.0399 | 24.07 | 60.3 |
| Mayonnaise | 200 | 0.1408 | 28.61 | 20.3 |

(3) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml

Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|-----------|--------------------------|---------------------|------------------------|----------------------|
| Sugar | 130 | 0.4853 | 3669 | 1.98 |
| Spices | 130 | 0.0412 | 5830 | 14.2 |

4. Confectionery**Key Points**

Because sugar is the main ingredient of confectionery, these items are dissolved in a sugar-type dehydrated solvent for titration. Volumetric titration is used.

Coulometric titration is normally avoided as these products will not dissolve in electrolytes. The moisture vaporization method is also in some cases unsuitable as heating causes sugars to break down and produce water.

Caramels, candies and similar items are titrated after they have been dissolved in a sugar-type dehydrated solvent that has been heated (up to 45°C). (If the temperature exceeds 45°C the formamide in the sugar-type dehydrated solvent will gradually break down. The Karl Fischer reagent will be consumed in small amounts and this will lead to uncertainty about the end point.) The moisture vaporization method can be used for snack-type confectionery.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent SU (or FM) at 40°C 25-50ml

| Substance | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|----------------------|---------------------|------------------------|----------------------|
| Malt syrup | 0.0505 | 12.59 | 24.9 |
| Candy | 0.1893 | 5.78 | 3.05 |
| Drops | 0.2674 | 5.77 | 2.16 |
| Milk caramel | 0.2869 | 23.42 | 8.16 |
| Cream caramel | 0.1206 | 9.93 | 8.24 |
| Chocolate | 0.3153 | 3.18 | 1.01 |
| Wafers | 0.5500 | 12.76 | 2.32 |
| Chocolate cream | 0.0999 | 12.13 | 12.1 |
| Chocolate emulsifier | 0.2527 | 5.83 | 2.31 |
| Chewing gum | 0.2978 | 5.63 | 1.89 |
| Corn snack | 0.2217 | 3.24 | 1.46 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|--------------|--------------------------|---------------------|------------------------|----------------------|
| Potato chips | 130 | 0.1814 | 3.73 | 2.06 |
| Biscuits | 130 | 0.3821 | 12.72 | 3.33 |
| Corn snacks | 130 | 0.2462 | 3.44 | 1.40 |

(3) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml

Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|---------------------|--------------------------|---------------------|------------------------|----------------------|
| Small rice crackers | 130 | 0.0377 | 2776 | 7.36 |

5. Dairy Products, Fat Products

Key Points

Because of their high moisture content, most dairy products are titrated directly using the volumetric method. A sugar-type dehydrated solvent is normally used as the titration solvent. However, products that have fats as their principal ingredients, such as butter, are dissolved in an oil-type dehydrated solvent for titration. When volumetric titration is used for fat products they are dissolved in an oil-type dehydrated solvent. The moisture content of vegetable oils, which contain little water, can be measured more accurately using coulometric titration.

If a product will not dissolve readily in the electrolyte, the addition of chloroform to the anolyte (equivalent to 20% by volume of anolyte) will allow the substance to dissolve for repeat titrations.

The moisture vaporization method can be used for samples of these types. However, the conditions must be determined with care. As a general rule, a heating temperature in the 110-180°C range is used.

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, OL II, SU (or MS, CM, FM) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-----------------|---------------------|---------------------|------------------------|----------------------|
| Powdered milk | General-use | 0.0572 | 2.64 | 4.56 |
| Cream cheese | " | 0.0485 | 25.04 | 51.6 |
| Natural cheese | " | 0.1143 | 72.16 | 63.1 |
| Milk powder | Sugar-type | 1.0888 | 30.55 | 2.81 |
| Condensed milk | " | 0.0730 | 19.42 | 26.6 |
| Fresh cream | " | 0.1142 | 16.74 | 14.7 |
| Powdered cheese | " | 0.1269 | 5.43 | 4.28 |
| Meat extract | " | 0.1067 | 18.59 | 17.4 |
| Rapeseed oil | Oil-type | 4.6163 | 0.51 | 110ppm |
| Butter | " | 0.0303 | 4.25 | 14.0 |
| Margarine | " | 0.0970 | 15.49 | 16.0 |

Sugar-type dehydrated solvent should be heated to 40°C before use in titration.

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|----------------|--------------------------|---------------------|------------------------|----------------------|
| Cream cheese | 130 | 0.1147 | 59.14 | 51.6 |
| Natural cheese | 130 | 0.0898 | 57.00 | 63.5 |
| Meat extract | 180 | 0.0705 | 12.17 | 17.3 |
| Margarine | 150 | 0.1281 | 19.97 | 15.6 |

(3) Coulometric titration

Reagents used: Aquamicon AX (or AS) 100ml

Aquamicon CXU 5ml

| Substance | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|---------------|---------------------|------------------------|----------------------|
| Powdered milk | 0.2071 | 5852 | 2.83 |
| Butter | 0.0422 | 5845 | 13.9 |
| Cheese | 0.0142 | 5840 | 41.1 |
| Palm oil | 0.3189 | 303 | 950ppm |
| Sesame oil | 0.9017 | 534 | 592ppm |
| Soy bean oil | 4.5118 | 29 | 51ppm |
| Salad oil | 2.7354 | 394 | 144ppm |

(4) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml

Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|---------------|--------------------------|---------------------|------------------------|----------------------|
| Powdered milk | 110 | 0.0648 | 2953 | 4.56 |
| Cheese | 130 | 0.0217 | 8982 | 41.4 |

6. Gourmet Foods, etc.

Key Points

Volumetric titration is normally used for gourmet foods because of their high moisture content. They are dissolved in a sugar-type dehydrated solvent and subjected to Karl Fischer titration. If a product will not dissolve readily the solvent can be heated to 40°C. An oil-type dehydrated solvent is used for high-fat foods. A general-purpose dehydrated solvent may be used for some samples. If the moisture content cannot be extracted fully using these solvents, Karl Fischer titration is used in conjunction with moisture vaporization. Either volumetric or coulometric titration can be used in such cases.

In the case of coulometric titration, direct titration should be avoided because of problems with the solubility of samples.

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, SU, OL II (or MS, FM, CM) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-------------------|---------------------|---------------------|------------------------|----------------------|
| Powdered egg yolk | General-use | 0.0610 | 2.96 | 4.85 |
| Dried beer yeast | " | 0.0820 | 3.02 | 3.68 |
| Coffee | Sugar-type | 0.1287 | 3.87 | 3.01 |
| Cocoa | " | 0.3632 | 5.60 | 1.54 |
| Juice powder | " | 0.4695 | 4.07 | 0.867 |
| Raw coffee beans | Sugar-type (40°C) | 0.0574 | 5.45 | 9.49 |
| Tea | Sugar-type (40°C) | 1.0516 | 5.80 | 0.552 |
| Gelatine | Sugar-type (40°C) | 0.0170 | 2.59 | 15.2 |
| Soy milk | Oil-type | 0.0663 | 57.26 | 86.4 |
| Curry roux | " | 0.1353 | 4.57 | 3.38 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|------------------|--------------------------|---------------------|------------------------|----------------------|
| Coffee beans | 130 | 0.1919 | 4.11 | 2.14 |
| Dried beer yeast | 200 | 0.0840 | 8.86 | 10.6 |
| Curry roux | 130 | 0.1217 | 4.31 | 3.54 |

(3) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml

Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|------------------|--------------------------|---------------------|------------------------|----------------------|
| Coffee | 90 | 0.1282 | 3229 | 2.52 |
| Raw coffee beans | 150 | 0.0555 | 5012 | 9.03 |
| Cocoa | 110 | 0.2486 | 3973 | 1.60 |
| Hops | 130 | 0.0189 | 1536 | 8.14 |
| Beet | 130 | 0.0913 | 7669 | 8.40 |
| Gelatine | 180 | 0.0114 | 1790 | 15.7 |

III-3. Pharmaceuticals

In this field, Karl Fischer titration is the most effective tool for precise moisture content measurement. Moisture content tends to be high, ranging from a few percent up to a few tens of percent. For this reason, volumetric titration is generally used.

The examples in this section show the application of Karl Fischer titration to biochemical and pharmaceutical products. Where the chemical ingredients of these products are known direct titration can be used as it is possible to determine whether or not interference will occur.

Even if products cause interference, they can still be measured using moisture vaporization and Karl Fischer titration, provided that they remain stable when exposed to heat.

Special pharmaceutical items are listed in the Japanese Pharmacopoeia. Aside from volumetric titration, the coulometric titration and moisture vaporization methods can also be used. This chapter gives examples based on the actual implementation of these methods.

1. Biochemical Products

Key Points

Sugar-type dehydrated solvents are generally used when applying volumetric titration to biochemical products such as amino acids, nucleic acids, sugars, enzymes and lipids. Even substances that do not dissolve in general-use dehydrated solvents can be titrated directly using a general-use dehydrated solvent, provided that the moisture content of the sample can be extracted adequately.

Direct coulometric titration is not suitable as many samples cannot be dissolved in the analytes used for this type of titration. Coulometric titration is carried out using the moisture vaporization method. Some samples break down at certain heating temperatures and there must be careful consideration of the temperature used for moisture vaporization.

L-cystine and vitamin C react with Karl Fischer reagent and cannot be titrated directly. Care is needed with general vitamin preparations that include vitamin C since these can also cause interference reactions. (Vitamin C reacts quantitatively with iodine. If the amount of vitamin C included in a sample is known, then the moisture content can be determined by adjusting the results. Refer to the Basic Knowledge section for more information.) Moisture vaporization is used with these substances.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, SU (or MS, FM) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|---------------------------------------|---------------------|---------------------|------------------------|----------------------|
| L-alanine | General-use | 0.5316 | 0.13 | 245ppm |
| Potassium asparaginate | " | 0.1026 | 5.29 | 5.16 |
| Glycylglycine | " | 0.2882 | 0.24 | 833ppm |
| Vitamin B12 | " | 0.1452 | 11.27 | 7.76 |
| Vitamin B1 hydrochloride | " | 0.2321 | 9.89 | 4.26 |
| ATP | Sugar-type | 0.0750 | 6.55 | 8.73 |
| Citidine (5') diphosphocholine sodium | " | 0.0466 | 1.92 | 4.12 |
| Dextran | " | 0.0901 | 5.93 | 6.58 |
| Chlorella | " | 0.0550 | 3.54 | 6.44 |
| Yeast extract | " | 0.0810 | 0.95 | 3.58 |
| Cyclodextrin | " | 0.0386 | 1.55 | 4.02 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|------------------------|--------------------------|---------------------|------------------------|----------------------|
| Adenosine triphosphate | 200 | 0.0430 | 3.28 | 8.41 |

(3) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml

Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|----------------------|--------------------------|---------------------|------------------------|----------------------|
| L-alanine | 150 | 0.7408 | 56 | 76ppm |
| Sodium asparaginate | 180 | 0.0366 | 2020 | 5.52 |
| Glycylglycine | 130 | 0.2765 | 70 | 253ppm |
| L-cystine | 130 | 0.1123 | 796 | 0.709 |
| Dextran | 180 | 0.0457 | 3093 | 6.76 |
| Vitamin preparations | 110 | 0.1211 | 2235 | 1.85 |
| Vitamin C | 100 | 0.1264 | 1275 | 1.01 |
| Vitamin B12 | 130 | 0.0403 | 3128 | 7.76 |
| Chlorella | 150 | 0.0659 | 4180 | 6.34 |
| Yeast extract | 80 | 0.0391 | 1446 | 3.70 |
| Yeast nucleic acid | 200 | 0.0230 | 5875 | 25.5 |

2. Pharmaceuticals

Key Points

The Japanese Pharmacopoeia (7th revision) designates Karl Fischer methodology as the general testing method for 28 pharmaceutical products. In addition to volumetric titration, the coulometric titration and moisture-vaporization methods have also been specified. Normally, samples are placed in a general-use dehydrated solvent and stirred for a period before titration. Alternatively, surplus Karl Fischer reagent may be added to the solution, which is then stirred for a period and reverse titrated with standard water-methanol. Depending on the solubility of the sample, a sugar-type or oil-type dehydrated solvent should be used.

The chemical constituents of pharmaceutical products are usually known so it is possible to determine in advance whether or not a particular product is suitable for Karl Fischer titration. Coulometric titration is convenient when only a limited amount of sample can be obtained (such as when a substance is too valuable to use more than a few milligrams), or when moisture content is low. The moisture vaporization method is used when it is difficult to draw the moisture into the dehydrated solvent, or when interference would occur.

As with other types of substances, the heating temperature must be selected with care.

Moisture vaporization should be used only after careful consideration.

[Examples of Measurement]

(1) Volumetric titration

| | |
|--|---------|
| Reagents used: Karl Fischer Reagent SS-Z (or SS) | |
| Dehydrated Solvent SU(or MS, FM) | 25-50ml |

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|---------------------------|---------------------|---------------------|------------------------|----------------------|
| Aminophylline | General-use | 0.2115 | 8.90 | 4.21 |
| Digitalis | " | 0.3502 | 5.46 | 1.56 |
| Antibiotics | " | 0.1245 | 8.35 | 6.71 |
| Gibberellin methyl ester | " | 0.2005 | 3.31 | 1.65 |
| Berberine chloride | " | 0.0433 | 4.23 | 9.55 |
| Glutathione | " | 0.2713 | 11.51 | 4.24 |
| Aspirin aluminum | " | 0.1638 | 2.33 | 1.42 |
| Carbetapeten citrate | " | 0.3053 | 0.13 | 0.043 |
| Chlorobutanol | " | 0.0896 | 4.35 | 4.85 |
| Patenol | " | 0.1243 | 0.13 | 0.10 |
| Erythromycin lactobionate | " | 0.0431 | 1.43 | 10.3 |
| Rutin | " | 0.1202 | 11.36 | 9.45 |
| Libotite | Sugar-type | 0.1337 | 31.18 | 23.3 |
| Hemin | " | 0.1838 | 1.47 | 0.800 |
| Phosphomycin Ca | " | 0.1533 | 14.65 | 9.49 |
| Pantechinan | " | 0.1375 | 28.30 | 20.6 |
| Sodium aspartate | Sugar-type (40°C) | 0.0543 | 5.77 | 10.6 |
| Throat drops | " (40°C) | 0.2970 | 10.79 | 3.63 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|------------------------|--------------------------|---------------------|------------------------|----------------------|
| Phosphomycin Ca | 250 | 0.1142 | 10.58 | 9.26 |
| Potassium xanthogenate | 150 | 0.5009 | 2.42 | 0.483 |

(3) Coulometric titration

Reagents used: Aquamicon AX (or AS) 100ml

Aquamicon CXU 5ml

| Substance | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|---------------|---------------------|------------------------|----------------------|
| Albumin | 0.2236 | 693 | 0.310 |
| Polypeptide | 0.0037 | 316 | 8.54 |
| Aminophylline | 0.0427 | 1795 | 4.20 |

(4) Moisture vaporization - Coulometric titration

Reagents used: Aquamicron AX (or AS) 150ml
 Aquamicron CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|----------------------|--------------------------|---------------------|------------------------|----------------------|
| Albumin | 110 | 0.1818 | 578 | 0.318 |
| Glutathione | 110 | 0.4208 | 1635 | 0.389 |
| Berberine chloride | 150 | 0.0288 | 2735 | 9.56 |
| Bufferin | 130 | 0.0662 | 2645 | 4.00 |
| Aspirin aluminum | 150 | 0.1715 | 2332 | 1.36 |
| Synthetic penicillin | 150 | 0.0837 | 2616 | 3.13 |

3. Chinese Herbal Medicines, Biological Tissue, etc.**Key Points**

Either a general-use or a sugar-type dehydrated solvent is used for chinese herbal medicines. In general, however, these products are difficult to dissolve. This means that insufficient moisture is extracted and accurate analytical results cannot be obtained. The moisture vaporization method is used for this reason. The heating temperature must be considered carefully as heating can cause some products to change color or break down.

In the examples shown, biological tissue was dispersed in a general-use dehydrated solvent and subjected to Karl Fischer titration.

Similar procedures should be used for capsules and other items.

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)
 Dehydrated Solvent GEX, SU (or MS, FM) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|---------------------|---------------------|---------------------|------------------------|----------------------|
| Pills (heart tonic) | General-use | 0.1356 | 8.86 | 6.53 |
| Muscle | " | 0.1018 | 75.74 | 74.4 |
| Brain | " | 0.0994 | 77.23 | 77.7 |
| Blood serum | " | 0.0916 | 83.90 | 91.6 |
| Pancreas | " | 0.6645 | 33.36 | 5.02 |
| Bile acid | " | 0.9185 | 15.15 | 1.65 |
| Licorice powder | " | 0.1111 | 9.91 | 8.92 |
| Crude drugs | Sugar-type | 0.0608 | 18.80 | 30.9 |
| Capsules | " (40°C) | 0.0697 | 9.81 | 14.1 |
| Soft capsules | " (40°C) | 0.0528 | 5.09 | 9.64 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|---------------------|--------------------------|---------------------|------------------------|----------------------|
| Pills (heart tonic) | 110 | 0.2215 | 14.51 | 6.55 |
| Crude drugs | 130 | 0.0532 | 16.46 | 30.9 |
| Medicinal wafers | 150 | 0.0776 | 12.82 | 16.5 |
| Capsules | 170 | 0.0726 | 10.14 | 14.0 |
| Toothpaste | 200 | 0.2069 | 64.33 | 31.1 |
| Black hair | 200 | 0.0726 | 8.09 | 11.1 |
| Blond hair | 200 | 0.1583 | 18.38 | 11.6 |

(3) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml

Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|-------------------|--------------------------|---------------------|------------------------|----------------------|
| Crude drugs | 130 | 0.0961 | 1254 | 1.30 |
| Licorice powder | 130 | 0.0439 | 3977 | 9.06 |
| Cinnamon | 130 | 0.0620 | 3464 | 5.59 |
| Mint | 110 | 0.0428 | 2411 | 5.63 |
| Soft capsules | 150 | 0.0463 | 4463 | 9.64 |
| Gelatine capsules | 150 | 0.0201 | 3262 | 16.2 |

III-4. Minerals and Natural Products

This chapter provides examples of the use of Karl Fischer titration to measure the moisture content of mineral substances such as rock, sand and iron ore. As these substances are not soluble in solvents the moisture vaporization method is, of course, used in most cases. Particular care must be taken with reference to the heating temperature as water of composition can cause problems.

Natural products vary widely and it is possible to present only a few examples here.

Refer to these when determining the analytical conditions.

1. Minerals

Key Points

With the traditional drying methodology, substances like ores and rock tended to oxidize. Measurement had to take place over long periods of time and the results were frequently inaccurate. By combining moisture vaporization with Karl Fischer titration moisture content can be measured quickly and accurately.

Karl Fischer titration can be carried out using either volumetric or coulometric methods. Volumetric titration is generally used for substances with a high moisture content. Since minerals commonly occur in lumps or granular form, samples must first be crushed into suitably fine grains. During this process care is needed to prevent moisture vaporization into, or absorption from the atmosphere.

With minerals, problems can arise not only with water of adhesion but also with water of composition (water of crystallization). Fractional measurement is achieved using the moisture vaporization method. The heating temperature is set between 100 and around 200°C for water of adhesion, and between 500 and 1,000°C when measuring water of composition. Thus, the temperature for moisture vaporization is set according to both the type of sample and the purpose of the measurement.

A commercially available dual-system heating oven provides a convenient way of obtaining accurate fractional measurements of water of adhesion and water of composition.

Reference: JIS M8211 "Iron Ores--Method for Determination of Combined Water Content"

[Examples of Measurement]**(1) Volumetric titration**

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-----------------|---------------------|---------------------|------------------------|----------------------|
| Soil | General-use | 0.0508 | 23.63 | 46.5 |
| Dried soil | " | 0.0858 | 4.21 | 4.91 |
| Powdered quartz | " | 1.6711 | 0.94 | 0.056 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|---------------|--------------------------|---------------------|------------------------|----------------------|
| Rocks | 900 | 0.0798 | 13.11 | 16.4 |
| Clay | 110 | 0.8837 | 34.46 | 3.90 |
| " | 700 | 0.1033 | 14.99 | 14.5 |
| Soil | 200 | 0.0483 | 22.88 | 47.2 |
| Iron ore | 750 | 0.5638 | 13.58 | 2.41 |
| Limestone | 700 | 0.2462 | 0.84 | 0.34 |
| Cement | 800 | 1.5555 | 11.20 | 0.720 |
| Ferrite | 200 | 0.8967 | 9.20 | 1.03 |
| Coal | 180 | 1.0022 | 33.47 | 3.34 |
| Amphibole | 1000 | 1.0283 | 16.04 | 1.56 |
| Black mica | 1000 | 1.1005 | 25.75 | 2.34 |
| Kaolin | 800 | 0.1414 | 19.94 | 14.1 |
| Talc | 1000 | 0.2003 | 14.40 | 7.19 |
| Bentonite | 800 | 0.1135 | 18.61 | 16.4 |
| Manganese ore | 750 | 0.2313 | 24.29 | 10.5 |

(3) Moisture vaporization - Coulometric titration

Reagents used: Aquamicon AX (or AS) 150ml
 Aquamicon CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|-----------------|--------------------------|---------------------|------------------------|----------------------|
| Black mica | 1000 | 0.0733 | 1716 | 2.34 |
| Amphibole | 1000 | 0.2167 | 3391 | 1.56 |
| Rocks | 700 | 0.1176 | 6331 | 5.38 |
| Silica | 900 | 0.0476 | 2333 | 4.90 |
| Casting sand | 110 | 1.5238 | 1515 | 994ppm |
| " | 900 | 1.1927 | 6688 | 0.561 |
| Clay | 110 | 0.0520 | 2048 | 3.94 |
| Soil | 180 | 0.0736 | 3747 | 5.09 |
| Talc | 200 | 0.4579 | 843 | 0.184 |
| " | 900 | 0.1871 | 9512 | 5.08 |
| Sintered ore | 750 | 0.0985 | 65 | 660ppm |
| Manganese ore | 110 | 0.1700 | 833 | 0.490 |
| " | 750 | 0.0185 | 1922 | 10.4 |
| Iron ore | 750 | 0.1115 | 2653 | 2.38 |
| Powdered quartz | 200 | 1.1064 | 564 | 510ppm |
| " | 900 | 0.8052 | 937 | 0.116 |

2. Natural Products

Key Points

Natural products vary widely and the appropriate Karl Fischer titration should be selected to suit the particular sample. Direct titration is used for substances that dissolve in dehydrated solvent or that are unstable when heated. If the sample is stable when heated, use the moisture vaporization method. The heating temperature must be considered carefully when using that method. If the temperature is too high the breakdown of the substance could lead to interference. (For example, the end point may not be reached, or the analytical results that are obtained may be abnormally high.)

Karl Fischer titration can be carried out using either volumetric or coulometric methods, but volumetric titration is probably more suitable since natural products tend to have a high moisture content.

[Examples of Measurement]

(1) Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX, KTX, SU (or MS, CM,FM) 25-50ml

| Substance | Dehydrated solvents | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|-------------------|---------------------|---------------------|------------------------|----------------------|
| Silver fir leaves | General-use | 0.0462 | 3.12 | 6.76 |
| Tree roots | " | 0.0279 | 2.53 | 9.07 |
| Pollen | Sugar-type | 0.0071 | 0.64 | 9.0 |
| Pine resin | Ketone-type | 1.0106 | 0.74 | 0.073 |
| Rosin | " | 0.7388 | 6.15 | 0.832 |

(2) Moisture vaporization - Volumetric titration

Reagents used: Karl Fischer Reagent SS-Z (or SS)

Dehydrated Solvent GEX (or MS) + PG (3:1) 50-100ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (mg) | Moisture Content (%) |
|------------|--------------------------|---------------------|------------------------|----------------------|
| Pine resin | 130 | 1.6708 | 0.83 | 0.050 |

(3) Coulometric titration

Reagents used: Aquamicron AX (or AS) 100ml
 Aquamicron CXU 5ml

| Substance | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|-------------------|---------------------|------------------------|----------------------|
| Raw lacquer | 0.0247 | 3466 | 14.0 |
| Processed lacquer | 0.1211 | 3810 | 3.15 |

(4) Moisture vaporization - Coulometric titration

Reagents used: Aquamicron AX (or AS) 150ml
 Aquamicron CXU 10ml

| Substance | Heating Temperature (°C) | Sample Quantity (g) | Measurement Value (µg) | Moisture Content (%) |
|-------------------|--------------------------|---------------------|------------------------|----------------------|
| Silver fir leaves | 130 | 0.0541 | 3800 | 7.02 |
| Tree roots | 100 | 0.0189 | 1723 | 9.12 |

Chapter IV: List of Karl Fischer Reagents

Volumetric Titration Reagents

The requirements for volumetric titration are a Karl Fischer reagent, standard water-methanol to assess the titer and a dehydrated solvent in which to dissolve or disperse the sample.

Mitsubishi Chemical Corporation has an extensive range of reagents suitable for all levels of moisture content. Choose the combination of products that is most suitable for your particular purpose.

Karl Fischer Reagent SS Series (Pyridine-Type)

The SS Series has enjoyed an excellent reputation for quality and performance for many years.

| Product | Standard | Packaging | Uses |
|--------------------------------------|---|------------------------|--|
| Karl Fischer Reagent SS (Mitsubishi) | Titer 2.5-3.5mgH ₂ O/ml | 500ml glass bottles | General-use This titration preparation can be used for a wide range of purposes. |
| | Titer 8-12mgH ₂ O/ml | 500ml glass bottles | High moisture content This product allows quick, accurate measurement of moisture content over about 40% in foodstuffs, cosmetics, etc. |
| | Titer 0.7-1.2mgH ₂ O/ml | 500ml glass bottles | Low moisture content This product is suitable for measuring moisture content below 100ppm in organic solvents, electrical insulating oils, gases, etc. |
| Dehydrated Solvent MS | Moisture content 0.2mgH ₂ O/ml or lower | 500ml glass bottles | General-use (*recommended product) Suitable for organic solvents, inorganic chemicals, agricultural chemicals, pharmaceuticals, fertilizers, detergents, foodstuffs, etc. |
| Dehydrated Solvent ML | Moisture content 0.2mgH ₂ O/ml or lower | 500ml glass bottles | General-use Suitable for organic solvents, inorganic chemicals, agricultural chemicals, pharmaceuticals, fertilizers, detergents, foodstuffs, etc. |

List of Karl Fischer Reagents

| Product | Standard | Packaging | Uses |
|-----------------------|--|------------------------|---|
| Dehydrated Solvent CM | Moisture content 0.3mgH ₂ O/ml or lower | 500ml glass bottles | Oil-type Suitable for naphtha, gasoline, diesel oil, heavy oil, electrical insulating oil, oils and fats (hardened oil, margarine, etc.), etc. |
| Dehydrated Solvent CP | Moisture content 0.5mgH ₂ O/ml or lower | 500ml glass bottles | Ketone-type (*recommended product) For ketones, silicon oils, acetic acid and other lower carboxylic acids, aldehydes (except acetaldehydes), anilines, etc. |
| Dehydrated Solvent PE | Moisture content 0.2mgH ₂ O/ml or lower | 500ml glass bottles | Ketone-type For ketones, silicon oils, acetic acid and other lower carboxylic acids, aldehydes (except acetaldehydes), anilines, etc. |
| Dehydrated Solvent PP | Moisture content 0.2mgH ₂ O/ml or lower | 500ml glass bottles | Aldehyde-type Acetaldehydes, propionaldehydes, butyraldehydes, etc. |
| Dehydrated Solvent FM | Moisture content 0.2mgH ₂ O/ml or lower | 500ml glass bottles | Sugar-type Sugars, proteins, gelatine, additives, animal feeds, etc. |
| Dehydrated Solvent ME | Moisture content 0.2mgH ₂ O/ml or lower | 500ml glass bottles | For gaseous samples Nitrogen, etc. |

Mix Dehydrated Solvent MS with propylene glycol (PG) in a 3:1 ratio (e.g. MS90ml: PG30ml) when using a moisture vaporization system.

Standard Reagents for Titer Assessment

Mitsubishi Chemical Corporation supplies two types standard water-methanol products that include a known amount of water. These products are used to assess the titer.

Select the product according to the titer of the Karl Fischer reagent that you are using. These standard reagents are also convenient for use in back titration.

| Product | Standard | Packaging | Uses |
|--------------------------------------|--|---------------------|--|
| Standard Water Methanol (Mitsubishi) | Moisture content: 2.0±0.04 mgH ₂ O/ml | 250ml glass bottles | Used to assess titer of Karl Fischer reagents(3-10mgH ₂ O/ml) |
| | Moisture content: 0.5±0.02 mgH ₂ O/ml | 250ml glass bottles | Used to assess titer of Karl Fischer reagents (1mgH ₂ O/ml) |

Karl Fischer Reagent SS-Z Series (Pyridine/Chloroform-Free Type)

Mitsubishi's SS-Z range of titration products is free of both pyridine and chloroform.

These products are kind to both people and the environment.

Karl Fischer Reagent SS-Z is a volumetric titration reagent that contains neither chloroform nor methyl cellosolve. It is also free of pyridine so there is almost no odor.

A low-toxicity solvent system has been used to develop a product that is kind to both people and the environment while providing the same performance as earlier products.

These products can be used with existing moisture content measuring systems. Combine them with the dehydrated solvent that is appropriate for the sample.

| Product | Standard | Packaging | Uses |
|--|---|-------------------------|---|
| Karl Fischer Reagent SS-Z (Mitsubishi) | Titer 4.5-5.5mgH ₂ O/ml | 500ml, 1L glass bottles | General-use This titration preparation can be used for a wide range of purposes. |
| | Titer 0.7-1.2mgH ₂ O/ml | 500ml glass bottles | Low moisture content This titration preparation is suitable for samples with low moisture content. |
| Dehydrated Solvent GEX | Moisture content: 0.2mgH ₂ O/ml or lower | 500ml glass bottles | General-use Suitable for organic solvents, inorganic chemicals, agricultural chemicals, pharmaceuticals, fertilizers, detergents, foodstuffs, etc. |
| Dehydrated Solvent OLX | Moisture content: 0.5mgH ₂ O/ml or lower | 500ml glass bottles | Oil-type Suitable for naphtha, gasoline, heavy oil, electrical insulating oil, oils, etc. |
| Dehydrated Solvent OL II | Moisture content: 0.3mgH ₂ O/ml or lower | 500ml glass bottles | Oil-type (*includes chloroform) Suitable for naphtha, gasoline, heavy oil, electrical insulating oil, oils and fats, etc. |

| Product | Standard | Packaging | Uses |
|------------------------|---|---------------------|--|
| Dehydrated Solvent KTX | Moisture content: 0.2mgH ₂ O/ml or lower | 500ml glass bottles | Ketone-type For ketones, silicon oils, acetic acid and other lower carboxylic acids, aldehydes (except acetaldehydes), etc. |
| Dehydrated Solvent SU | Moisture content: 0.2mgH ₂ O/ml or lower | 500ml glass bottles | Sugar-type Sugars, proteins, gelatine, additives, animal feeds, etc. |

Mix Dehydrated Solvent GEX with propylene glycol (PG) in a 3:1 ratio (e.g. GEX90ml:PG30ml) when using a moisture vaporization system.

Coulometric Titration Reagents

Coulometric titration reagents consist of anolytes which are placed in the anode chamber and catholytes which are placed in the cathode chamber. These products have a worldwide reputation for excellent performance and can be used in all manufacturers' coulometric titration systems. A general-use product and a ketone-type product (for ketones, lower carboxylic acids, silicon oils, etc.) are available. These products can be used with Aquamicron CXU catholyte.

These products are kind to both people and the environment. They contain no carbon tetrachloride, methyl cellosolve, pyridine or chloroform.

Aquamicron Series

| Product | Standard | Packaging | Uses |
|----------------------------|--|--------------------------|--|
| Aquamicron AX (anolyte) | Moisture content: 0.15mgH ₂ O/ml or lower | 500ml glass bottles | General-use Used with organic solvents, inorganic chemicals, petroleum products, gases, and a wide range of other substances. |
| Aquamicron CXU (catholyte) | Moisture content: 0.6mgH ₂ O/ml or lower | 5ml ampoules/10 per case | |
| Aquamicron AKX (anolyte) | Moisture content: 0.15mgH ₂ O/ml or lower | 500ml glass bottles | Ketone-use Ketones, silicon oils, lower carboxylic acids, etc. |
| Aquamicron CXU (catholyte) | Moisture content: 0.6mgH ₂ O/ml or lower | 5ml ampoules/10 per case | |

Single-Solution Coulometric Titration Reagent

Aquamicon FLS is a single-solution coulometric titration reagent. It should be used in single-solution electrolytic cells without diaphragm.

Use this product in combination with single-solution electrolytic cells.

This product is kind to both people and the environment. It contains no carbon tetrachloride, methyl cellosolve, pyridine or chloroform.

| Product | Standard | Packaging | Uses |
|---------------|--|---------------------|---|
| Aquamicon FLS | Moisture content: 0.15mgH ₂ O/ml or lower | 500ml glass bottles | Used for moisture vaporization method. Organic solvents. |

Using Single-Solution Karl Fischer Titration

As the single-solution coulometric titration version of Karl Fischer titration has not been adopted as an official method (JIS, etc.), it should be regarded only as a convenient methodology. (It may not be possible to use this product in some types of equipment.)

Aquamicon Solid Water Standard

| Product | Standard | Packaging | Uses |
|--------------------------------|------------------------------|-------------------|---|
| Aquamicon Solid Water Standard | Moisture content: 3.83±0.05% | 10g glass bottles | For evaluation a moisture meter with a water vaporizer. |

Aquamicon Standard Solution

Mitsubishi Chemical Corporation has traditionally supplied standard water-methanol as a standard reagent for assessing titer. Recently we have begun to sell a new product which has been developed in response to growing awareness of the importance of day-to-day management needs. It also reflects the demand for products that are easy to use and manage.

This product is the result of long years of experience in the fields of production technology and moisture measurement technology. For added peace of mind, it is also environmentally friendly thanks to the use of low-odor, low-toxicity solvents.

List of Karl Fischer Reagents

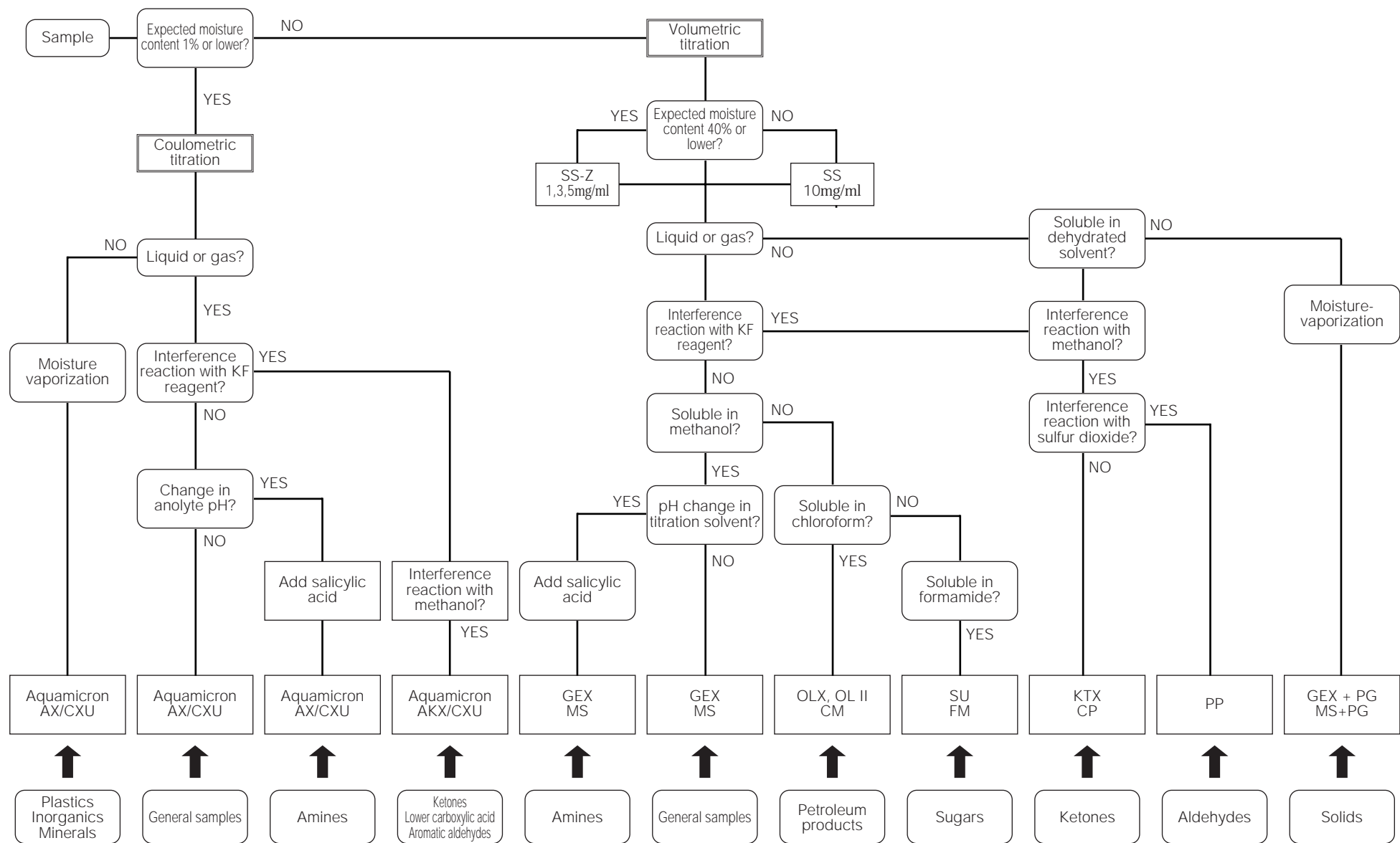
| Product | Titer | Packaging | Uses |
|--------------------------------|-------------------------|--------------------------|---|
| Aquamicon water Standard 0.2mg | 0.2mgH ₂ O/g | 5ml ampoules/10 per case | Used to check the accuracy of coulometric titration systems. |
| Aquamicon water Standard 1mg | 1mgH ₂ O/g | 5ml ampoules/10 per case | Used to check the accuracy of coulometric titration systems. |
| Aquamicon water Standard 10mg | 10mgH ₂ O/g | 8ml ampoules/10 per case | Used to assess the titer of KF reagents used in automatic volumetric titration systems. |

Mitsubishi Check Solution P

This end-point adjustment solution can be used with both general-use and ketone-type products. It can also be used for day-to-day management of coulometric moisture measurement systems.

| Product | Moisture Content | Packaging | Uses |
|-------------------------------|------------------------------|--------------------------------------|--|
| Check Solution P (Mitsubishi) | 3.8~4.2mgH ₂ O/ml | 100ml glass bottles with septum caps | Used when the presence of free iodine in the analyte has caused reddish-brown discoloration. Add a suitable amount to restore a water surplus. Normally a 100µl microsyringe is used. The readiness of a coulometric moisture measurement system for normal use can be checked periodically by measuring a specific volume of Check Solution (e.g. 100µl). |

ChapterV: Summary of Selection Procedures for Karl Fischer Reagents



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Afterword

Nine years have passed since I first thought of the production of this Karl Fischer Reagent Manual and the work was suspended for a considerable period. Now that the project is finally complete, it feels as if a heavy load has been lifted from my shoulders. I hope that this book will assist you with the use of the various Karl Fischer reagent products.

At the completion of the project, I should like to acknowledge the contribution of Mr. Shin'ichi Kuwata (formerly leader of this group) who created the basic framework for the book, Professor Kaname Muroi who has spent many years researching the Karl Fischer moisture measurement method and Mr. Mitsumasa Ono (currently with Daia Instruments Co., Ltd.) who carried out the actual Karl Fischer moisture measurements used as examples in this book. I should like also to thank Mr. Akiyoshi Nozawa (currently of Nippon Rensui Co., Ltd.), Ms. Hiroko Fujino, Ms. Akiyo Sekino (retired), Ms. Yuka Nitta (nee Fujimoto, retired) and Ms. Naoko Katayama. Thanks are due also to Mr. Kazuo Kikuchi, Director, Business Department, Deputy General Manager Masaki Hayashi, Acting Department Manager Takazumi Kanekiyo, Acting Department Manager Toshiyuki Narikiyo, Mr. Toshihiko Yamashita, Mr. Takashi Kowada, Mr. Mitsunari Morishita and Kengo Ito of Mitsubishi Chemical Corporation's Functional Chemical Company, and to Mr. Yasuo Koike and Kazuo Kumamoto, Directors and Group Leader Toshio Kaneko of the Analytical Sciences Laboratory at the Yokohama Research Center. Without their assistance this project would not have been possible.

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