

# HYDRANAL®-Manual



Eugen Scholz Reagents  
for Karl Fischer Titration

## Dear Colleague,

This Sigma-Aldrich HYDRANAL®-Manual is intended to be a useful reference handbook for analysts performing routine Karl Fischer (KF) titration. It contains practical recommendations and is the culmination of many years of diligent product development and close collaboration with our customers. We have tried to organize the information systematically according to product groups and application areas to make it both informative and easy to use.

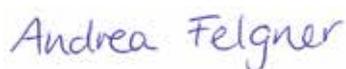
Besides this handbook, we have also published many results in the literature and listed them in the Literature Appendix. For analysts wanting a deeper understanding of KF principles, we highly recommend the textbook by Eugen Scholz "Karl-Fischer Titration" [1].

Over the years, we have investigated the KF titration of many diverse products and substances. Details of each particular case are beyond the scope of this manual, but are available in our comprehensive Laboratory Applications library. Available Laboratory Applications are noted in the text with the prefix "L" and are also listed in the Appendix.

Our HYDRANAL®-Laboratory or our HYDRANAL®-Technical Center personnel would be happy to send you any Laboratory Applications you may be interested in. We have always adhered to the principle of recommending only those working methods and applications that we have tried and verified ourselves. We never accept nor copy any untested publications or methods. By using this principle, we hope to ensure a high level of working safety and optimum results for you.

We are here to serve you, to help you choose and use the right HYDRANAL®-Reagents and develop reliable working methods. Please feel free to contact us. We look forward to helping you solve your most routine or challenging KF titration needs.

Kind regards,



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# HYDRANAL<sup>®</sup>-Manual

Eugen Scholz Reagents for Karl Fischer Titration

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## 1. Introduction: Innovations by Riedel-de Haën

Moisture content plays an important role in many chemical processes, product performance, organoleptic properties and stability. A defined, reliable and truly practical method for moisture measurement was introduced in 1935 when chemist Karl Fischer published his manuscript "New procedure for the determination of the water content in liquids and solids." (K. Fischer; *Angew. Chemie* 1935, 48, 394). Karl Fischer titration, as it was to be known, could be followed by nearly any laboratory interested in moisture determination. Consequently, it has become one of the most frequently employed methods in analytical chemistry.

But the technique was open to improvement. Beginning in 1979, Riedel-de Haën chemists Eugen Scholz and Helga Hoffmann investigated ways to improve Karl Fischer titration, making it safer, more accurate, easier to use and applicable to a wider range of substrates. These improvements became the foundation of the HYDRANAL® product line described in this Manual.

Three important innovations define the HYDRANAL® line:

- Noxious pyridine was replaced by bases that are both safer and more effective.
- New reagents and techniques reduce the number of required components, make endpoints clearer and more stable, and give faster and more sensitive reactions.
- Safety innovations beyond pyridine replacement include removal of halogenated hydrocarbons and replacement of methanol.

The results of Dr. Scholz and his team's investigations were of such fundamental importance that patents were received for many of the new reagents and their use. So far, more than fifty patents have been issued or are pending in Europe, the US, Japan and other countries. Research continues to this day toward the development of new, innovative HYDRANAL® products and working methods.

### 1.1 New bases

The original KF method and many currently commercially available products use noxious pyridine as the base. Beginning in 1979, Riedel-de Haën initiated a series of systematic investigations led by Dr. Eugen Scholz aimed at replacing pyridine. The result of these investigations soon showed that pyridine could be replaced by bases that are superior for such applications. The most significant results were published in the Fresenius "Zeitschrift für Analytische Chemie" in the series entitled "Karl Fischer Reagents without Pyridine" [2-9]. The initial publications reported on the use of diethanolamine as a base [2-5]. Subsequent articles [8] reported on the use of imidazole, which has since proven to be the best Karl Fischer base. Imidazole, an integral HYDRANAL® component, proved to be an ideal buffer for the KF system; it is safe and ensures a rapid and accurate KF titration.

### 1.2 New reagents

As a result of the investigations undertaken, new reagents for the determination of water were developed that surpass the classic Karl Fischer solutions. The first two-component reagent containing diethanolamine as the base, HYDRANAL®-Solvent and HYDRANAL®-Titrant, was introduced in 1980. This reagent allows a rapid titration with a stable end point. The base of this reagent was changed to imidazole in 1986 to improve the buffering of the KF system and increase the water capacity of the solvent to 7 mg/mL. This reagent is described in detail in section 2.2.

HYDRANAL®-Composite, a one-component reagent that contains imidazole as the base, was introduced to the market in 1980. Details of this reagent can be found in section 2.1.

In later years the coulometric reagents HYDRANAL®-Coulomat A and HYDRANAL®-Coulomat C followed and enabled the coulometric technique for water determination (see section 2.3). In 1991 a new set of coulometric reagents free of halogenated hydrocarbons was introduced. Next were introduced special methanol-free reagents for

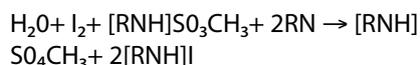
the determination of water in aldehydes and ketones, designated HYDRANAL®-K reagents. This product line comprises the HYDRANAL®-Composite 5 K and HYDRANAL®-Medium K for the volumetric determination of water and HYDRANAL®-Coulomat AK, and HYDRANAL®-Coulomat CG-K for coulometric determination (section 2.4).

The range of KF titration reagents was completed with the addition of HYDRANAL®-Standards (section 2.5), titration reagents for back titrations and buffering substances (sections 2.6 and 2.7, respectively).

The most recent developments include ethanol-based reagents, the HYDRANAL®-E Types. Research into additional non-toxic reagents is ongoing.

### 1.3 Scientific investigations

In conjunction with the development work undertaken, fundamental questions required satisfactory answers. The introduction of new reagents demanded the verification of the stoichiometry of the reaction. We came to the conclusion that the well known equations for the reaction did not fully describe the course of the KF reaction observed and necessitated further investigation. The results of the investigations undertaken by Dr. Eugen Scholz and his team have since been published in both English and German by Springer Verlag [1].



(RN = Base)

The sulfur dioxide reacts with the alcohol to form an ester that is subsequently neutralized by the base. The anion of the alkyl sulfurous acid is the reactive component and is already present in the KF reagent. The titration of water constitutes the oxidation of the alkyl-sulfite anion to alkyl sulfate by the iodine. This reaction consumes water.

This means that two significant prerequisites must be fulfilled in order to assure a stoichiometric course of the KF reaction. The first is the presence of a suitable alcohol to esterify the sulfur dioxide completely [1]. The practical consequences of the results are explained in section 4.1.

A suitable base is necessary for the complete neutralization of the acids produced during the reaction. The basicity of pyridine is too low to completely neutralize the acid and is the cause of the sluggish titration observed using the classic (non-HYDRANAL®) KF titration reagents. If the base is too strong, the solution becomes too alkaline and an end point will not be reached. A titration in the pH range of 5-7 is preferred and this can be achieved by the use of imidazole. The pH adjustment is therefore of prime importance for the course of an efficient KF titration (see section 4.2).

### 1.4 Patents

The results of our investigations were of such fundamental importance that patents were filed for many of the new HYDRANAL®-Reagents and their use. More than 50 patents have been filed, many of which have since been granted and are, therefore, binding. Of particular note are patents DP 3008421, EP 0035066, EP 0127740, EP 0075246, EP 0135098, GB 2,234,066, JP 61-54182, USP 4,740,471, USP 4,378,972, USP 4,748,126, USP 4,429,048, USP 4,619,900 and the USP 5,139,955. Additional patents have been granted in other countries, including Spain, Brazil, South Africa, etc. Further patents are pending.

It is important to note that Sigma-Aldrich does not permit the manufacture of patented reagents for commercial or personal use. This also applies to the application of such reagents. The procurement of the patented reagent also grants the right of its usage.

### 1.5 Analytical support

The determination of water using the KF method is carried out using specialized instrumentation. There are a number of commercially available instruments that are designed specifically for KF titrations. Our HYDRANAL®-Reagents are compatible with these titrators and our well-equipped HYDRANAL®-Laboratories have the most important KF instruments available on the international market.

Often we are asked by customers for technical assistance to help them determine the water content of their specific products. In most cases we were able to find an acceptable solution to their application. When we deem these methods to be of general interest, which is often the

case, we mention them in this manual, and sometimes publish a Laboratory Application on the subject.

Take advantage of our vast experience with KF Titration by contacting our HYDRANAL®-Laboratories for help and information on:

- KF titration in general
- How to deal with difficult samples
- Method development work on your samples, free of charge
- How to receive detailed application protocols from us
- How to obtain HYDRANAL® product information

Our experts at the HYDRANAL®-Hotline can be accessed by mail, phone, FAX or E-mail at the following locations:

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## 2. HYDRANAL®-Reagents

Sigma-Aldrich reagents for moisture determination by Karl Fischer titration are sold under the registered trademark HYDRANAL®. HYDRANAL® is a result of our dedicated investigations into improving the safety, accuracy and ease-of-use of the KF technique. HYDRANAL®-Reagents fulfill all the requirements of practical laboratory analysis and enable analysts to choose the optimum reagent for their specific application and instrumentation. The HYDRANAL® product line consists of one-component and two-component reagents for volumetric determinations, coulometric reagents and special reagents for the determination of water in ketones and other difficult substances. The product range is complemented by calibration standards for the determination of the titer (water concentration) and buffer solutions.

The HYDRANAL® range of reagents uses imidazole or diethanolamine (available in a few reagents) as the base, rather than pyridine. Imidazole and diethanolamine are both safe and effective and guarantee reliable analyses. The composition of HYDRANAL®-Reagents, their target applications and usage guidelines are summarized in the following sections.

### 2.1 HYDRANAL®-Composite one-component reagents for volumetric titrations

One-component reagents contain all the reactants (i.e. iodine, sulfur dioxide and imidazole) dissolved in a suitable alcohol. These reagents are intended for the volumetric KF titration of water.

#### 2.1.1 Applications

HYDRANAL®-Composite is a universal reagent for volumetric KF titration methods of determining water. It is suitable for all commercially available instrumentation. HYDRANAL®-Composite one-component reagent is preferred because it is relatively simple to use. All necessary reactants are conveniently contained in one solution. The working medium (i.e. the solvent required) is chosen according to the dissolution properties of the sample substance being analyzed.

#### 2.1.2 General procedure

The following procedure is recommended for titrations with HYDRANAL®-Composite. The titration procedure is described in detail in section 5.1. Variations to the procedure as a result of differences arising from the sample matrix are discussed in section 8. Specific procedures for many products are described in section 9 to 13. Suitable instrumentation for these titrations is listed in section 6.

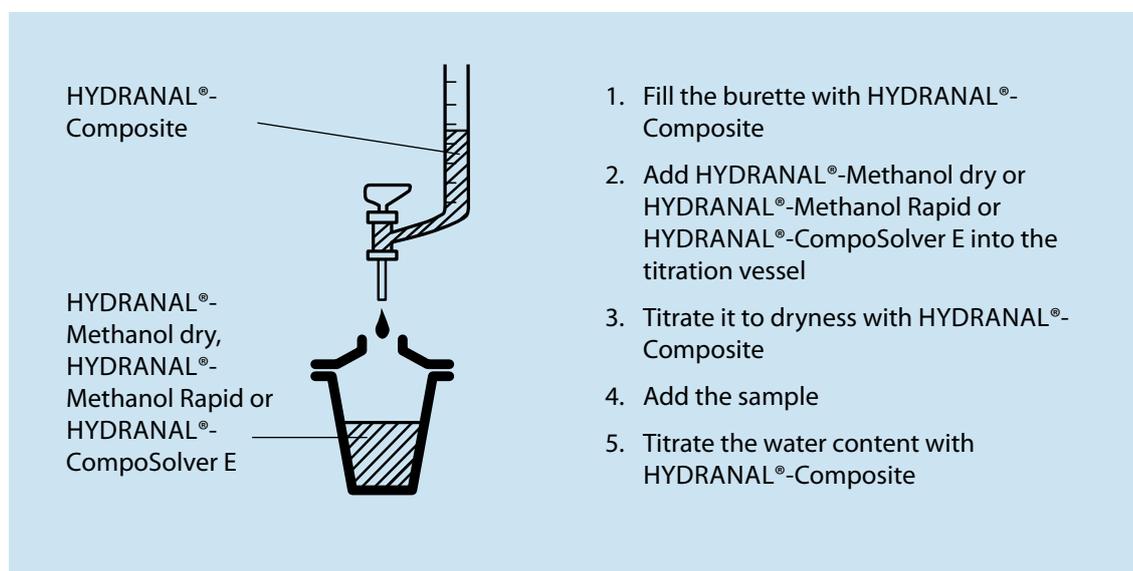


Diagram 2.1.2

### 2.1.3 The product line

There are currently four different HYDRANAL®-Composites; each one is designed for a specific application.

HYDRANAL®-Composite 5<sup>1</sup> has a titer of 5 mg H<sub>2</sub>O/mL. It is the preferred reagent for most applications. It contains imidazoles, sulfur dioxide and iodine in diethylene glycol monoethyl ether (DEGEE). HYDRANAL®-Composite 5<sup>1</sup> is very stable and has a shelf life of three years. The titer decay is approximately 0.3 mg H<sub>2</sub>O/mL per year.

HYDRANAL®-Composite 2<sup>2</sup> has a nominal titer of 2 mg H<sub>2</sub>O/mL and is used for the titration of samples with lower water contents. It contains imidazoles, sulfur dioxide and iodine in diethylene glycol monoethyl ether (DEGEE). HYDRANAL®-Composite 2<sup>2</sup> is very stable and has a shelf life of three years. The titer decay is approximately 0.1 mg H<sub>2</sub>O/mL per year.

HYDRANAL®-Composite 1<sup>3</sup> has a titer of 0.7 to 1.0 mg H<sub>2</sub>O/mL and is used for the titration of samples with very low water levels. It is distinguished from the other titrants by its high reaction sensitivity, meaning that trace amounts of water can be titrated rapidly. This reagent has a shelf life of three years.

HYDRANAL®-Composite 5 K<sup>4</sup> is a special reagent intended for the determination of water in aldehydes and ketones (hence the designation "K"). Applications using this reagent are described in sections 2.4 and 9.6.

HYDRANAL®-Composite 5 K<sup>4</sup> consists of the same components as in HYDRANAL®-Composite 5<sup>1</sup> and can therefore be used for any application. However, a titration with this reagent is slightly slower because of its modified composition.

HYDRANAL®-Methanol Rapid<sup>5</sup> contains accelerators for the KF reaction and reduces titration times significantly.

HYDRANAL®-Methanol dry<sup>6</sup> is a medium for the titration vessel and contains a maximum of 0.01% H<sub>2</sub>O. For general applications the titration speed can be improved by the addition of a titration accelerator, like HYDRANAL®-Solvent<sup>7</sup> (section 2.2.3) or HYDRANAL®-Buffer Acid<sup>8</sup> (section 2.7). An efficient titration can be achieved in practice by using a 3:1 mixture of methanol and HYDRANAL®-Solvent<sup>7</sup> as solvent for the sample and working medium for the titration.

HYDRANAL®-CompoSolver E<sup>9</sup> contains accelerators and is based on ethanol. It can be used instead of methanol.

## 2.2 HYDRANAL®-Solvent and HYDRANAL®-Titrant two-component reagent for volumetric titrations

The two-component reagents consist of all the necessary reactants for the titration, but in two different solutions. HYDRANAL®-Solvent<sup>7</sup> is the solvent solution consisting of sulfur dioxide and imidazole in methanol. HYDRANAL®-Titrant<sup>10</sup> is a solution of iodine with a pre-determined titer (water equivalent). HYDRANAL®-Solvent E<sup>11</sup> and HYDRANAL®-Titrant E<sup>12</sup> contain ethanol instead of methanol as solvent.

In the two-component system, both HYDRANAL®-Solvent and HYDRANAL®-Titrant are necessary for the titration.

### 2.2.1 Applications

When combined HYDRANAL®-Solvent and HYDRANAL®-Titrant are virtually a universal reagent for the determination of water by KF titration. These reagents can be used with all commercially available titration equipment. In practice, the two-component reagent is preferred when rapid titrations and highly accurate results are required. The two-component system is more accurate due to its faster rate of reaction. By reacting with the water faster it does not experience as much influence from atmospheric moisture as the slower one component system. Both reagents are very stable: titrants have a three year shelf life, while the solvents have a five year shelf life. The titer of HYDRANAL®-Titrant will not change as long as the bottle remains tightly sealed.

### 2.2.2 General procedure

We recommend the following procedure for the two-component titration technique. HYDRANAL®-Solvent serves as the working medium; HYDRANAL®-Titrant is used to titrate the sample (see diagram 2.2.2).

<sup>1</sup> 34805

<sup>2</sup> 34806

<sup>3</sup> 34827

<sup>4</sup> 34816

<sup>5</sup> 37817

<sup>6</sup> 34741

<sup>7</sup> 34800

<sup>8</sup> 34804

<sup>9</sup> 34734

<sup>10</sup> 34801 or 34811

<sup>11</sup> 34730

<sup>12</sup> 34732 or 34723

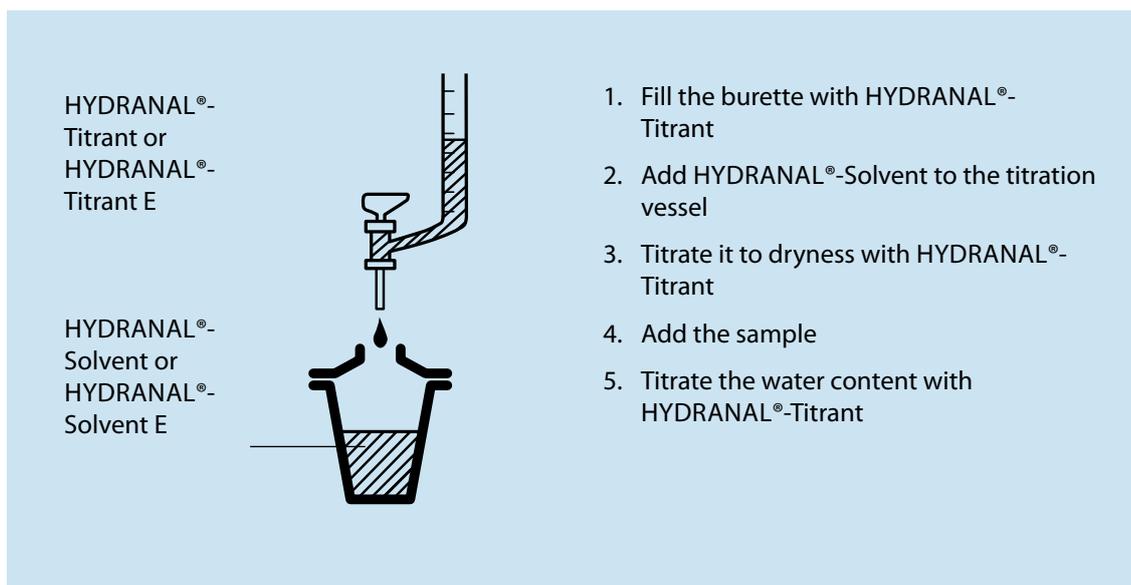


Diagram 2.2.2

This titration procedure is described in detail in section 5.2. Variations in the procedure to accommodate different sample matrices are given in section 8. Specific procedures for many products are described in sections 9 to 13.

(Note: Although the HYDRANAL®-Solvent and HYDRANAL®-Titrant can be premixed and used as a one-component reagent, the stability of the mixture is significantly reduced. We do not recommend this practice.)

### 2.2.3 The product line

Different grades of HYDRANAL®-Solvent and HYDRANAL®-Titrant reagents are available for different applications.

HYDRANAL®-Solvent<sup>1</sup> is the preferred working medium for the two-component titration techniques. It consists of a solution of imidazole and sulfur dioxide in methanol and has a nominal capacity of 7 mg H<sub>2</sub>O/mL. The solution has been pre-dried to maximum water content of 0.02%. HYDRANAL®-Solvent<sup>1</sup> has a five-year shelf life, during which the water content will not increase as long as the bottle remains unopened.

HYDRANAL®-Solvent E<sup>2</sup> is the same as HYDRANAL®-Solvent<sup>1</sup> except it contains ethanol instead of methanol. It is preferred from safety (ethanol is less toxic than methanol) and solubility (some samples are more soluble in ethanol) standpoints.

HYDRANAL®-Solvent CM<sup>3</sup> contains imidazole and sulfur dioxide in a mixture of methanol

and chloroform and was developed for the determination of water in oils and fats. The capacity for water of this solution is approximately 3 mg H<sub>2</sub>O/mL.

HYDRANAL®-Solvent Oil<sup>4</sup> contains imidazole and sulfur dioxide in a mixture of methanol and a long-chain aliphatic alcohol. It does not contain chloroform. HYDRANAL®-Solvent Oil<sup>4</sup> is designed for the determination of water in oils and fats. The capacity for water of this solution is approximately 3 mg H<sub>2</sub>O/mL. The HYDRANAL®-Solvent CM<sup>3</sup> and HYDRANAL®-Solvent Oil<sup>4</sup> have different solubilizing properties, giving analysts choices in the ability to dissolve oily samples.

HYDRANAL®-Titrant 5<sup>5</sup> is the standard titrating agent for general applications. It is a methanolic solution of iodine with an exact titer adjustment of 5.00 ± 0.05 mg H<sub>2</sub>O/mL. The titer remains unchanged even after prolonged storage, as long as the bottle remains unopened. The titer however may drop slightly through handling, since methanol is hygroscopic.

HYDRANAL®-Titrant 5E<sup>6</sup> is the same as HYDRANAL®-Titrant 5<sup>5</sup> except the methanol has been replaced by ethanol. HYDRANAL®-Titrant 2<sup>7</sup>

<sup>1</sup> 34800

<sup>2</sup> 34730

<sup>3</sup> 34812

<sup>4</sup> 34749

<sup>5</sup> 34801

<sup>6</sup> 34732

<sup>7</sup> 34811

is a titrating agent for small amounts of water. The titer is adjusted to  $2.00 \pm 0.02$  mg H<sub>2</sub>O/mL. The methanolic solution of iodine can show a slight drop in titer during handling.

HYDRANAL®-Titrant 2 E<sup>1</sup> is the same as HYDRANAL®-Titrant 2<sup>2</sup> except the methanol has been replaced by ethanol.

### 2.3 HYDRANAL®-Coulomat reagents for coulometric determinations

For standard coulometric KF titrations, two reagent solutions, an anolyte (the solution about the anode) and a catholyte (the solution about the cathode), are necessary. The anolyte is a modified KF reagent containing iodide instead of iodine. The Karl Fischer reaction occurs in the anolyte [1]. The catholyte enables the counterpart cathode reaction that must proceed so that the by-products of the KF reaction produced at the cathode are not disturbed [1]. HYDRANAL® products for coulometric KF titration are given the name HYDRANAL®-Coulomat.

#### 2.3.1 Applications

HYDRANAL®-Coulomat A<sup>3</sup> and HYDRANAL®-Coulomat CG<sup>4</sup> are the standard reagents for coulometric KF titration. HYDRANAL®-Coulomat AG<sup>5</sup>, AD<sup>6</sup> and AG-H<sup>7</sup> are anolytes free of halogenated solvents, HYDRANAL®-Coulomat CG<sup>4</sup> is the corresponding catholyte. HYDRANAL®-Coulomat E<sup>8</sup> is a new reagent where methanol is replaced by ethanol. It is also free of halogenated solvents.

#### 2.3.2 General procedure

The following general procedure is used for the coulometric determination of water (see diagram 2.3.2).

This titration procedure is described in detail in section 5.3. Alterations to the procedure due to the sample matrix are given in section 8. Procedures for many specific samples are described in sections 9 to 13.

#### 2.3.3 The product line

HYDRANAL®-Coulomat A<sup>3</sup> is the anodic reagent (anolyte) for coulometric titration. It contains sulfur dioxide, imidazole and iodide in a solvent mixture of methanol and chloroform. A volume of 100 mL in the anodic compartment will suffice for the determination of approximately 1000 mg H<sub>2</sub>O.

HYDRANAL®-Coulomat AD<sup>6</sup> is a chloroform-free anolyte reagent especially designed for coulometric cells without a diaphragm.

HYDRANAL®-Coulomat AG<sup>5</sup> is a chloroform-free anolyte. It contains two suitable bases, along with sulfur dioxide, imidazole, iodide and methanol as solvent. It has a water capacity of 1000 mg per 100 mL. HYDRANAL®-Coulomat AG<sup>5</sup> is also suitable for use in coulometry without a diaphragm.

HYDRANAL®-Coulomat E<sup>8</sup> contains the same components as HYDRANAL®-Coulomat AG<sup>5</sup>, but the majority of the methanol is replaced by ethanol. It is suitable for cells with and without diaphragm. In cells with a diaphragm it can be used as catholyte as well.

HYDRANAL®-Coulomat AG-H<sup>7</sup> is an anolyte for the investigation of hydrocarbons. It contains a long-chain alcohol and similar components as HYDRANAL®-Coulomat AG<sup>5</sup>. It is also suitable for cells without a diaphragm.

HYDRANAL®-Coulomat AG Oven<sup>9</sup> is an anolyte with minimal and extremely stable drift. It was developed for the determination of water in gases or with a KF Oven connected to a coulometer.

HYDRANAL®-Coulomat Oil<sup>10</sup> is an anolyte for the water determination in oils, including crude oil. It contains chloroform and xylene as the solubilizing agents. HYDRANAL®-Coulomat Oil<sup>10</sup> must be used in the cells with a diaphragm.

HYDRANAL®-Coulomat CG<sup>4</sup> is the catholyte free of halogenated solvents. It contains a patented formulation containing ammonium salts as the reactive component and methanol as the solvent. A volume of 5 mL is sufficient for the determination of 200-300 mg water.

HYDRANAL®-Coulomat AK<sup>11</sup> and HYDRANAL®-Coulomat CG-K<sup>12</sup> are complementary, methanol-free reagents intended for the coulometric determination of water in ketones and other substances that react with methanol. Further information on these products is found in sections 2.4 and 8.4.

<sup>1</sup> 34723

<sup>2</sup> 34811

<sup>3</sup> 34807

<sup>4</sup> 34840

<sup>5</sup> 34836

<sup>6</sup> 34810

<sup>7</sup> 34843

<sup>8</sup> 34726

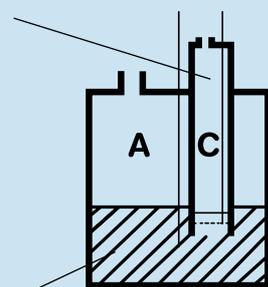
<sup>9</sup> 34739

<sup>10</sup> 34868

<sup>11</sup> 34820

<sup>12</sup> 34821

HYDRANAL®-Coulomat CG or HYDRANAL®-Coulomat E



Analyte solution:  
HYDRANAL®-Coulomat A,  
HYDRANAL®-Coulomat AG,  
HYDRANAL®-Coulomat AD,  
HYDRANAL®-Coulomat AG-H, or  
HYDRANAL®-Coulomat E

1. Fill the anodic compartment (A) with HYDRANAL®-Coulomat A/AG/AD/AG-H/E
2. Fill the cathodic compartment (C) with HYDRANAL®-Coulomat CG/E
3. Switch on the instrument (cell is automatically titrated to dryness)
4. Push the analysis button
5. Inject the sample
6. Record the water content at the end of the analysis
7. Repeat steps 4-6

Diagram 2.3.2

## 2.4 HYDRANAL® products for the determination of water in aldehydes and ketones

Historically, aldehydes and ketones have posed problems for KF titration because they react with some conventional reagents to produce acetals and ketals [1]. The water formed in this reaction is also titrated, leading to erroneously high results and vanishing end points.

Additionally, a second side reaction, the well-known bisulfite addition, can occur during the titration of aldehydes. This unwanted side reaction consumes water leading to erroneously low results [1].

We have developed and patented HYDRANAL®-Reagents that do not produce these side reactions, eliminating or significantly reducing these sources of error. These innovations include specific amines and alcohols not found in competitive KF reagent formulations.

The reagent for the volumetric titration of water in aldehydes and ketones consists of two components: HYDRANAL®-Composite 5 K<sup>1</sup> and HYDRANAL®-Working Medium K<sup>2</sup>, HYDRANAL®-Medium K<sup>3</sup> or HYDRANAL®-KetoSolver<sup>4</sup>.

HYDRANAL®-Composite 5 K<sup>1</sup> is the titrating reagent for the determination of water in aldehydes and ketones. It consists of a solution

of imidazole, sulfur dioxide and iodine in diethylene glycol monoethyl ether.

HYDRANAL®-Working Medium K<sup>2</sup> is the corresponding solvent system for HYDRANAL®-Composite 5 K<sup>1</sup> titrant. It contains 2-chloroethanol and chloroform. HYDRANAL®-Working Medium K<sup>2</sup> is added to the titration vessel and serves as the working medium and as the solvent for the sample. Both solutions are used like a one-component reagent, i.e. in accordance with the procedures described in sections 2.1.2 and 5.1.

HYDRANAL®-Medium K<sup>3</sup> is a new, less toxic medium that can replace HYDRANAL®-Working Medium K<sup>2</sup>.

HYDRANAL®-KetoSolver<sup>4</sup> is free of halogenated solvents. It gives a slightly slower titration rate.

The HYDRANAL®-Reagents described above can be used for the determination of water in substances other than aldehydes and ketones. The HYDRANAL® Medium K<sup>3</sup>, HYDRANAL®-Working Medium-K<sup>2</sup> and HYDRANAL®-KetoSolver<sup>4</sup> can act as the solvent for the

<sup>1</sup> 34816

<sup>2</sup> 34817

<sup>3</sup> 34698

<sup>4</sup> 34738

determination of water in any substance where methanol can interfere with the titration and must be avoided. Further information can be found in section 8.4.

HYDRANAL®-Composite 5 K<sup>1</sup> can be used as a universal titrating reagent. It does, however, have a slower titration rate than HYDRANAL®-Composite 5<sup>2</sup> (refer to section 2.1.3). In many cases, HYDRANAL®-Medium K<sup>2</sup> can be used in conjunction with the standard volumetric reagent, HYDRANAL®-Composite 5<sup>2</sup>. For the determination of water in aldehydes and certain reactive ketones however, it is strongly recommended that only HYDRANAL®-Composite 5 K<sup>1</sup> be used (section 9.6.1).

HYDRANAL®-Coulomat AK<sup>3</sup> is an anolyte for the coulometric determination of water in ketones. It contains imidazole, sulfur dioxide and iodide dissolved in a suitable solvent mixture. Its capacity is approximately 100 mg of water per 100 mL.

HYDRANAL®-Coulomat CG-K<sup>4</sup> is the corresponding catholyte. It does not contain halogenated hydrocarbons. The water capacity of 5 mL HYDRANAL®-Coulomat CG-K<sup>4</sup> is 100 mg.

Both HYDRANAL®-Coulomat AK<sup>3</sup> and HYDRANAL®-Coulomat CG-K<sup>4</sup> reagent solutions are used in the same way as the standard HYDRANAL®-Reagents for coulometry, i.e. according to the procedures described in sections 2.3.2 and 5.3.

## 2.5 HYDRANAL®-standardization products

It is good analytical practice to check the titer of KF titration reagents prior to performing new titrations, especially if the reagent bottle has been previously opened or is otherwise suspect. The titer can be calibrated using a number of substances that have differing advantages and varying limitations [1]. We recommend the use of sodium tartrate-2-hydrate or HYDRANAL®-Water Standard 10.0<sup>5</sup> for an exact standardization of titer.

### HYDRANAL®-Standard Sodium tartrate-2-hydrate<sup>6</sup>

**Water Content: 15.66 ± 0.05%, tested against NIST SRM 2890**

This standard is the primary standard for KF applications. The bottle is supplied with

a Certificate of Analysis that indicates this standard is tested against NIST SRM 2890.

Sodium tartrate forms a dihydrate, which, under normal conditions, remains stable and does not lose or adsorb moisture. This dihydrate has a water content of 15.66%, which can be ensured by drying the dihydrate at 150 °C. It is presented in a finely-powdered form that dissolves relatively quickly in methanol.

### HYDRANAL®-Standard Sodium tartrate-2-hydrate<sup>7</sup>

**Water Content: 15.66 ± 0.05%**

This standard is dedicated for the same application, but it is not tested against the NIST standard.

### HYDRANAL®-Standard 5.0<sup>8</sup>

**Water Content: 5.00 ± 0.02 mg H<sub>2</sub>O/mL (20 °C) = 5.91 ± 0.02 mg H<sub>2</sub>O/g**

This calibration standard is intended for the titer determination of reagent solutions for volumetric KF titration. It contains a mixture of solvents of a defined partial pressure of water, which, under normal atmospheric conditions, neither absorbs nor releases moisture. The determination of titer using this standard is described in detail in section 5.5.

### HYDRANAL®-Water Standard 10.0<sup>5</sup>

**Water content: 10.0 mg/g = 1%**

This standard is intended for calibrating volumetric KF reagents. One package contains ten 8 mL glass ampoules and a Certificate of Analysis that shows the exact water content of the particular batch. The standard is tested against NIST SRM 2890.

### HYDRANAL®-Water Standard 1.0<sup>9</sup>

**Water content: 1.0 mg/g = 0.1%**

This standard is intended to verify coulometric water determinations. One package contains ten 4 mL glass ampoules and a Certificate of Analysis that shows the exact water content of the particular batch. The standard is tested against NIST SRM 2890.

<sup>1</sup> 34816

<sup>2</sup> 34805

<sup>3</sup> 34820

<sup>4</sup> 34821

<sup>5</sup> 34849

<sup>6</sup> 34696

<sup>7</sup> 34803

<sup>8</sup> 34813

<sup>9</sup> 34828

**HYDRANAL®-Water Standard 0.1<sup>1</sup>****Water content: 0.1 mg/g = 0.01%**

This standard is intended to verify coulometric determinations of small amounts of water. One package contains ten 4 mL glass ampoules and a Certificate of Analysis that shows the exact water content of the particular batch. The standard is tested against NIST SRM 2890.

**HYDRANAL®-Water Standard Oil<sup>2</sup>**

Mineral-oil based matrix standard for KF titration in oils. Exact water content stated on Certificate of Analysis. Tested against NIST SRM 2980.

**HYDRANAL®-Water Standard KF-Oven<sup>3</sup>  
140-160°C****Water content: ~5% (exact value on Certificate of Analysis.) The standard is tested against NIST SRM 2890.****HYDRANAL®-Water Standard KF-Oven<sup>4</sup>  
220-230°C****Water content: 5.55% ± 0.05%**

These two solid standards are intended to check the reliability of a KF Oven. The standard is tested against NIST SRM 2890.

## 2.6 HYDRANAL® for back titration

The back titration method, described in section 5.4, is rarely used. However, we supply a standard for back titration applications.

**HYDRANAL®-Water-in-Methanol 5.0<sup>6</sup>**

This solution contains 5.00 ± 0.02 mg H<sub>2</sub>O/mL.

## 2.7 HYDRANAL®-Buffers

The KF reaction is pH dependant, with pH 6-7 being the ideal range. Strongly acidic samples slow the reaction and must be neutralized without inducing an alkaline reaction of the working medium prior to starting the titration. Details are given in section 8.6.

HYDRANAL®-Buffer Acid<sup>7</sup> is a suitable buffer solution to stabilize the pH to within the ideal range of 6-7. The buffer capacity is approximately 5 mmol acid/mL. HYDRANAL®-Buffer Acid<sup>7</sup> also enhances the visual indication of the end point as the yellow background color is suppressed. A distinct color change to brown can be better observed. HYDRANAL®-Buffer

Acid<sup>7</sup> has a shelf life of 5 years.

HYDRANAL®-Buffer Base<sup>8</sup> is a ready-made working medium for water determination in bases. It contains salicylic acid and has a buffer capacity of 1 mmol base per mL.

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<sup>1</sup> 34847

<sup>2</sup> 34694

<sup>3</sup> 34693

<sup>4</sup> 34748

<sup>5</sup> 37943

<sup>6</sup> 34802

<sup>7</sup> 34804

<sup>8</sup> 37859

### 3. The advantages of HYDRANAL®

The HYDRANAL®-Reagents, initially only intended as an alternative to the original pyridine-containing reagents, have surpassed the popularity of classical Karl Fischer solutions in many application areas. Many of the HYDRANAL® advances, like more effective bases and safer reagents have equaled the replacement of pyridine in importance; an unexpected but certainly welcome observation. The classical KF reagents titrate very slowly and with vanishing end points making it difficult to determine the actual end of the titration. Accurate reagent consumption, and hence the accurate water measurement, depends on the working conditions and the results of the analysis are somewhat uncertain using the classical KF reagents. A significant problem with slow titration times is that moisture has time to permeate into the system. The uncertainty of the results increases as the expected amount of water in the sample decreases. Also, the determination of trace amounts of water using the original KF reagents is nearly impossible because of the insufficient basicity of the pyridine used in those reagents [1].

#### 3.1 Titration speed

HYDRANAL®-Reagents are characterized by a rapid course of titration. Diagram 3.1 compares the course of 3 titrations of 40 mg of water. The titration using a pyridine-containing one-component reagent takes approximately ten minutes (curve C). HYDRANAL®-Composite 5<sup>1</sup> shortens this titration time to about four minutes (curve B). The most rapid titration, taking less than two minutes, is achieved with the HYDRANAL® two-component reagent (curve A). The high reactivity of HYDRANAL®-Reagents has been achieved by an optimization of the reactants and an adjustment of the pH of the total titration system.

#### 3.2 End point stability

The titration curves in diagram 3.1 show that the end point stability improves as the titration time is reduced. The advantages of HYDRANAL®-Reagents become even more apparent when trace amounts of water are determined, as

depicted in diagram 3.2. A definite end point was reached using the HYDRANAL® two-component reagent (curve A) while the titration curve of the pyridine-containing KF reagent (curve C) gives the impression that the instrument aborted without having reached a finite end point. This is of particular significance when determining small amounts of water; exactly the case when the solvent is titrated to dryness by the instrument. Each uncertainty in the pre-titration phase of the analysis adds to the inaccuracy of the resultant determination of water content.

#### 3.3 Accuracy

The greater reliability of HYDRANAL® Reagents was tested by running a series of side-by-side water determinations on HYDRANAL®-Reagents and a conventional KF reagent. In each case, the titer of each titrant was standardized using 100 mg of water. Different amounts of water were titrated by each reagent and the standard deviation (scatter) of twenty analyses was calculated. The results are presented in the Table below.

The consumption of the HYDRANAL® two-component reagent was directly proportional to the total water content over the entire range tested, clearly indicating that the KF reaction remains stoichiometric. The pyridine-containing KF reagent showed a systematic deviation of +2.5% in the range 10-20 mg H<sub>2</sub>O and a scatter of 1-2%, which infers a total error of as much as 4%. HYDRANAL®-Composite one-component reagent showed a systematic error of 0.5%, which is still better than the pyridine-containing KF reagent. The most accurate results were obtained using the HYDRANAL® two-component reagent.

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<sup>1</sup> 34805

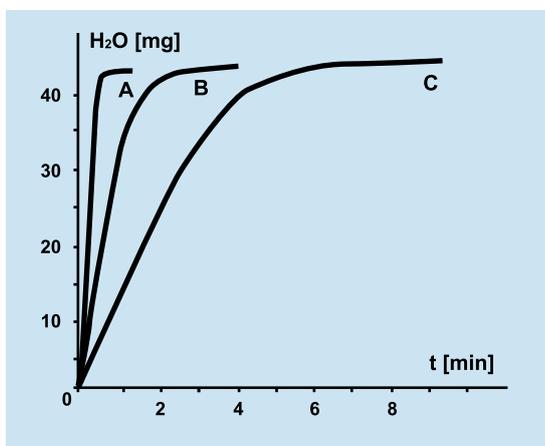


Diagram 3.1

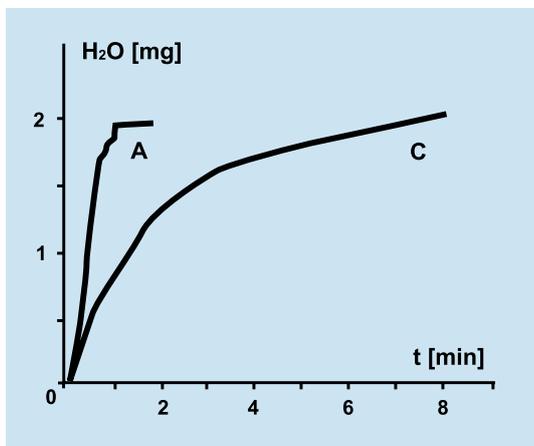


Diagram 3.2

Water content	Conventional KF reagent containing pyridine	One-component HYDRANAL®-Composite	Two-component HYDRANAL®-Solvent & HYDRANAL®-Titrant
100 mg	$\pm 0.44\%$	$\pm 0.30\%$	$\pm 0.20\%$
50 mg	$+0.56 \pm 0.62\%$	$+0.06 \pm 0.24\%$	$+0.01 \pm 0.30\%$
20 mg	$+1.68 \pm 0.93\%$	$+0.33 \pm 0.60\%$	$+0.02 \pm 0.25\%$
10 mg	$+2.59 \pm 1.85\%$	$+0.84 \pm 0.6\%$	$-0.1 \pm 0.5\%$
5 mg	$+2.40 \pm 2.5\%$	$+0.72 \pm 1.2\%$	$+0.2 \pm 1.0\%$

Table: Error and scatter in the determination of water [1]. 20 individual analyses

## 4. Chemical fundamentals behind Karl Fischer titration

In order to assure a stoichiometric course of the KF reaction, certain fundamental requirements must be met and several potential interferences must be avoided. The working medium, which is the solvent used to dissolve and titrate the sample, and the pH of the system are the two most important considerations.

### 4.1 Working medium

The working medium is the solvent or solvent mixture in which the sample is dissolved and in which the KF titration is carried out. The correct working medium assures the stoichiometry of the KF reaction. The working medium must be able to dissolve the sample and the products of the titration reaction and allow confident end point determination [1]. Only a few solvents can fulfill all of these requirements.

Methanol is the preferred choice for a working medium; methanol permits a rapid and stoichiometric course of the KF reaction. Most samples dissolve easily in methanol, and it gives a sensitive and reliable indication of the end point. Often, other solvents are added to the methanol, although the methanol content should always be at least 25%.

1-Propanol, ethanol and other long-chained alcohols are better at dissolving lipophilic molecules than methanol and can be added to the methanol (section 8.1) to improve solubility of the sample. Occasionally, they can be used alone as the solvent while developing methods for these types of compounds (section 8.4).

2-Methoxyethanol (ethylene glycol monomethyl ether) and 1-methoxy-2-propanol are other alcohol solvents. They are preferred when side reactions (esterification, ketal formation, etc.) can occur in the presence of methanol. Titrations in these solvents are slower than in methanol (section 8.4).

We have investigated 2-chloroethanol as a methanol alternative or additive. It suppresses side reactions and enables a rapid KF reaction (section 8.4).

Chloroform is a good solvent for solubilizing fats and can be combined with methanol. The

methanol content should be at least 25% and preferably 50% (see section 8.2). The use of 100% chloroform changes the stoichiometry of the KF reaction and is therefore not suitable to use on its own.

Formamide improves the solubility of polar substances and can be mixed with methanol for the determination of water in proteins (section 8.3). The methanol content should not be less than 50% [1]. A 30% proportion of formamide usually suffices and is preferred.

Other solvents can be used in specific cases. Caution is called for when using aprotic solvents as they alter the stoichiometry of the KF reaction towards the Bunsen equation [1], i.e. the titer of the titrant appears erroneously high. The change in titer does not remain constant, but depends on the ratio of the alcohol to the aprotic solvent. This ratio changes throughout the titration since the titrating agent contains alcohol. The result is an indefinable ratio, a continuously changing stoichiometry and inaccurate results. To be accurate, this approach requires an exact determination of the titer under the identical working parameters. Therefore, we do not recommend the use of pure aprotic solvents as the working medium for KF titrations.

These fundamental rules also apply for KF titrations with HYDRANAL<sup>®</sup>-reagents. With the one-component reagent HYDRANAL<sup>®</sup>-Composite, the working medium can be selected by the user. Methanol is used in the majority of cases because of the advantages previously mentioned. Mixtures of methanol and chloroform or methanol and formamide are used in specific cases in order to improve the solubility of the sample. HYDRANAL<sup>®</sup>-CompoSolver E<sup>1</sup>, which is based on ethanol, can also be used. When working with the two-component reagent, HYDRANAL<sup>®</sup>-Solvent<sup>2</sup>, which contains methanol as the solvent, is used as the working medium. The addition of

<sup>1</sup> 34734

<sup>2</sup> 34800

chloroform or formamide is possible in specific cases. Replacing these solvent components by other solvents is not permissible. Proven mixtures of solvents are described in detail in section 8.

## 4.2 pH

In the ideal pH range 5-7, the Karl Fischer reaction runs quickly and stoichiometrically. At higher pH values a side reaction occurs that consumes iodine. It can be observed by a reversal of the end point. In strongly acidic conditions the reaction constant of the KF reaction decreases and the course of the titration is slower [1]. In practice, a pH range of 4-7 is acceptable.

The titration of water produces acids that must be neutralized. The HYDRANAL®-reagents contain imidazole as the base to neutralize these acids and buffer the titration system. The pH is thus stabilized around the ideal value of 5, ensuring a rapid and stoichiometric course of the reaction.

The pH balance of the titration can be upset by the introduction of large amounts of strong acids or bases; for example when the water content of such substances is to be determined [1]. These substances must be neutralized by adding an appropriate weak base or acid or a buffer solution to the working medium. Details are given in section 8.5 and 8.6.

Sluggish or vanishing end points can be an indication of a fluctuation of the pH of the system outside the optimal range. When this is suspected the pH should be measured. A glass pH electrode, previously calibrated in an aqueous solution, can be used for this. The pH of the system should not however be determined directly in the titration cell because the pH electrode will introduce water to the system. Instead, the pH should be measured on a portion of the working medium that has been taken from the titration cell.

The log K vs. pH curve for a KF titration appears in diagram 4.2. Note the optimal range of pH 5-7 over which the log K does not change significantly.

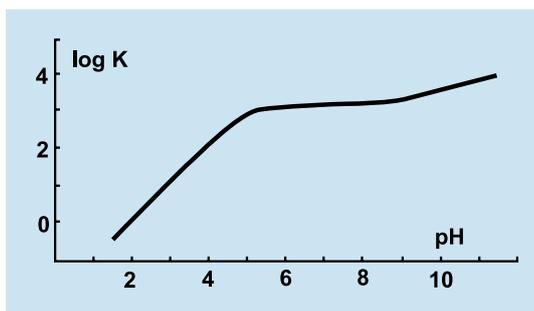


Diagram 4.2. Dependence of the reaction rate constant  $K$  on the pH (Verhoef, J. C. and Barendrecht, E.; *Mechanism and Reaction Rate of the Karl-Fischer Titration Reaction*. *J. Electroanal. Chem.* **1976**, 71, 305-315.

## 5. Standard procedures for KF titrations

The KF titration has been carried out in many different ways in the past 70 years. Originally, organic solvents were titrated directly with the KF reagent. Later, solvents used as diluents were introduced where water content was determined by so-called “blank titrations” and subtracted in the subsequent calculations. Today, a suitable solvent is usually added to the titration vessel, dehydrated by a pre-titration and used as the working medium for the titration of the sample. The function of the working medium was covered in more detail in section 4.1.

Three basic forms of the KF titration have evolved:

- Volumetric titration using a one-component reagent
- Volumetric titration using a two-component reagent
- Coulometric titration

Volumetric titrations are used when water content is high, i.e. 1-100 mg per sample.

Coulometry is a micro-method and is particularly suitable for samples with low water content, on the order of 10 µg up to 10 mg of water per sample.

The fundamental techniques of each of the three titration methods are described in this section. They can be used to analyze many different substances. When difficulties in analyzing a sample are encountered, modifications to the basic technique are made. Suggested variations to the titration procedures to accommodate different sample matrices are given in section 8. Titrations of specific products are described in sections 9-13.

### 5.1 Volumetric titrations using the one component reagent HYDRANAL®-Composite

HYDRANAL®-Composite are the one-component KF reagents; the preferred reagents because of convenience; they contain all the necessary reactive components in one solution. The

working medium it requires (the solvent for the sample) is not prescribed and can be chosen by the analysis within limits. HYDRANAL®-Composite can be used with all commercially available titration equipment with only minor changes to the working procedures. The sequential steps of a titration of water using the one-component reagent are described in the following section.

#### 5.1.1 Addition of the reagent

First, the burette is filled with HYDRANAL®-Composite. With many instruments, the original bottle is connected to the equipment. Whatever the set-up, it is imperative that the burette, stock vessel and their inter-connection are absolutely dry. Residual water can cause local changes in the titer and lead to errors in the results. The stock vessels should be protected from infiltration of atmospheric moisture by using drying tubes (see section 6.4).

#### 5.1.2 Addition of the working medium

Next, 20-40 mL of working medium are added to the titration vessel. The amount of working medium added depends on the size of titration cell and on the size of the sample to be titrated (section 6.5). The titration cell is closed immediately after the addition of working medium in order to keep the amount of unavoidable atmospheric moisture to an absolute minimum. HYDRANAL®-Methanol dry<sup>1</sup> or HYDRANAL®-Methanol Rapid<sup>2</sup> or HYDRANAL®-CompoSolver E<sup>3</sup> can be used as a working medium.

#### 5.1.3 Pre-titration

Next, the solvent in the titration vessel is titrated to dryness with HYDRANAL®-Composite. This pre-titration is important because it removes the residual water that was in the solvent and the moisture adhering to the surfaces in the cell and on the electrode. The atmosphere of the cell is also dried of moisture. A completely anhydrous working medium is achieved in this way. The

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<sup>2</sup> 37817

<sup>3</sup> 34734

pre-titration must be carried out very carefully since any error will influence the subsequent determination of the water content of the sample. A titration to a stable end point is the prerequisite for a reliable analysis. Because the amount of water removed by the pre-titration is relatively small, this titration is carried out as slowly as possible. An excess of reagent during pre-titration also induces an error of the same magnitude in the subsequent determination of water. A perfectly dried titration cell has a maximum drift consumption of 0.01 mL of KF reagent per minute.

#### 5.1.4 Weighing the sample

After pre-titration of the working medium and titration cell to dryness, a pre-determined quantity of the sample to be investigated is added to the working medium. The cell is opened for as short a time as necessary and then closed again immediately after the sample was added to keep intrusion of atmospheric moisture to an absolute minimum. Recommended sample addition techniques (pipettes, weighing boats, etc.), are described in detail in section 7.3.

The size (mass or volume) of the sample per titration depends on its water content, the volume of the burette, the titer of the titration agent and the desired accuracy. Details are given in section 7.2. We recommend using as much sample as to consume approximately half a burette volume of reagent. When using HYDRANAL®-Composite (water equivalent 5 mg H<sub>2</sub>O/mL) and a 10 mL burette, the amount of sample is chosen so it contains approximately 25 mg of water. In many cases, like in the determination of trace amounts of water, the sample size will be significantly lower.

#### 5.1.5 Titration of the water content

Once the sample has been added, the titration should be started immediately. The dosage rate of the titration agent can be adjusted to the anticipated amount of water. The titration rate should be rapid initially, but reduced when the end point is imminent. Modern KF instrumentation automatically adjusts the titration rate to the amount of water still remaining in the titration vessel.

A definite determination of the end point is as important as the pre-titration step. Generally, one titrates to an end point of 10 seconds stability (section 5.6).

A stable end point is a significant indication of the course of a titration with no complications. A vanishing end point indicates that the water in the sample was released too slowly or that there were interferences from side reactions.

#### 5.1.6 Calculation of the results

After a stable end point has been reached, the amount of HYDRANAL®-Reagent used is read from the burette scale. The water content is calculated from the volume consumed and the water equivalent (WE) of the reagent:

$$\text{mg H}_2\text{O} = a \cdot \text{WE}$$

$$\% \text{ H}_2\text{O} = \frac{a \cdot \text{WE}}{10 \cdot e}$$

Where:

- a = the consumption of reagent in mL
- WE = water equivalent of the reagent in mg H<sub>2</sub>O/mL
- e = weight of the sample in g

The following formula is applied for the statistical evaluation of a series of titrations:

$$\text{Mean} \quad m = \frac{1}{n} \sum x_i$$

Standard deviation

$$S_{\text{abs}} = \sqrt{\frac{\sum x_i^2 - \frac{1}{n} (\sum x_i)^2}{n - 1}}$$

$$S_{\text{rel}} = \frac{100 \cdot S_{\text{abs}}}{m} \%$$

Where:

- x<sub>i</sub> = Result of each analyses
- n = Number of analysis
- m = Mean
- S = Standard deviation

#### 5.1.7 Replacement of the working medium

Following the completion of a titration, the spent solutions should be removed from the titration cell. Most instruments are equipped with pumps that not only empty the titration cell, but dry the atmosphere within it. A plastic wash bottle proves very useful for the manual removal of the spent solution (section 6.5). The titration cell should be opened for as short a time as possible in order to keep the introduction of atmospheric moisture to an absolute minimum.

Usually the titration cell is immediately refilled with fresh solvent and dehydrated by a pre-titration. Automatic titration instruments are programmed for continuous titrations. Modern instruments allow an automatic “conditioning.” The solvent is continuously kept at its equivalency point. Thus, a prepared working medium and a dry titration cell are constantly available and ready for the next sample.

Sequential titrations in the same working medium are possible. The solvent mixture of the previous titration is immediately used as the working medium for the titration of the next sample. In this way, the use of a fresh solvent and a pre-titration for each titration is not required. When performing sequential titrations, the substance being investigated should be of the same type. Also, the methanol content in the working medium must not fall below 25% or the end point may be altered.

## 5.2 Volumetric titrations using the two-component reagent HYDRANAL®-Titrant (E) and HYDRANAL®-Solvent (E)

The HYDRANAL® two-component system consisting of HYDRANAL®-Titrant and HYDRANAL®-Solvent is distinguished by a rapid titration rate, stable end points and highly accurate results. The titer of HYDRANAL®-Titrant is absolutely stable as long as moisture does not penetrate into the reagent.

A proven method has been established when using two-component-reagents. HYDRANAL®-Solvent serves as the working medium and is added to the titration cell. HYDRANAL®-Titrant is used as the titrating agent and is added to the sample from the burette. This reagent can be used with all commercially available equipment. The actual KF titration is carried out in a similar fashion as the one-component reagents described above.

**5.2.1 Addition of HYDRANAL®-Titrant/Titrant E**  
First, HYDRANAL®-Titrant is added to the burette, i.e. it is the stock vessel for the burette. Stock vessel, valves and interconnections must be completely dry. The stock vessels are protected from atmospheric moisture by the addition of drying tubes (see section 6.4).

### 5.2.2 Addition of HYDRANAL®-Solvent<sup>1</sup>/Solvent E<sup>2</sup>

Next, a 20-40 mL volume of HYDRANAL®-Solvent<sup>1</sup> or <sup>2</sup> is added to the titration vessel. The exact amount added depends primarily on the size of the titration cell. The titration cell is sealed immediately following the addition of HYDRANAL®-Solvent<sup>1</sup> or <sup>2</sup> in order to keep the unavoidable intrusion of atmospheric moisture to a minimum.

### 5.2.3 Pre-titration

The HYDRANAL®-Solvent<sup>1</sup> or <sup>2</sup> added to the titration vessel is then titrated to dryness with HYDRANAL®-Titrant. This pre-titration is analogous to that of the one-component reagent and requires the same care (see section 5.1.3). The instrumentation used should be equipped with a particularly fast stirrer to ensure complete mixing of reactants within the cell. The stir rate should, however, preclude the inclusion of potential moisture from the cell atmosphere.

### 5.2.4 The sample

The same rules apply as for the one-component reagent (section 5.1.4). In addition, it must be remembered that the HYDRANAL®-Solvent<sup>1</sup> or <sup>2</sup> has a defined and limited capacity for water that cannot be exceeded (see section 2.2.3). Usually, an effective water capacity of approximately 7 mg H<sub>2</sub>O per mL of HYDRANAL®-Solvent<sup>1</sup> or <sup>2</sup> is anticipated, i.e. if 20 mL HYDRANAL®-Solvent are available, a maximum water content of 140 mg H<sub>2</sub>O can be titrated.

### 5.2.5 Titration of the water content

The titration of water is started immediately after the sample has been added to the vessel. The initial stages of the titration should be rapid, but reduced in rate as the end point approaches. A stable end point must be achieved or the results will be in doubt (see section 5.1.6).

### 5.2.6 Calculation of the results

The results are calculated in the same manner as for the one-component reagent (see section 5.1.6).

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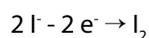
<sup>2</sup> 34730

### 5.2.7 Replacement of HYDRANAL<sup>®</sup>-Solvent<sup>1</sup>/Solvent E<sup>2</sup>

As with a one-component reagent, following completion of the titration the spent working medium should be removed from the cell. Fresh HYDRANAL<sup>®</sup>-Solvent<sup>1</sup> or <sup>2</sup> is then added and the pre-titration repeated, ensuring a prepared working medium ready for the next titration. Subsequent titrations are also possible using the two-component titration system. However, the water capacity (7 mg H<sub>2</sub>O/mL) of the solvent component must be taken into consideration. If 20 mL HYDRANAL<sup>®</sup>-Solvent<sup>1</sup> or <sup>2</sup> have been applied, a maximum of 28 mL of HYDRANAL<sup>®</sup>-Titrant can be consumed during the subsequent titrations. Otherwise, the water content of the solvent component will be exceeded and accurate results will not be obtained.

### 5.3 Coulometric titrations with HYDRANAL<sup>®</sup>-Coulomat A<sup>3</sup>/AG<sup>4</sup>/AD<sup>5</sup>/E<sup>6</sup>/AG-H<sup>7</sup>/AG Oven<sup>8</sup> and HYDRANAL<sup>®</sup>-Coulomat CG<sup>9</sup>

In coulometric titration of water, the iodine required for the KF reaction is produced by anodic oxidation of iodide to iodine [1]:



The iodine reacts with the water present according to the Karl Fischer reaction (see section 1.3). Iodine is consumed as long as water is present. An excess of iodine indicates the end point of the titration. Because the amount of water titrated is proportional to the total current consumption (current X time), the water content can be determined from the current required for the titration.

Because the titration current is low, a maximum of 5-10 mg H<sub>2</sub>O can be determined in an economically acceptable time period of 10 minutes. Coulometry is principally intended for the determination of water in substances with low water content (0.1 - 0.0001%). Particular advantages are to be seen in the ppm range. This is a micro-method and is therefore the ideal complement to volumetric titration methods for smaller amounts of water.

In practice, commercially available instruments directly indicate the water content, either in µg H<sub>2</sub>O or ppm H<sub>2</sub>O. The coulometric cell is the main component of the equipment.

The most commonly used cell consists of an anodic compartment, where the Karl Fischer titration takes place, and a smaller cathodic compartment where the corresponding cathodic reaction (a reduction reaction) occurs. The anodic compartment contains the necessary anolyte; the cathodic compartment contains the suitable catholyte. The compartments are separated by a diaphragm that prevents an interchange of the two reagent solutions.

The purpose of each solution is different. The elemental iodine generated in the anodic compartment of the cell reacts with the other reactants ultimately consuming the water in the sample. The anolyte is basically a modified KF solution; it enables the anodic oxidation of iodide to iodine with a 100% yield of current.

The counterpart reaction, which the catholyte must be capable of producing, takes place in the cathodic compartment. Since diffusion of the reactive components cannot be ruled out in spite of the diaphragm separating the two compartments, the components of the catholyte must be compatible with the anolyte. Therefore, we cannot recommend the use of an anolyte in the cathodic compartment. This would enhance the danger of reductive products from the cathode diffusing through the diaphragm to the anode. A subsequent oxidation by elemental iodine leads to erroneously higher water content results.

HYDRANAL<sup>®</sup>-Coulomat A<sup>3</sup>/AG<sup>4</sup>/E<sup>5</sup> and HYDRANAL<sup>®</sup>-Coulomat CG<sup>9</sup> are reagents that have been developed especially for coulometric cells with a diaphragm. HYDRANAL<sup>®</sup>-Coulomat A<sup>3</sup>/AG<sup>4</sup> is the anolyte, HYDRANAL<sup>®</sup>-Coulomat CG<sup>9</sup> is the catholyte (see section 2.3.3). Their proper use is described in the following sections. When handling the reagents, particular care should be taken to ensure the exclusion of moisture since coulometry is a micro-method and even the smallest amounts of water can result in serious errors. A 1 mL volume of normal laboratory atmosphere contains about 10 µg of H<sub>2</sub>O; a value easily detected by the sensitive coulometric method. The absolutely anhydrous titration cell must therefore never be exposed to the atmosphere, not even when adding the sample.

<sup>1</sup> 34800

<sup>2</sup> 34730

<sup>3</sup> 34807

<sup>4</sup> 34836

<sup>5</sup> 34810

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<sup>7</sup> 34843

<sup>8</sup> 34739

<sup>9</sup> 34840

Coulometric cells without a diaphragm consist of only one chamber. The anode and cathode reactions take place in the same electrolyte solution. The cathode reaction must not produce any by-products that could be oxidized and give the impression of extra water in the cell. HYDRANAL®-Coulomat AD<sup>3</sup>/E<sup>4</sup>/AG<sup>2</sup>/AG-H<sup>5</sup>/AG Oven<sup>6</sup> are suitable for this form of coulometric titration.

Coulometric titration is in principle very easy to carry out. The machine is switched on and the sample is injected into the sealed cell via a syringe through a septum. After a few minutes, the water content of the sample is digitally displayed by the machine. The next sample can be injected immediately.

### 5.3.1 Filling the anodic compartment with HYDRANAL®-Coulomat

#### A<sup>1</sup>/AG<sup>2</sup>/AD<sup>3</sup>/E<sup>4</sup>/AG-H<sup>5</sup>/AG Oven<sup>6</sup>

It is important that the titration cell be completely dry. Once the spent reagent from the previous determination has been removed, the cell has to be refilled with fresh reagent solution. If the cell was dismantled for cleaning or other reasons, it must be dried at 50 °C in a drying cabinet prior to using it again. The drying of the diaphragm requires special care. Consult the titration instrument manufacturer's instructions.

A slight excess of iodine during the manufacture of HYDRANAL®-Coulomat A<sup>1</sup>/AG<sup>2</sup>/AD<sup>3</sup>/E<sup>4</sup>/AG-H<sup>5</sup>/AG Oven<sup>6</sup> removes the last traces of moisture from the reagent. The light brown color of the reagent can disappear during transport and/or storage because the solution is hygroscopic. When colorless, any absorbed moisture can be removed by adding several drops of HYDRANAL®-Titrant, or any other 5% solution of iodine in methanol, until the slightly brown coloration of the reagent has been re-established. An excess of iodine should, however, be avoided. The solution is added to the anodic compartment of the coulometric titration cell using a dry funnel. During this process the coloration should disappear again.

The amount of reagent used depends upon the titration instrument. Usually, it requires approximately 100-150 mL. The titration cell is immediately closed after the addition of reagent. A titration cannot be initiated if the solution still shows an excess of elemental iodine, in which case an appropriate addition of water, or preferably aqueous methanol, will remove the iodine and ensure a properly functioning anolyte.

### 5.3.2 Filling the cathodic compartment with HYDRANAL®-Coulomat CG<sup>7</sup> or HYDRANAL®-Coulomat E<sup>4</sup>

The cathodic compartment is filled with HYDRANAL®-Coulomat CG<sup>7</sup>/E<sup>4</sup>. The amount of reagent used is in accordance with the manufacturer's instructions, usually 5 mL. Relative to the anolyte, the level of the catholyte in the cathodic compartment should be lower in order to prevent diffusion into the anodic compartment.

The cathodic compartment must also be anhydrous, as otherwise the moisture will diffuse into the anodic compartment and cause sluggish end points and erroneous results. This solution is dehydrated in a similar manner. A slight excess of elemental iodine is not detrimental.

### 5.3.3 Drying the titration cell

The design and construction of the titrator is such that the titration cell is self-drying upon initiation of the instrument. A titration cannot be started unless the titration cell is dry.

The instrument determines and indicates the degree of dryness of the equipment automatically. This is shown as a "drift" or "background" in µg H<sub>2</sub>O/min or µg H<sub>2</sub>O/sec, depending on the instrument. It reflects the amount of water that the equipment removes per minute, i.e. residual moisture or penetrating moisture. Other instruments indicate only the background titration current.

The drift of the instrumentation used for the coulometric determination of water should not exceed 50 µg H<sub>2</sub>O/min or 0.90 µg H<sub>2</sub>O/sec. The drift value of a freshly-replenished titration cell should not exceed 10 µg H<sub>2</sub>O/min (0.10 µg H<sub>2</sub>O/sec); ideally 4 µg H<sub>2</sub>O/min can be achieved.

This self-dehydration process exists only for the anolyte. Moisture retained in droplets in the cell and moisture adhering to the walls is slowly released and is the cause of high drift values. This residual moisture can be quickly removed by gently shaking the filled titration vessel.

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<sup>2</sup> 34836

<sup>3</sup> 34810

<sup>4</sup> 34726

<sup>5</sup> 34843

<sup>6</sup> 34739

<sup>7</sup> 34840

Moisture from the cathodic compartment can sometimes be the cause of a high drift resulting from the slow diffusion of water through the diaphragm into the anodic compartment. Reductive substances produced in an unsuitable (or spent) catholyte have the same effect. Therefore we highly recommend replacing the catholyte at least once a week, irrespective of how long the anolyte was used.

The drift value of a freshly filled titration cell is less than  $10 \mu\text{g H}_2\text{O}/\text{min}$ . The drift can increase during a series of determinations. This does not appreciably influence the accuracy of the analyses as the instrumentation automatically compensates for the inherent drift value. This is only true when the drift rate is relatively stable.

#### 5.3.4 Addition of the sample

The drift should be controlled before the sample is added. In order to obtain reliable drift compensation by the instrument, the drift should be stable. Some instruments will go into "wait" mode and not titrate when the drift is too high or not sufficiently stable.

The titration is initiated by pressing the start button. The sample to be analyzed is then injected through the septum into the anolyte. This means that only samples in liquid form can be added. The addition of solid samples is not possible, as the titration cell may not be opened. Solid samples can be dissolved in suitable solvents and added in solution form. Also, the moisture can be evaporated from the solid sample in an oven, collected and added as a vapor to the titration cell (see section 8.11). Gaseous samples are introduced into the anolyte via a gas inlet tube. Further details are given in section 8.10.

The size of the sample depends on the anticipated water content and the desired accuracy. The maximum sample size can be easily calculated (section 7.2).

For practical reasons, the sample size should not exceed 10 mL. The volume of a coulometric titration cell will hold another 50 mL, approximately. A single titration of 10 mL of sample means a total of 5 determinations possible per reagent fill. The smallest sample size is dependent upon the desired accuracy. The reproducibility of results varies from 1-10  $\mu\text{g H}_2\text{O}$  per determination depending on the instrument used.

Generally, 0.5-5.0 mL samples in liquid form are added. Gaseous samples range from 100 mL to 10 L.

#### 5.3.5 Calculation of the results

Modern coulometric titration equipment indicates the amount of water digitally in mg and thus enables an easy conversion to mass units. Most instruments will show the results in mass or volume units, i.e. % or ppm if the sample size was entered.

#### 5.3.6 Reliability

Coulometry is often referred to as an "absolute method," which implies the "absolute" and total reliability of the results. Only the total current measured is absolute. Whether the current measured is proportional to the actual amount of water in the sample cannot be assured absolutely. There are many causes for the errors in titration results. Inaccurate addition of the sample, moisture in the titration cell, spent or unsuitable reagents, penetration of reductive substances from the cathodic compartment through the diaphragm, side reactions that produce water, poisoned electrodes and instrumentation defects are a few sources of error.

We therefore recommend determining the recovery rate of water at regular intervals. Such a control determination is relatively simple: 1.0 g (exactly weighed by difference) HYDRANAL®-Water Standard 0.1<sup>1</sup> or 1.0<sup>2</sup> is injected into the titration cell using a calibrated syringe to determine the water content. Recovery rates for water of  $\pm 0.03 \text{ mg H}_2\text{O}$  for HYDRANAL®-Water Standard 1.0<sup>2</sup> or  $\pm 0.005 \text{ mg/g}$  for HYDRANAL®-Water Standard 0.1<sup>1</sup> from the value given on the certificate can be considered acceptable. Such a control titration can be carried out following a series of water determinations. It should be conducted if the reagent or equipment appears suspect. A daily control will give the analyst additional assurance.

#### 5.3.7 Replacement of the reagents

The spent reagent can be replaced relatively easy. The spent anolyte is removed from the anodic compartment with a pump or through the sample port opening by means of a plastic suction bottle (section 6.5). Certain instruments are equipped with pumps. The anodic compartment is subsequently re-filled

<sup>1</sup> 34847

<sup>2</sup> 34828

with HYDRANAL®-Coulomat A<sup>1</sup>/AG<sup>2</sup>/AD<sup>3</sup>/E<sup>4</sup>/AG-H<sup>5</sup>/AG Oven<sup>6</sup>, as described in section 5.3.1. The cathodic compartment is similarly replenished with HYDRANAL®-Coulomat CG<sup>7</sup> (section 5.3.2). It is common practice to replenish both reagents at the same time.

Changing the reagent in a diaphragm-less cell is relatively easy. After the spent reagent is removed, fresh HYDRANAL®-Coulomat AD<sup>3</sup>/E<sup>4</sup>/AG<sup>2</sup>/AG-H<sup>5</sup>/AG Oven<sup>6</sup> is added to the cell.

Determining whether or not the reagent is spent and requires changing is more complicated. There are many factors that influence this decision, including:

- If the drift or background is significantly increased
- If the titration cell is full
- If the water capacity of the reagent has been exhausted
- If the instrument is defective

Usually, it is a full titration cell that causes the replacement of the reagent. Most cells have a 100 mL reagent capacity and a total cell volume of 150-160 mL. The reagent must be replenished after 50-60 mL of sample have been added. Furthermore, the successive dilution reduces the conductivity and necessitates replenishment of the reagent.

The capacity limit of HYDRANAL®-Coulomat AG<sup>2</sup>/AD<sup>3</sup>/E<sup>4</sup>/AG-H<sup>5</sup>/AG Oven<sup>6</sup> (the anolyte) is seldom reached. The chemical composition together with the known equation for the KF reaction ensures a total capacity of 1000 mg H<sub>2</sub>O per 100 mL volume. This water capacity can be fully utilized. HYDRANAL-Coulomat Oil<sup>8</sup> has a water capacity of 300 mg per 100 mL.

The capacity limit of the catholyte cannot be calculated because exchange reactions take place with the anode. The capacity of the catholyte must be determined empirically. The water capacity of 5 mL HYDRANAL®-Coulomat CG<sup>7</sup> is 200-300 mg. Gases develop when approximately 200 mg H<sub>2</sub>O are analyzed. They do not however influence the function of the catholyte. A dissipation of sulfur can take place when more than 300 mg H<sub>2</sub>O is determined per 5 mL of catholyte. This is avoided by replenishing the reagent early.

A calculation of the total amount of water is relatively difficult as not only the water from the sample, but also the blank consumption of reagent during the self-drying time must be considered. Certain instruments are equipped

to register the total water consumption since the last replacement of reagent. This enables an accurate calculation of the remaining capacity of the reagent.

A drift increase often means the reagent must be replaced. An increase in the drift can have different causes. Side reactions such as esterification or the formation of ketals lead to a production of water. A continual infiltration of moisture into the cell can also be the source. However, a spent catholyte solution is most often the cause. When reductive substances from the cathodic compartment diffuse through the diaphragm into the anodic compartment, they react like water and cause an increase in the drift. A drift increase can equally be caused by the diffusion of moisture from the cathodic into the anodic compartment. Whatever the cause, it is recommended to replenish the reagent in order to guarantee an accurate and error-free water determination.

In case of doubt, the recovery rate of water should be determined as described in section 5.3.6. This method is a reliable way of determining whether the equipment is functioning properly and capable of producing acceptable results.

### 5.3.8 Machine always switched on

The coulometric cell should always be dry and operational to enable a fast water determination. This can be achieved if the machine remains permanently switched on. Moisture penetrating the cell will be immediately eliminated this way. No additional reagent is consumed by using this working method since the amount of reagent used is determined by the amount of free moisture. If the machine is switched off, the same amount of water collects in the cell and will be eliminated only when the machine is switched on, which can take a long time and uses up the same amount of reagent.

## 5.4 Coulometry without a diaphragm

For cells without a diaphragm, HYDRANAL®-Coulomat AD<sup>3</sup>/E<sup>4</sup>/AG<sup>2</sup>/AG-H<sup>5</sup>/AG Oven<sup>6</sup> is used.

<sup>1</sup> 34807

<sup>2</sup> 34836

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<sup>7</sup> 34840

<sup>8</sup> 34868

The same principle as described in section 5.3 applies to carrying out this form of coulometry. A catholyte is not necessary, so section 5.3.2 is not applicable.

## 5.5 Back titrations

The back titration method was used more often in the past. This method was of significance when the KF reagents contained pyridine and were thus slow. The determination of water could be accelerated using the back titration technique.

Titration with HYDRANAL®-Reagents are rapid and back titrations are not usually necessary. The need to perform a back titration with HYDRANAL®-Reagents is rare [1], although it is possible in principle with all one- and two-component HYDRANAL®-Reagents. The individual steps are as follows:

1. HYDRANAL®-Methanol dry<sup>1</sup> is added to the titration cell and titrated to dryness using HYDRANAL®-Composite according to section 5.1.3. If the two-component reagent is used HYDRANAL®-Solvent<sup>2</sup> is added to the cell and dried using HYDRANAL®-Titrant according to section 5.2.3. The working medium can be modified through the addition of other solvents.
2. The sample is then weighed into the cell according to the procedure outlined in section 5.1.4 or 5.2.4.
3. An excess of titrant is added, e.g. 10 mL HYDRANAL®-Composite or HYDRANAL®-Titrant. The quantity of titrant is calculated to ensure that the expected water content is exceeded.
4. After waiting for a time determined by the sample being investigated, the working medium is back-titrated with HYDRANAL®-Water-in-methanol 5.0<sup>3</sup>.

The water content of the sample is calculated from the difference between the water capacity of the added titrant and the water content of the methanol used for the back titration:

$$\text{mg H}_2\text{O} = (\text{WE}_{\text{KF}} - \text{mL}_{\text{KF}}) - (\text{WE}_{\text{meth.}} \times \text{mL}_{\text{meth.}})$$

For back titration, two solutions of known titer are required: the KF solution and the HYDRANAL®-Water-in-methanol 5.0<sup>3</sup>. The titer of the KF solution is determined according to the procedure in section 5.6. The titer of the HYDRANAL®-Water-in-methanol 5.0<sup>3</sup> is determined against the adjusted KF solution.

## 5.6 Standardization of titer

Determining the titer of reagents is part of the routine work in a KF laboratory. It is a necessary task as the titer of standard solutions changes or can change by the penetration of atmospheric moisture [1]. The frequency of the titer control depends mainly on the choice of the titrating agent employed and how tightly sealed the equipment is against permeation by atmospheric moisture.

The stability of the titer of HYDRANAL®-Composite is exceptionally good and a weekly control of its titer is sufficient.

The determination of the titer of HYDRANAL®-Titrant is really not necessary since it can be stored indefinitely. The titer should, however, be controlled occasionally. This apparent contradiction arises from the hygroscopic nature of absolute methanol. Improper handling of the titrant can lead to infiltration of atmospheric moisture and a decrease in the titer of the reagent for subsequent titrations.

We prefer to frequently control the titer, which we consider to be more a control of the titration conditions. The titer of HYDRANAL®-Composite changes approximately 0.01 water equivalent per week (see next section for WE definition); such changes are hardly significant for a daily control of the titer. If, however, large deviations are detected the titration conditions must be inspected.

Titer fluctuations can arise from the infiltration of moisture, the equipment being no longer airtight, spent drying agent and other causes. Titer values that fluctuate from day to day, increasing and decreasing, are a proven indication of scatter in the analysis and are not due to a fluctuation of the titer.

We do not recommend determining the titer in the morning, even though it is a common practice. Because the plastic tubing on the instruments is permeable to moisture, the titer of the KF reagent typically decreases slightly during the night. The tubes should be

<sup>1</sup> 34741

<sup>2</sup> 34800

<sup>3</sup> 34802

flushed several times with fresh reagent prior to determining the titer. The determined titer must always be compared with the previous day's results to ensure it does not vary in value outside the normal, expected range.

A fluctuation in the room temperature of the laboratory can cause fluctuations in the titer. KF reagents consist of organic solvents whose coefficients of thermal expansion are significantly greater than that of water. A temperature increase of 1 °C will usually result in a titer decrease of about 0.1%.

The titer is determined in the same manner as described in sections 4.1 and 4.2. Instead of titrating the water in a sample, a substance of known water content or a known amount of water is added and titrated. The same working conditions, i.e. the same solvent(s), the same volumes and the same temperature are used as for the subsequent investigation of the sample.

Different standards offer advantages and limitations and are used for the titer determination [1]. We recommend the use of HYDRANAL®-Standard sodium tartrate-2-hydrate<sup>1</sup> for an exact titer determination or HYDRANAL®-Water Standard 10.0<sup>2</sup> which is a certified liquid standard in sealed glass ampoules. HYDRANAL®-Standard 5.0<sup>3</sup> is intended for the rapid control of the titer. The use of pure water is equally acceptable.

#### 5.6.1 HYDRANAL®-Standard sodium tartrate 2-hydrate<sup>1</sup>

Sodium tartrate dihydrate is the primary titer standard for KF titrations. It remains stable, does not effloresce (which means to become a powder by losing water of crystallization) and is not hygroscopic under normal laboratory conditions.

HYDRANAL®-Standard sodium tartrate 2-hydrate<sup>1</sup> has a guaranteed water content of  $15.66 \pm 0.05\%$ . It dissolves relatively quick in methanol and the titration can be started within three minutes. In HYDRANAL®-Solvent<sup>4</sup> it dissolves so rapidly that the titration can be started at once. Depending on the titer to be determined, 0.1-0.5 g (= 15-75 mg H<sub>2</sub>O) are used. The amount of titrating reagent to be standardized should be about 10 mL. The titration is carried out according to the procedures described in sections 5.1 or 5.2. The titer is calculated as the water equivalent, WE (in mg H<sub>2</sub>O per mL of reagent) for Karl

Fischer titrations:

$$WE = \frac{\text{weight of water in mg}}{\text{consumption of reagent in mL}}$$

#### 5.6.2 HYDRANAL®-Water Standard 10.0<sup>2</sup>

This standard is a certified liquid standard. It is each delivered in 8 mL glass ampoules. One package contains 10 ampoules and a Certificate of Analysis giving the exact water content for the batch. To determine the titer, an ampoule is opened and portions of about 2 g (exactly weighed) are added to the titration vessel using a syringe.

#### 5.6.3 HYDRANAL®-Standard 5.0<sup>3</sup>

Standards in liquid form are easy to handle and are therefore preferred for routine analyses. The methanol standards used in the past are not recommended since they are hygroscopic and the water content can change easily [1]. HYDRANAL®-Standard 5.0<sup>3</sup> has a guaranteed water content of  $5.00 \pm 0.02$  mg H<sub>2</sub>O per mL at 20 °C. By choosing the appropriate solvents, this standard is not hygroscopic under normal conditions. It can be added via pipette without any change of water content from contamination by atmospheric moisture. In order to determine the titer of a KF solution, 5, 10 or 20 mL are added using an appropriately gauged pipette. The titer is determined according to the procedures described in section 5.1 and 5.2. A high degree of accuracy is achieved this way. The water equivalent, WE, is calculated in the same way as when using sodium tartrate-2-hydrate.

#### 5.6.4 Water

Pure water can also be used as a standard calibration substance. This would appear to be the simplest method. However, it is not trivial to accurately weigh and add precisely 20-50 mg of water. Weighing by difference of a micro-syringe proves to be the most suitable method.

### 5.7 End point indication

All of the customary methods of KF end point indication can be employed when using

<sup>1</sup> 34803

<sup>2</sup> 34849

<sup>3</sup> 34813

<sup>4</sup> 34800

HYDRANAL<sup>®</sup>-Reagents. This is also valid for the preferred biamperometric and bipotentiometric methods [1], as well as for the seldom-used method of visual indication. The indication of the end point is improved by the use of HYDRANAL<sup>®</sup>-Reagents no matter which method of end point indication is used.

### 5.7.1 Electrometric indication

The antiquated KF reagents containing pyridine were notorious for how difficult it was to determine the end point of a titration. The equivalency point of the reaction was reached slowly with these reagents, primarily due to the weak basicity of pyridine. Actual reversal of the end point was not uncommon.

To obtain unambiguous end point determination, a special technique was developed. The end point was established when a defined potential (bipotentiometric indication), or current (biamperometric indication) was not only reached but remained constant for a specified length of time, e.g. 20 seconds. This end point delay is typical of the KF titration and all the instruments available incorporate an end point duration setting, which can be adjusted individually (see section 6.6). A duration or delay setting of twenty seconds has proven to be preferred time in practice. Changing this delay time often changes the consumption of KF solution and thus alters the results.

The latest development for end point determination is the "drift-stop." Using this method, the titration is stopped when a chosen drift is measured in the titration cell.

Special protocols for end point determination are not necessary when using HYDRANAL<sup>®</sup>-Reagents. A stable end point is reached (see section 3) quickly. The delay time can be adjusted according to the substance under investigation. The delay time can be reduced to five seconds if only the adherent moisture is being determined. This also applies to titrations where the influence of side reactions should be suppressed. If, on the other hand, the water in the sample can be released and titrated only slowly, the end point delay time can be set to 60 seconds in order to ensure a complete determination of the total amount of water present. There is no influence on the titration result in either case; the titer remains constant independent of the titration conditions.

### 5.7.2 Visual indication

Conventional KF reagents yield a color change from yellow to brown that is relatively vague. A sulfur dioxide-iodide complex  $[\text{SO}_2\text{I}]^-$  is present in the system at a pH of 4-5 just before the equivalence point is reached and causes the yellow coloration.

This complex dissociates at pH values of 6-7 and the titration solution becomes colorless. Since HYDRANAL<sup>®</sup>-Reagents have a higher pH than conventional reagents, there is less yellow coloration and the color change to brown is easier to recognize. A complete decolorization of the working medium can be achieved by the addition of HYDRANAL<sup>®</sup>-Buffer Acid<sup>1</sup>. The pH of the system is raised to 6-7 and the solution becomes completely colorless. In practice, a sufficient (5 mL), amount of HYDRANAL<sup>®</sup>-Buffer Acid<sup>1</sup> is added to the working medium prior to the pre-titration. The titration is then carried out in the normal manner. Refer to sections 4.1.3 and 4.2.3 for the appropriate procedures.

### 5.7.3 Photometric indication

Use of photometric methods to measure the end point is currently used only in flow injection methods of analysis. Wavelengths of 525 or 600 nm are monitored. The absorption spectrum of HYDRANAL<sup>®</sup>-Reagents is depicted in diagram 5.7.3. Curve A shows the absorption spectrum with excess iodine, curve B with an excess of water. The greatest sensitivity is achieved in the 460-480 nm range. If the excess iodine is to be measured, the less sensitive range (520-620 nm)

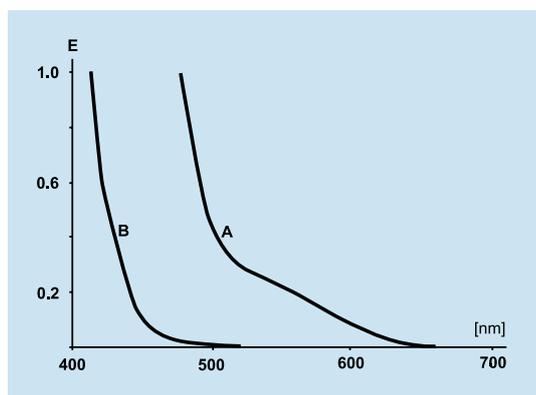


Diagram 5.7.3

<sup>1</sup> 34804

## 6. Laboratory recommendations

is chosen.

Successful Karl Fischer titration requires techniques and considerations beyond those of normal volumetric titrations because of the acute need to prevent contamination of the system by extraneous moisture. In this section, we will discuss certain details that demand particularly close attention.

### 6.1 The KF laboratory

Karl Fischer titrations do not require a specialized laboratory. When using HYDRANAL®-Reagents a fume hood is not required because these reagents do not contain pyridine and do not possess a noxious odor. A KF titration should be carried out under normal ambient conditions whenever possible. Room temperatures higher than normal should be avoided since the organic solvents, such as methanol or diethyleneglycol monoethyl ether, have relatively low thermal expansion coefficients (approximately 0.1% per °C). Temperature fluctuations can influence the titer significantly. Furthermore, equipment such as water baths, which can increase the relative humidity of the atmosphere, should not be placed in the vicinity of KF instrumentation.

### 6.2 Titration instrumentation

Many different titration instruments are used for KF titration. Commercially available equipment is preferred. These instruments are available from a variety of manufacturers world-wide. There is a wide range of options from simple to complex. Simple instruments consist of a burette and an indication system. Titrators carry out the titration automatically, register the weight of the sample being determined, adapt the titration rate to the amount of water in the sample and print out the titration results [1].

Simple titration apparatus are also available that enable KF titrations to be carried out with minimum equipment and at minimum cost [1]. These systems are desirable when KF titrations are performed only occasionally or when investigating the potential for the method before investing in more expensive equipment.

HYDRANAL®-Reagents are suited for all types of KF instrumentation. We have tested and/or

used equipment from Metrohm, Mettler-Toledo, SI Analytics, Radiometer, Orion, Prolabo, Fisher Scientific, Photovolt, Mitsubishi, Hiranuma, Kyoto Electronic and CSC Scientific. We use many of these instruments in our HYDRANAL®-Laboratories to ensure compatibility of our methods.

The different KF titration instruments differ in their design and concept, their ease of use and handling. It is not possible to give detailed instructions on the specifics of each instrument. Instead, we will mention a few basic rules that we consider to be important for everyday practice and are common to all types of instruments.

### 6.3 Titration cells

Commercially available volumetric titration cells are usually glass vessels kept tightly closed by plastic seals. The penetration of atmospheric moisture is kept to a minimum. The cell is hermetically sealed when in use, and is only briefly opened in order to add the sample or to replenish the solvent. When titration cells are disassembled, the residual adherent solvent adsorbs atmospheric moisture making the subsequent titration of the re-assembled titration cell very difficult. When this happens, a complete overhaul and drying of the cell is required. Best results are achieved by a thorough, final rinse with methanol following the removal of solids, etc. by water-miscible solvents. The cell is then dried with a dryer, or in a drying cabinet at 50-70 °C.

The size of the titration cell should not be larger than absolutely necessary because the unused volume is a source of extraneous moisture. The inner surfaces of the cell should be smooth, enabling a uniformly thin film of methanol; any surface defects where methanol can collect will retain water and cause sluggish end points. Corners and seals that enable the formation of pockets of solvent are particularly detrimental. Titration cells should be gas-tight to allow venting with dried air.

Titrations demanding high accuracy, like coulometric titrations, should be carried out only in glass titration cells. Titration cells with plastic seals have a higher permeability for water vapor. We determined the permeation rate being as high as 1 mg H<sub>2</sub>O/hour into titration

cell of such construction. This is equivalent to a reagent consumption rate of 0.003 mL/min. Corresponding consumption rates for titration cells constructed completely from glass are much lower, approximately 0.05 mg H<sub>2</sub>O/hour.

In our HYDRANAL®-Laboratories and other facilities that use KF titration, we use titration apparatus with ground glass connections for titrations requiring high accuracy. Such apparatus can be easily dried by the customary pre-titration. Commercially available titration cells are preferred for routine work as these provide acceptable accuracy and are very practical.

Even glass titration cells are not absolutely impermeable to water vapor. They will absorb moisture from the atmosphere when left unused. This causes sluggish end points in subsequent titrations. It is recommended to keep the equipment programmed to a continuous overnight titration in order to prevent an accumulation of moisture in the cell when not in use. The same effectiveness can be achieved by the addition of a sufficient amount of titration agent to the cell. The cell should then be shaken the next day to remove the moisture in any solvent pockets and adherent on the cell walls. This procedure is strongly recommended for coulometric titration cells.

The titration cell should be completely disassembled if it will be unused for long periods of time. The parts should be rinsed with methanol and dried. Atmospheric drying will normally suffice, or it can be dried overnight in a drying cabinet at 50 °C or for 5-10 minutes using a fan. Higher drying temperatures are not recommended because they can lead to deformation of plastic parts of the cell.

Most titration cells have a variable speed stirring mechanism, usually a magnetic stirrer. During a titration, the stirring rate should be set to a maximum to ensure a rapid mixing of the reagent added. Insufficient stirring can easily lead to an over-titration. However, excessive stirring draws cell atmosphere into the titration medium and can alter the end point. Atmospheric moisture will be absorbed and can lead to a reversal of the end point.

Proper positioning of the burette and electrodes is important. The burette tip should be centered above the stirrer to ensure a rapid distribution of the reagent added. The indicator electrodes should be near the titration cell wall to ensure sufficient contact with the titration medium.

## 6.4 Burettes

Both dispensing and piston burettes can be used for KF titration. Dispensing burettes should be permanently attached to the stock bottle to prevent contact with atmospheric moisture when refilling the burette. The burette should be vented only by an anhydrous atmosphere and be equipped with appropriate drying tubes. Such drying tubes should be large enough to completely remove the moisture intrusion into the venting atmosphere. The burette should be filled via the upper opening, rather than filled by pressurization through the lower inlet. The latter requires a larger quantity of air with consequent introduction of atmospheric moisture.

The burette tip should be inserted deeply enough into the titration vessel solution to be well submerged below the liquid level.

Piston burettes should be used for KF titrations. Modern commercial KF titration instruments are almost exclusively equipped with piston burettes. These are connected to the suction side of the reagent stock bottle. Certain titration instruments have standard connections that enable a direct connection to the HYDRANAL®-Reagent bottle. The KF reagent is drawn into the burette from the stock bottle. The filling rate should not be too high as this leads to bubbles that can cause inaccuracies in the reading of the volume.

The KF reagent is portioned into the titration vessel from the burette, which should have sufficiently large volume to accommodate the number of desired titrations. The dispensing rate is automatically determined and controlled by the course of the titration and the remaining water to be titrated. The volume of reagent dispensed is displayed.

The stock reagent bottles should be protected from atmospheric moisture by drying tubes that contain molecular sieves. However, if the stock bottle contains reagents that contain water, like HYDRANAL®-Water-in-methanol 5.0<sup>1</sup> or the HYDRANAL®-Standard 5.0<sup>2</sup>, the water content can be reduced by the use of drying tubes. This can be avoided by using drying tubes containing

<sup>1</sup> 34802

<sup>2</sup> 34813

the same reagent as in the stock bottle. Today's piston burettes are usually connected to stock bottles and to titration vessels by means of plastic tubing that is permeable to water vapor. Use of this tubing will cause a slow decrease in the titer of the KF titrating agent held in the tubing. We observed a 5% decrease in titer overnight. The reagent can completely decolorize within a few days. The remaining reagent in the connecting tubes should be discarded since it will mix with fresh reagent from the subsequent suction into the burette and cause a change in titer of the initial titration reagent fill. It remains debatable whether the first burette filling should be used for a titration. However, it should never be used to determine the titer as the results could be erroneous.

### 6.5 Working medium renewal

A suitable working medium (sample solvent) is added to the titration vessel prior to the determination of water. The criteria governing the choice of solvent are described in section 8 and in the product-specific methods. The amount of reagent depends on the size of the titration cell and on the size of the sample to be investigated. Volumetric titrations normally require 20-50 mL of reagent, coulometry usually requires 100 mL.

The simplest method for adding the working medium to the titration cell is by using a funnel. However, we recommend using pipettes since they ensure a more accurate addition of the amount of reagent and are a better protection against infiltration by atmospheric moisture. Although any moisture adsorbed when filling the cell with working medium will be removed by the pre-titration, it requires additional KF reagent which is essentially wasted.

Dispensing bottles are practical as they enable a quick and sufficiently accurate addition of the required amount of working medium. It should be pointed out however, that plastic is not impervious to water vapor and any working medium in the bottles will have increasing moisture content over time.

Today most titration instruments are equipped with automated dosage systems that add the reagents to the titration cell either manually or automatically as determined by the course of the titration reaction. These systems usually have an automatic pumping device for the

removal of spent reagent from previous titrations. This automated filling and emptying reduces the exposure of the cell to atmospheric moisture and ensures that the flow of air into the cell is dry.

Most titration instruments are equipped with drainage valves that enable easy emptying the cell. However, the stopcocks must be regularly lubricated to avoid valve seizure. An alternative, simple technique for the manual removal of spent working medium from the titration cell is by using a plastic wash bottle. The tip of the compressed bottle is introduced into the titration cell and pressure on the bottle is released to suck out the desired amount of spent working medium. Care should be taken during the drainage operation to ensure that no foreign atmosphere is drawn into the titration cell.

A suction bottle is suitable for the anodic compartment of a coulometric titration cell. We use pipettes fitted with suction bulbs for the removal of spent reagent from the cathodic compartment.

A modified working medium must sometimes be used, as for the addition of benzoic acid for the titration of a base. In such cases a funnel is a useful tool by which to add the benzoic acid, or any other solid. Particles of the solid that remain on the funnel are rinsed into the cell with the working medium.

### 6.6 End point stability and instrumentation delay

A delay in the cut off of the instrumentation at the end point is typical because of the previously-used slow reacting KF reagents (refer to section 5.6.1). Today, all commercially available instruments are equipped with a timer to pre-set this delay time. Each manufacturer uses different designations for this function, such as Delay, Stop-Delay, End Point Time and Temps Fin. Delay times between 5 and 100 seconds can be pre-set. The end point sensitivity of some Japanese instruments is set differently.

The commonly accepted end point duration of twenty seconds is now in question due to the development of new instruments and the availability of new, improved KF reagents capable of much faster titrations. The micro-dosage systems of modern piston

burettes enable titrant volumes as small as 0.5 to 1  $\mu\text{L}$  to be added accurately to the reaction. These micro-titration systems cannot tolerate an excess reagent of as little as one drop, approximately 0.01 mL, in the titration cell. End points that endure longer than twenty seconds are rare under such micro-titration conditions because the influence of extraneous moisture increases as the titration volume decreases. The delay time of the end point sensitivity must be adapted to modern methods of reagent addition.

A long end point delay time is not necessary when using HYDRANAL<sup>®</sup>-Reagents. These reagents reach the equivalence point of the KF reaction rapidly. The equivalence point of the reaction is reached immediately with HYDRANAL<sup>®</sup>-Solvent/Titrant; the final end point depends upon the time required for the added reagent to mix. An end point time delay of five seconds is sufficient for HYDRANAL<sup>®</sup>-Composite. Because of the speed and flexibility of HYDRANAL<sup>®</sup>-Reagents, it is possible to adjust the end point delay to the individual requirements of the sample under investigation (refer to section 5.6.1).

Although bipotentiometric and biamperometric methods of end point indication are excellent for KF titrations, interferences are sometimes encountered. The interference is caused by the coating on the platinum electrodes, a common occurrence during the titration of samples containing oils or sugars. These titrations are characterized by a delayed end point indication and an over-titration. A dark brown colorization of the reacted constituents is indicative of this type of contamination, which is solved by a thorough cleaning of the platinum electrodes.

The end point is also influenced by the choice of solvent system. When 1-propanol is used instead of methanol, an over-titration can occur. The indication potentials/currents are apparently dependent on the solvent system of the reaction. Certain instruments can be adjusted to compensate for the use of specific solvents.

## 7. Sample preparation

It is a rule of thumb that the analysis can only be as good as the sample. Analytical laboratories have valuable expertise in the vagaries of handling samples within their particular application areas. However, samples destined for moisture determination require additional analytical considerations [1].

### 7.1 Sampling and sample treatment

Water is everywhere and it can come into contact with the sample in numerous ways. Hygroscopic substances, both solids and liquids, adsorb moisture readily and exhibit high water content, even if the adsorption of water is restricted to the surface of the sample being investigated. Care should be taken when sampling to ensure that it is indeed representative of the bulk and not from the outer or surface regions of the sample that are more likely to have a higher water content. Conversely, substances that easily release water contain less water in the surface layers than in the bulk. The water content of samples can also change. Adherent water on solid samples can diffuse into colder areas of the bottle, for example if the sample is left on a window ledge or next to warm equipment. Water can separate from samples of dispersions. The same applies when the temperature of the sample drops below the solubility of water for the sample. The addition of a solubilizing agent, 2-propanol for example, can stabilize the sample in solution in either case. Further preventive measures are described in the literature [1].

Sampling and analyzing gaseous samples presents particular difficulties. The water content of gaseous samples is typically low; it can easily be changed through contact of the sample with the vessel walls and connections. Samples taken from gases must therefore be treated immediately with scrubber liquids that absorb the moisture. The most practical method is to direct the gas through the KF titration cell, preferably a coulometric titration cell. This technique eliminates the influence of the otherwise necessary determination of a blank value for the solvent or correction for the volume factor of the absorption agent. Further details are given in sections 7.3.5 and 8.10.

Liquefied gases can be kept in pressurized cylinders provided that a homogeneous distribution of the water content can be assured. However, if the water separates upon pressurization, the sample is no longer representative and cannot be used for subsequent analyses.

### 7.2 Sample size

The sample size (mass, volume) is dictated by the sample's expected water content and the desired accuracy of the determination.

A high degree of accuracy can be achieved by volumetric titration when the water content of the sample titrated consumes approximately half of the reagent in the burette. This corresponds to approximately 50 mg H<sub>2</sub>O for a reagent of 5 mg/mL titer in a burette containing 20 mL reagent.

It is important to remember that as the water content of the sample decreases, the sample size must increase to maintain accuracy. For this to be practical a change in burette size, a reduction in reagent titer or both may be required to accommodate the sample. Instrument manufacturers offer burettes as small as 1 mL, and when coupled with a titer 1 mg/mL reagent, 0.1 mg of water may be titrated.

The sample size for a coulometric determination should be such that it contains approximately 100-5000 µg H<sub>2</sub>O to achieve a high degree of accuracy. Amounts as low as 100 µg H<sub>2</sub>O can also be determined by trace analysis. Optimized conditions can determine water contents of 10 µg, although the reproducibility of such determinations obviously decreases.

A selection of samples sizes is presented in the following table. The actual amounts used for the titration will, of course, depend upon the titer of the reagent used, the burette and the desired accuracy of the titration.

### 7.3 Addition of the sample

When adding sample to the titration vessel, whether the sample is a solid or a liquid, care must be taken to avoid introduction of atmospheric moisture along with the sample into the vessel. Preventative measures correspond to the individual properties of the particular matrix. Samples should be weighed and added under their normal conditions to prevent changes in moisture content due to differences in environmental conditions. Weighing and adding samples into the titration vessel should be done as quickly as possible to keep contamination by atmospheric moisture to a minimum.

Resorting to working in a glove box should be the exception rather than the rule. Particular care is required when working with samples that are frozen or refrigerated. Cold samples will collect water via condensation and should therefore be allowed to warm to room temperature in an airtight vessel prior to weighing and addition. The homogenization of samples in liquid form by ultrasonic methods is possible, but determined on a case-by-case basis.

#### 7.3.1 Pipettes

The use of a pipette enables a very accurate addition of liquid samples. Pipettes are preferred for larger sample volumes (2-50 mL). Obviously, the pipette must be absolutely dry. We rinse our pipettes thoroughly with methanol and leave them overnight in a 50 °C drying cabinet. It is our experience that pipettes dried in this fashion have a residual water content of less than 50 µg and do not constitute significant error in volumetric determinations.

If the pipette is not dry, it should be rinsed 2-3 times with the substance being investigated

prior to the titration.

If the sample is hygroscopic we strongly recommend using a fresh pipette between subsequent sample additions. For these types of samples, we determined water content of 250 µg H<sub>2</sub>O after 1 minute and 1000 µg H<sub>2</sub>O after 15 minutes in a 25 mL pipette used to add the methanol.

#### 7.3.2 Calibrated syringes

Syringes with calibrated cylinder (e.g. Hamilton brand syringes) are often used for the volumetric addition of small sample volumes (<5 mL). Such syringes enable a sufficient degree of accuracy. However, they require extreme care in their handling.

Glass syringes should be disassembled for cleaning with a suitable solvent and then rinsed with methanol before drying. After allowing them to air dry, the syringe and injection needle should be further dried in a desiccator chamber. Our experience shows that it takes several days to thoroughly dry such needles. We therefore prefer to first dry glass syringes using air and then flush them with the substance under investigation 2-3 times prior to adding the sample.

The syringe is used to inject the sample into the titration cell, preferably through a septum. This method excludes the infiltration of atmospheric moisture into the titration, an absolute prerequisite for a coulometric determination of water. However, such sealants can also be a potential source of error if droplets from the needles are retained by the septum. The syringe cylinder should therefore be retracted before puncturing the seal, as well as before removal, to ensure that extraneous droplets are not retained

#### Recommended sample sizes

Water Content of the sample %	Sample size, Volumetry (g)	Sample size, Coulometry (g)
100	0.05	-
10	0.5	0.05
1	5	0.2
0.1	10	2
0.01	10	5
0.001	20	10
0.0001	-	10

by the needle.

The accuracy can be improved by weighing the syringe before and after adding the sample. This method of weighing by difference is described in the next section.

### 7.3.3 Plastic syringes

Injecting the sample through a septum stopper prevents the inclusion of atmospheric moisture, which is an absolute prerequisite for coulometric methods because they are used to determine extremely small amounts of water. It is also to be recommended for volumetric titrations.

Plastic syringes, which are quite common since they are disposable and inexpensive, eliminate tedious cleaning procedures between samples. They are supplied air-dry and can be used without any additional treatment. Nevertheless, we rinse our plastic syringes 2-3 times with the substance under investigation prior to use. This method is recommended for micro-determinations of water, like coulometry. Weighing by difference is a technique to improve the accuracy over that of a volumetric addition. The syringe is filled with the sample and weighed. The desired amount of sample is injected into the titration cell as described in section 7.3.2. The syringe is then reweighed and the difference in weight constitutes the actual weight of the sample that was added.

The syringe used for sample addition is usually equipped with a sufficiently long injection needle to go beneath the surface of the liquid in the titration cell. Thin needles are preferred to prevent excessive wear of the rubber stopper. Sturdier needles are required for viscous samples.

Plastic syringes have proven to be excellent vessels for weighing pastes and highly viscous liquids. The syringe needle is not used with these samples. The viscous liquid or paste sample is drawn into the plastic syringe and added to the titration cell. The actual amount of sample added is determined by weighing by difference.

Waxes and similar substances can also be added

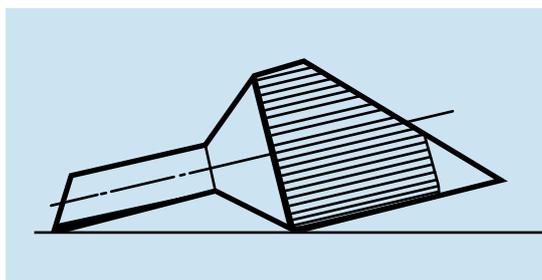


Diagram 7.3.4

by this method. They are first melted in a drying cabinet or air-tight vessel at 50 °C. The plastic syringe is warmed at the same time to prevent solidification of the wax during the subsequent weighing and addition of the sample.

### 7.3.4 Funnels for solid samples

Solid samples should be weighed and added directly to the titration cell whenever possible. This method ensures a reliable addition of sample and a rapid titration. Direct addition also avoids the need to measure separately the moisture content of solvents used to dissolve the solid.

Various accessories are available for volumetric titration instruments to assist the addition of solid samples. Certain titration instruments are equipped with a plastic dipper for this purpose. Other instruments have so-called sample locks. We often use a plastic weighing funnel as depicted in illustration 7.3.4. Such a funnel is cut to size from an empty FIXANAL®-Ampoule<sup>1</sup>. It is then filled with the sample and weighed. The funnel tip is then inserted into the previously dried opening in the lid of the titration vessel and the contents tipped into the cell. The emptied funnel is then re-weighed. This type of funnel is also suitable for samples as large as 10 g if a large FIXANAL®-Ampoule<sup>1</sup> is used.

### 7.3.5 The addition of gases

Gases are introduced either directly into the titration cell or via an adsorption medium. Suitable measurement methods and a diagram of the equipment are given in section 8.10.

The volume of gas is measured using a flowmeter (R in diagram 8.10). The flow rate is usually 6-10 L/hour or 100-150 mL/min. The flow meter can also be used to determine the amount of gas when calculating the flow time. Prerequisites are an accurate flow meter and a constant gas flow. New instruments require a gas flow of only 70 mL/min. Instruments based on aqueous measurement principles are more accurate. The KF titration cell must be completely air-tight so that the gaseous sample introduced passes first through the 0.3nm HYDRANAL®-Molecular sieves<sup>2</sup> in the drying tube (T in diagram 8.10) and then into

<sup>1</sup> For the FIXANAL® complete range please check [sigma-aldrich.com/fixanal](http://sigma-aldrich.com/fixanal)

<sup>2</sup> 34241

the instrument.

Liquified gases should be added as liquids to the KF titration cell. If the sample is allowed to boil, the water may remain in the sample container in liquid form and the water content of the sample will not be representative. Bottles containing the liquified gas should be inverted in order to add samples only in liquid form into the titration cell.

#### 7.4 Pre-dissolution of the sample

Although direct addition of the sample into the titration cell is preferred, it is not always possible. This is often the case when a large amount of an inhomogeneous sample is required, e.g. butter, or when solids have to be dissolved for a coulometric determination of their water content.

The sample should be first dissolved in a suitable solvent. The solvent should be as anhydrous as possible. An aliquot of this solution is measured and added to the titration cell and the titration carried out.

Such methods of sample addition require particular care if error is to be eliminated or at least minimized. All equipment, including flasks, funnels, pipettes, weighing boats, etc., must be completely dry. The water content of all solvents used for dissolution should be intrinsically low and be determined by a separate titration. That is, the water content of the solvent used for the dissolution of the sample must be determined and taken into account in the final calculation of the water content of the sample.

(Note: If 20 g of substance have been dissolved in a 100 mL measuring cylinder made up to the mark, a volume of 80-100 mL of solvent has been used. Accuracy is called for.)

The volume or mass fraction of the sample and solvent components must be taken into account when calculating the total moisture of solutions. If the correction factor is relatively large, the solvent cannot be considered 100% pure. It is necessary in those cases to calculate the mass fraction of each component in order to obtain accurate calculation of the total residual water. This is particularly important in coulometric titrations when the sample is introduced via syringe and the amount calculated by the weighing by difference method. If the correction factor is relatively large, the solvent cannot be considered 100%. It proves appropriate in those cases to determine the

mass of each component in certain cases, as their addition can often ease the calculation of the total residual water. This is particularly useful in coulometric determinations when the sample is injected into the cell from a syringe, and the weight of the sample is determined from weighing by difference.

The ability to prepare sample solutions and add them to the titration vessel without introducing any omnipresent moisture takes time and experience to master. It is not trivial to eliminate this source of error. We strongly recommend that whenever possible, the sample should be added to the titration cell directly without pre-dissolution.

#### 7.5 Extraction of water from the sample

Some samples release water very slowly or are so inhomogeneous that large sample masses are required. These types of samples require the pre-extraction of the moisture to obtain accurate KF titrations.

The simplest means of pre-extracting is to soak the sample in a suitable solvent, usually methanol, in an Erlenmeyer flask for several hours. An aliquot of the solvent is then titrated. It is important to consider that the volume of the solvent must be able to dissolve the amount of moisture extracted from the sample or the resulting water content measured will be erroneously low. As a general rule, 1 mL methanol should not be expected to extract more than 1 mg H<sub>2</sub>O.

The extraction process can be accelerated by increasing the extraction temperature. The moisture can also be extracted by refluxing the sample. However, the apparatus must be equipped with sufficiently large drying tubes filled with activated molecular sieves. The inherent water value of the extraction instrumentation must also be determined, i.e. a correction factor for the extraction equipment must be evaluated.

It is obvious from these discussions on the additional measures necessary for the pre-extraction of water from the sample that these methods should only be employed when a direct titration of the sample is not possible (refer to section 8.9).

## 8. Variants of the KF titration caused by the matrix

KF titration is applied to multifarious substances. The nuances in sample properties influence differentially the course of the KF titration. There are a number of ways to adjust the working conditions in order to enable a direct KF titration of the sample and avoid complicated and error-prone pre-dissolution and pre-extraction steps. Many of these variants are generally applicable and, as such, are described in this section. For example:

- Fats, oils and long-chained hydrocarbons have limited solubility in methanol. Solubility can be improved by the addition of long-chain alcohols or chloroform to the working medium.
- Proteins, carbohydrates and inorganic salts are either insoluble or dissolve only slightly. An addition of formamide improves the dissolution, dispersion and the extraction of water from these samples.
- In certain samples, methanol can cause interfering side reactions. It can be replaced by other solvents that do not react.
- Acids and bases can alter the pH of the KF system outside the desirable range and must be neutralized.
- The influence of slow side reactions can be suppressed by carrying out the titration at a lower temperature.
- Natural substances slowly release water. A titration at 50 °C or in boiling methanol accelerates the extraction of water and/or dissolution of the sample.
- Ovens are used to drive off the moisture from solids that only release water at temperatures higher than 60 °C. An inert gas is used to carry the moisture into the KF cell.
- KF solutions can absorb the moisture from gaseous samples.

If the working conditions of the titration are modified, the requirements of the KF reagents must also be considered. The solvent constituent of the HYDRANAL®-Composite one-component reagent can be extensively modified. However, the basic prerequisites for the KF titration must be maintained (see section 4).

Only a limited modification of the solvent component of the two-component reagent, HYDRANAL®-Solvent<sup>1</sup>/Titrant, is possible since

the solvent contains reactants for the KF reaction system. The coulometric KF reagents, HYDRANAL®-Coulomat A<sup>2</sup>/AD<sup>3</sup>/E<sup>4</sup>/AG<sup>5</sup>/AG-H<sup>6</sup>, may only be modified in exceptional cases. Any modification must not only assure the KF reaction takes place, but must also retain sufficient electrolytic conductivity within the cell (the minimum conductivity is dictated by the type of instrument used). Furthermore, a 100% current yield from the anodic oxidation of iodide must be assured.

Summarized working procedures are presented in this section for each of the titration variants. Procedures for the one-component reagent are designated "O", two-component reagents are designed with "T" and coulometry is given "C." Section 5 provides the foundations of KF titration that the practical methods in this section are based upon.

### 8.1 Addition of alcohols

Methanol does not satisfactorily dissolve long-chained hydrocarbons; a biphasic solution can form in the titration vessel. This does not necessarily impede the KF titration since the water in the hydrocarbon phase is quickly extracted and titrated during the titration. However, problems can occur if the indication electrode is situated in the hydrocarbon phase rather than in the methanol, or when oily deposits coat the electrode. These problems are avoided by adding 1-propanol to the working medium. A mixture of HYDRANAL®-Methanol dry<sup>7</sup> and 1-propanol is used as the working medium of one-component reagent, HYDRANAL®-Composite. For the two-component reagent, HYDRANAL®-Solvent/Titrant, a portion of the solvent component is replaced by 1-propanol. The amount of solvent component used depends upon the amount of water expected to be determined (1 mL HYDRANAL®-Solvent<sup>1</sup> approximates 7 mg H<sub>2</sub>O).

<sup>1</sup> 34800

<sup>2</sup> 34807

<sup>3</sup> 34810

<sup>4</sup> 34726

<sup>5</sup> 34836

<sup>6</sup> 34843

<sup>7</sup> 34741

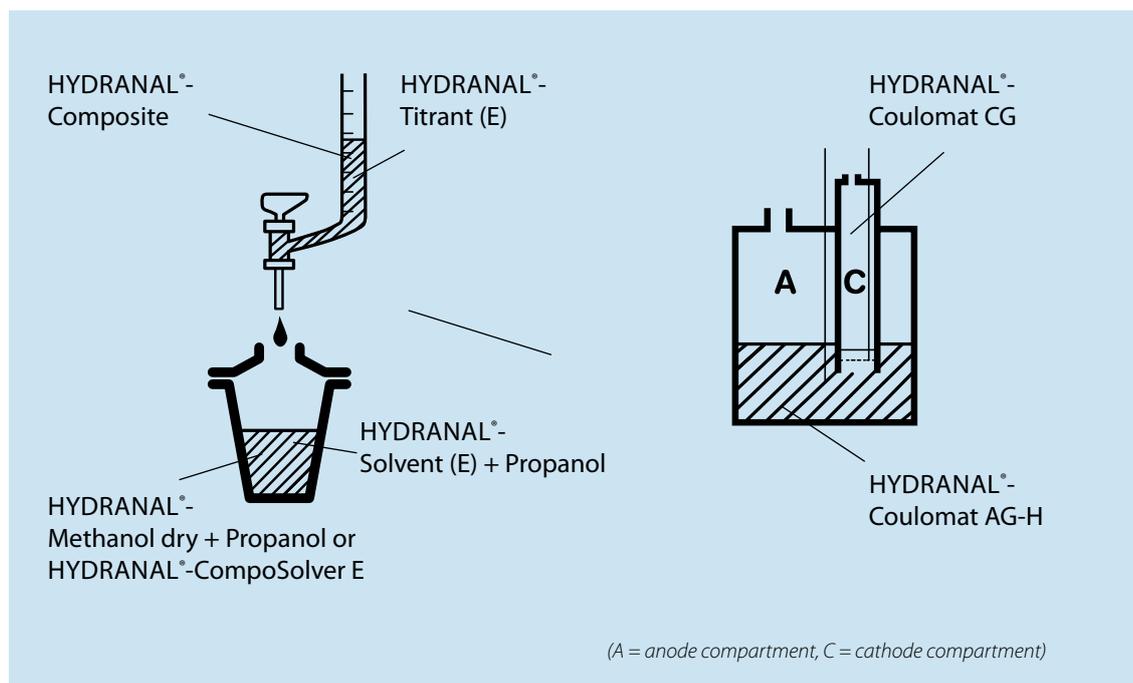


Diagram 8.1

Long-chain alcohols can be used in the same way as 1-propanol. Occasionally it is necessary to investigate alcohols of various chain lengths, and choose the alcohol based on its solubility toward the sample being investigated.

For coulometric determination, HYDRANAL®-Coulomat AG-H<sup>1</sup> is used as analyte since it contains a long-chain alcohol.

**Procedure 8.1 O Alcohols, one-component, volumetric titration**

10 mL HYDRANAL®-Methanol dry<sup>2</sup> and 20 mL 1-propanol, or 30 mL HYDRANAL®-CompoSolver E<sup>3</sup> are added to the titration vessel and titrated to dryness with HYDRANAL®-Composite. The weighed sample is then added and titrated in the same manner.

**Procedure 8.1 T Alcohols, two-component, volumetric titration**

10 mL HYDRANAL®-Solvent<sup>4</sup> or HYDRANAL®-Solvent E<sup>5</sup> and 20 mL 1-propanol are added to the titration vessel and titrated to dryness with HYDRANAL®-Titrant or HYDRANAL®-Titrant E. The sample (water content <70 mg H<sub>2</sub>O) is then added and titrated in the same manner.

**Procedure 8.1 T1 Alcohols, two-component, volumetric titration**

30 mL HYDRANAL®-Solvent Oil<sup>6</sup> are added to the titration vessel and titrated to dryness with HYDRANAL®-Titrant. The sample is then added and titrated in the same manner.

**Procedure 8.1 C Alcohols, coulometric titration**

The anodic compartment of the coulometric cell is filled with 100 mL HYDRANAL®-Coulomat AG-H<sup>1</sup>. The cathodic compartment is filled as usual with 5 mL HYDRANAL®-Coulomat CG<sup>7</sup>. The determination is carried out in the usual way.

**8.2 Addition of chloroform**

Fats, long-chained hydrocarbons and other lipophilic substance have limited solubility in alcohols. Addition of HYDRANAL®-Chloroform<sup>8</sup> greatly improves their solubility. Because chloroform reduces the dissolution of inorganic salts in methanol, adding it enables the determination of the salts' adherent (not bulk) water content. However, some methanol is always required; it can only be partially replaced (see section 4.1). For an exact determination of water, the methanol content should not be less than 35% by volume, although a 25% HYDRANAL®-Methanol dry<sup>2</sup> / 75% HYDRANAL®-Chloroform<sup>8</sup> solvent mixture is acceptable for trace analyses, in spite of the possibility of a slight change in the stoichiometry of

<sup>1</sup> 34843  
<sup>2</sup> 34741  
<sup>3</sup> 34734  
<sup>4</sup> 34800

<sup>5</sup> 34730  
<sup>6</sup> 34749  
<sup>7</sup> 34840  
<sup>8</sup> 37863

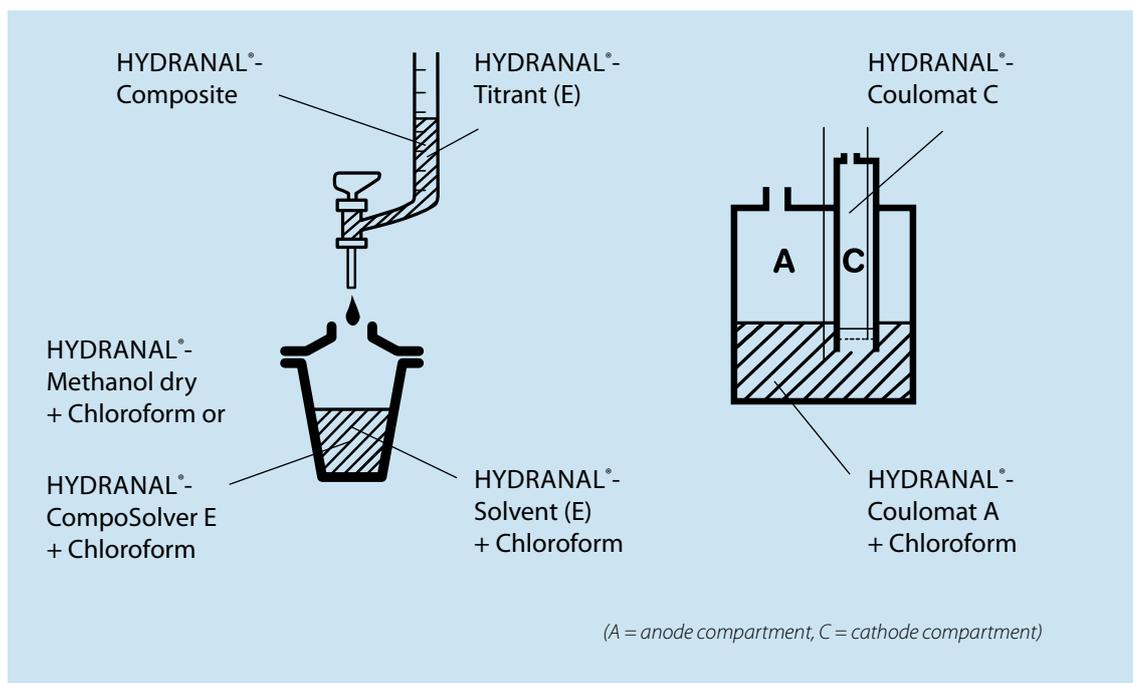


Diagram 8.2

the KF reaction. (The factor for the titrating agent apparently increases.) An addition of HYDRANAL®-Chloroform<sup>1</sup> also accelerates the KF reaction.

The coulometric reagent, HYDRANAL®-Coulomat A<sup>2</sup>, already contains chloroform and as such has better solubility of fatty substances. The chloroform content can be increased, but should not exceed 30% by volume or the conductivity will be decreased to levels that can cause interferences with certain coulometric instruments. The minimum conductivity differs from instrument to instrument, so an exact maximum chloroform volume cannot be given here.

#### Procedure 8.2 O Chloroform addition, one-component, volumetric titration

10 mL HYDRANAL®-Methanol dry<sup>3</sup> or HYDRANAL®-Methanol Rapid<sup>4</sup> and 10 mL HYDRANAL®-CompoSolver E<sup>5</sup>, respectively, and 20 mL HYDRANAL®-Chloroform<sup>1</sup> are added to the titration vessel and titrated to dryness with HYDRANAL®-Composite. The sample is then added and titrated in the same manner.

#### Procedure 8.2 T Chloroform addition, two-component, volumetric titration

30 mL HYDRANAL®-Solvent CM<sup>6</sup> (or 10 mL HYDRANAL®-Solvent<sup>7</sup> or HYDRANAL®-Solvent E<sup>8</sup> and 20 mL chloroform<sup>1</sup>) are added to the titration vessel, and titrated to dryness with HYDRANAL®-Titrant or HYDRANAL®-Titrant E. The sample (<70 mg H<sub>2</sub>O) is then added and titrated in the same manner.

#### Procedure 8.2 C Chloroform addition, coulometric titration

The anodic compartment of the coulometric titration cell is filled with 70 mL HYDRANAL®-Coulomat A<sup>2</sup> and 30 mL HYDRANAL®-Chloroform<sup>1</sup>. The water content is determined according to the general recommendations given in section 5.3.

### 8.3 Addition of formamide

HYDRANAL®-Formamide dry<sup>9</sup> improves the solubility of polar substances in methanol and is therefore preferred for the determination of water in carbohydrates, proteins and inorganic salts. HYDRANAL®-Formamide dry<sup>9</sup> also accelerates the extraction of moisture from solids and is used in the titration of starch and other foodstuffs and naturally occurring substances, as well as in titrations at elevated temperatures. HYDRANAL®-Formamide dry<sup>9</sup> accelerates the course of the reaction. Because

<sup>1</sup> 37863

<sup>2</sup> 34807

<sup>3</sup> 34741

<sup>4</sup> 37817

<sup>5</sup> 34734

<sup>6</sup> 34812

<sup>7</sup> 34800

<sup>8</sup> 34730

<sup>9</sup> 34724

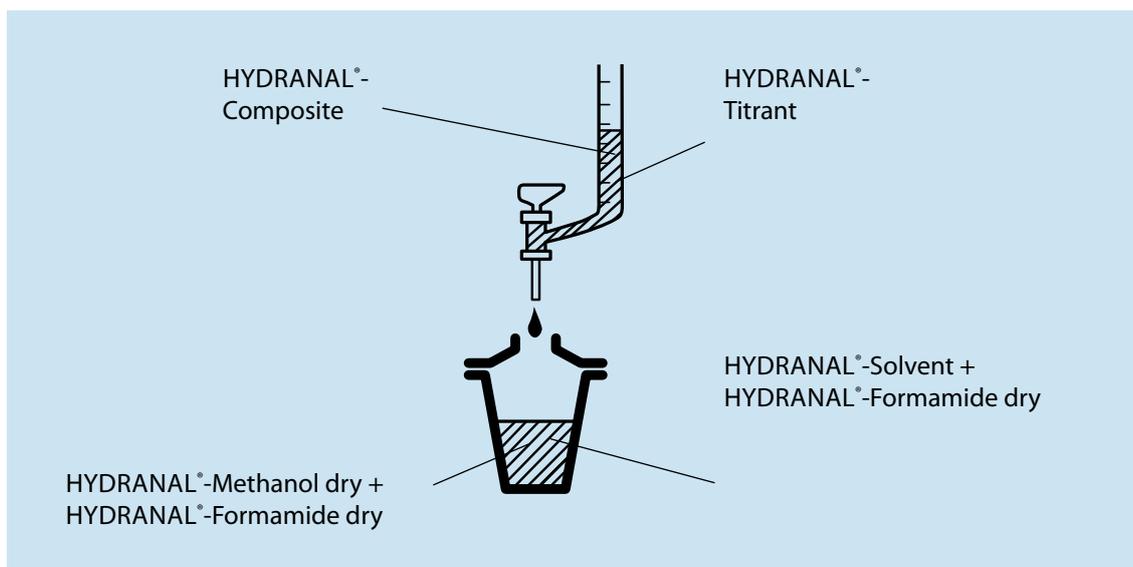


Diagram 8.3

it can also influence the stoichiometry of the KF reaction, formamide should not be used at concentrations >50% by volume.

**Procedure 8.3 O Formamide addition, one-component, volumetric titration**

20 mL HYDRANAL®-Methanol dry<sup>1</sup> or HYDRANAL®-Methanol Rapid<sup>2</sup> and 20 mL HYDRANAL®-Formamide dry<sup>3</sup> are added to the titration vessel and titrated to dryness with HYDRANAL®-Composite. The sample is then added and titrated in the same manner.

**Procedure 8.3 T Formamide addition, two-component, volumetric titration**

20 mL HYDRANAL®-Solvent<sup>4</sup> and 20 mL HYDRANAL®-Formamide dry<sup>3</sup> are added to the titration vessel and titrated to dryness with HYDRANAL®-Titrant. The sample (<140 mg H<sub>2</sub>O) is then added and titrated in the same manner.

We have tried the use of formamide in the coulometric titration with diaphragm. Side reactions blacken the cathode, and after one day the analyte has to be discarded.

In the coulometric titration without diaphragm 10-20% HYDRANAL-Formamide<sup>3</sup> dry can be added to HYDRANAL-Coulomat AG<sup>5</sup>.

<sup>1</sup> 34741

<sup>2</sup> 37817

<sup>3</sup> 34724

<sup>4</sup> 34800

<sup>5</sup> 34836

## 8.4 Methanol-free working media

Methanol is the normal working solvent, but it can sometimes cause undesirable side reactions that interfere with the desired KF titration reaction. Examples of such side reactions are esterification with certain mineral acids, the formation of acetals and ketals with aldehydes and ketones, respectively, or reactions with certain amines and siloxanes.

When such reactions may occur, it is advantageous to replace the methanol with non-reactive solvents. Although solvents such as pyridine, dioxane, formamide, dimethylformamide and propylene carbonate are quoted in the literature as being suitable replacements for methanol, we strongly disagree with this assertion. Non-alcoholic solvents alter the stoichiometry of the KF reaction (section 4.1).

Methyl glycol (2-methoxyethanol) is also often recommended, and in certain cases is a suitable replacement for methanol. However, the course of the KF titration with this solvent is slower and very sluggish with certain instruments. The indication potentials are changed so that a greater or lesser degree of over-titration occurs, depending on the instrument. The formation of acetals and ketals is not completely suppressed. The same applies to use of ethanol or 1-propanol. Benzyl alcohol is also suitable, however it iodizes slightly and the reaction products are irritating to the eyes.

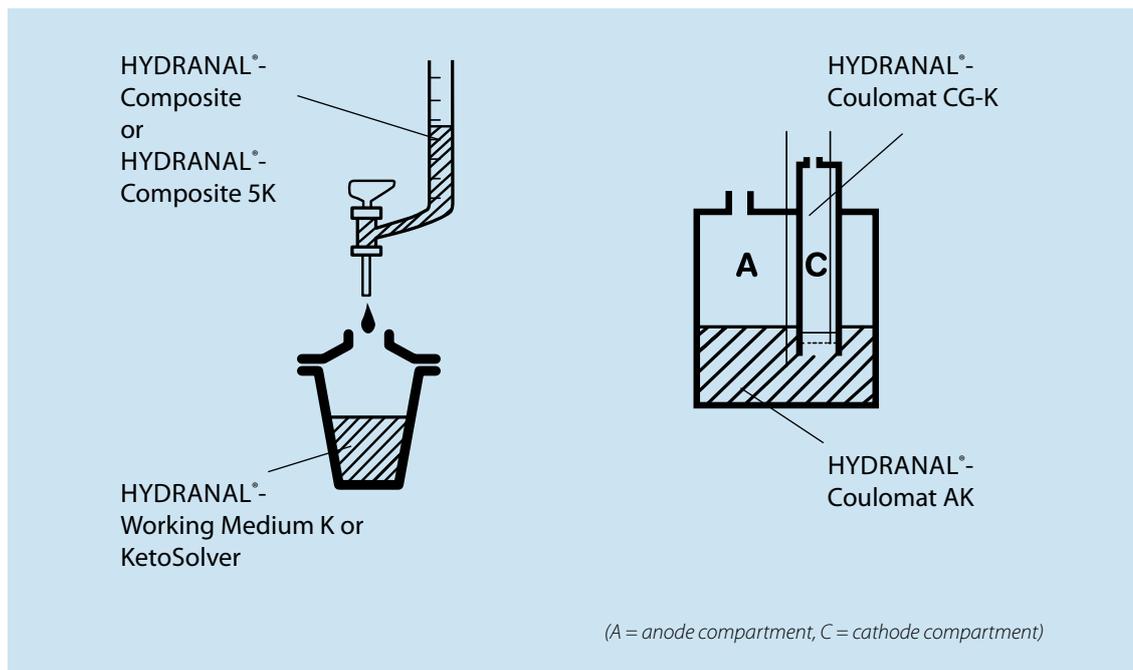


Diagram 8.4

Our systematic search for suitable KF alcohols found that certain halogenated alcohols (2-chloroethanol, trifluoroethanol) and 1-methoxy-2-propanol are particularly suitable. We used this work as the basis of our methanol-free KF reagents [11]. These reagents are designated as HYDRANAL®-K reagents because they were primarily developed for determination of water in ketones and aldehydes (section 2.4). These reagents are also suitable for moisture determination of amines (section 9.8), siloxanes (section 9.10) and other titrations in methanol-free working media.

Our further research into alternate alcohols lead to the line of halogen-free KF solvents called HYDRANAL®-KetoSolver<sup>1</sup>.

The "K" type reagents are available in both a one-component system for volumetric determinations and for coulometry. Both reagents are described in detail in section 2.4 and used like the corresponding non-K reagent. A variety of ketones can also be titrated in the new working medium, the ethanol-based HYDRANAL®-CompoSolver E<sup>2</sup>.

<sup>1</sup> 34738

<sup>2</sup> 34734

<sup>3</sup> 34817

<sup>4</sup> 34698

<sup>5</sup> 34805

<sup>6</sup> 34816

<sup>7</sup> 34820

<sup>8</sup> 34821

#### Procedure 8.4 O HYDRANAL®-K Reagents, one-component, volumetric titration

30 mL HYDRANAL®-Working Medium K<sup>3</sup> or HYDRANAL®-Medium K<sup>4</sup> or HYDRANAL®-KetoSolver<sup>1</sup> are added to the titration vessel and titrated to dryness with HYDRANAL®-Composite 5<sup>5</sup>. (The titration of aldehydes or ketones requires HYDRANAL®-Composite 5K<sup>6</sup>.) The sample is then added and titrated using the same reagent.

#### Procedure 8.4 C HYDRANAL®-K Reagents, coulometric titration

The anodic compartment of the coulometric titration cell is filled with 100 mL HYDRANAL®-Coulomat AK<sup>7</sup> and 5 mL HYDRANAL®-Coulomat CG-K<sup>8</sup> are added to the cathodic compartment. The general procedure given in section 5.3 is then followed. Methanolic solutions of iodine must not to be used to dry the reagents! We recommend a solution of iodine in 2-methoxyethanol or HYDRANAL®-Composite 5<sup>5</sup> for this purpose.

### 8.5 Neutralization of bases

Strong bases can increase the pH of the KF system if the basicity exceeds the buffering capacity of the reagent solutions. A titration end point will not be reached. Strong bases must be neutralized prior to starting the titration by the addition of an adequate amount of HYDRANAL®-

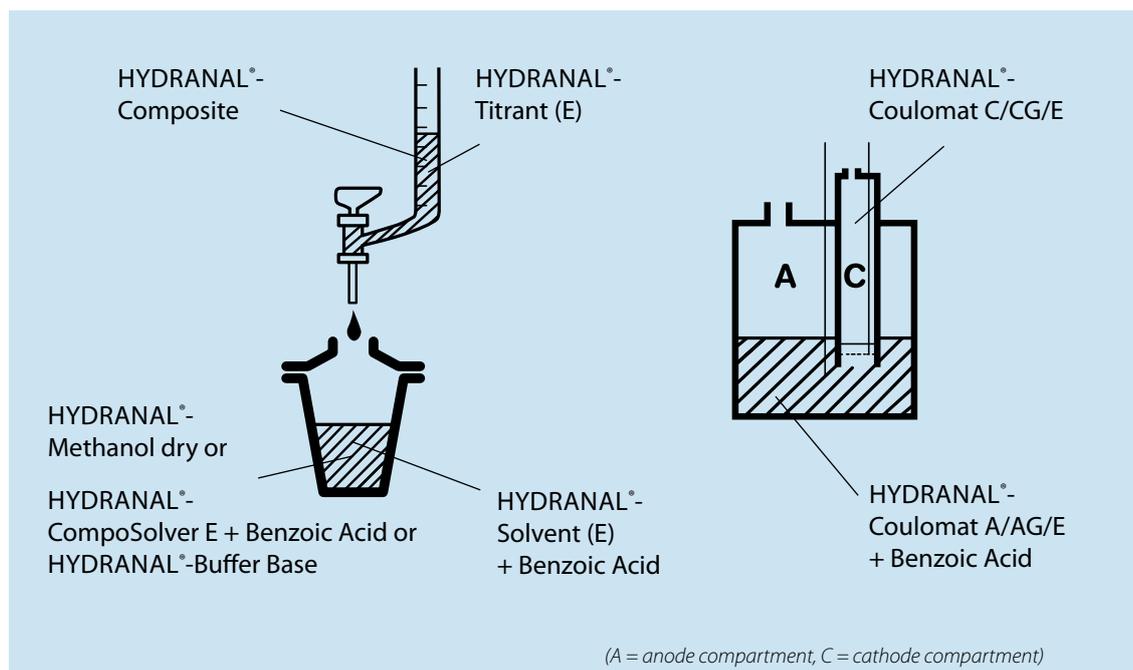


Diagram 8.5

Salicylic<sup>1</sup>, HYDRANAL®-Benzoic<sup>2</sup> or propionic acid. HYDRANAL®-Buffer Base<sup>3</sup> is a ready-made working medium for water determination in basic samples. It contains salicylic acid and has a buffer capacity of 1mmol base per mL.

HYDRANAL®-Benzoic acid<sup>2</sup> is typically used because it is easy to handle and does not have an unpleasant odor. Salicylic acid is stronger and can reduce the pH to 4-5, which is outside the desirable pH range and can slow down the course of the titration slightly. HYDRANAL®-Salicylic acid<sup>1</sup> is especially useful for the moisture determination of phenols. Propionic acid has similar acidification properties as HYDRANAL®-Benzoic acid<sup>2</sup>. Because it is a liquid it can be pipetted. However, propionic acid has an unpleasant odor.

**Procedure 8.5 O Basic compounds, one-component, volumetric titration**

30 mL HYDRANAL®-Buffer Base<sup>3</sup> or 30 mL HYDRANAL®-Methanol dry<sup>4</sup> or HYDRANAL®-CompoSolver E<sup>5</sup> and 5 g HYDRANAL®-Benzoic acid<sup>2</sup> or HYDRANAL®-Salicylic acid<sup>1</sup> are added to the titration vessel as follows:

The HYDRANAL®-Benzoic acid<sup>2</sup> or HYDRANAL®-Salicylic acid<sup>1</sup> is put into a funnel and rinsed into the titration cell with the methanol. The alcoholic solution is then titrated to dryness with HYDRANAL®-Composite. The base being determined (<40 mmol) is then added and titrated with HYDRANAL®-Composite.

**Procedure 8.5 T Basic compounds, two-component, volumetric titration**

30 mL HYDRANAL®-Solvent<sup>6</sup> or HYDRANAL®-Solvent E<sup>7</sup> and 5 g HYDRANAL®-Benzoic acid<sup>2</sup> or HYDRANAL®-Salicylic acid<sup>1</sup> are added to the titration vessel as follows: The HYDRANAL®-Benzoic acid<sup>2</sup> or HYDRANAL®-Salicylic acid<sup>1</sup> is put into a funnel and rinsed into the titration cell with the HYDRANAL®-Solvent<sup>6</sup> or HYDRANAL®-Solvent E<sup>7</sup>. The solution is titrated to dryness with HYDRANAL®-Titrant or HYDRANAL®-Titrant E. The base being determined (<50 mmol) is then added and titrated in the same manner with HYDRANAL®-Titrant or HYDRANAL®-Titrant E.

**Procedure 8.5 C Basic compounds, coulometric titration**

HYDRANAL®-Coulomat A<sup>8</sup>/AD<sup>9</sup>/E<sup>10</sup>/AG<sup>11</sup>/AG-H<sup>12</sup> is acidified by approximately 20% by weight of benzoic acid for the coulometric determination of bases. 20 g HYDRANAL®-Benzoic acid<sup>2</sup> is added to the anodic compartment of the cell using a funnel (approximately 160 mmol acid). The

<sup>1</sup> 37865  
<sup>2</sup> 32035  
<sup>3</sup> 37859  
<sup>4</sup> 34741  
<sup>5</sup> 34734  
<sup>6</sup> 34800  
<sup>7</sup> 34730  
<sup>8</sup> 34807

<sup>9</sup> 34810  
<sup>10</sup> 34726  
<sup>11</sup> 34836  
<sup>12</sup> 34843

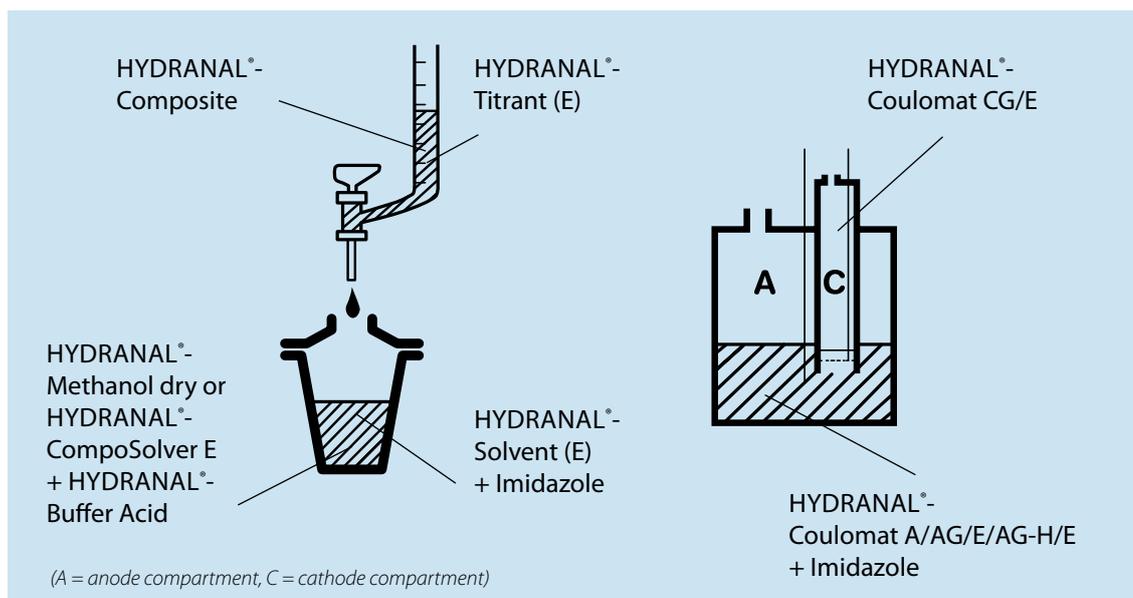


Diagram 8.6

HYDRANAL<sup>®</sup>-Benzoic acid<sup>1</sup> is rinsed into the cell with 100 mL HYDRANAL<sup>®</sup>-Coulomat A<sup>2</sup>/AD<sup>3</sup>/E<sup>4</sup>/AG<sup>5</sup>/AG-H<sup>6</sup>. A 5 mL aliquot of HYDRANAL<sup>®</sup>-Coulomat CG<sup>7</sup>/E<sup>4</sup> is added to the cathodic compartment of the cell in the usual manner. The instrument is then turned on and the titration cell titrated to dryness. Approximately 200 mmol of the base can be analyzed using this method.

### 8.6 Neutralization of acids

Moderately strong to strong acids can reduce the pH of the working medium and cause significant reduction in the titration reaction rate. Acids must be neutralized prior to starting the titration. The most practical approach is to neutralize the acid by the addition of a suitable base to the working medium. However, the base should not cause an increase in the pH to such a degree that no end point of the pre-titration is reached. Pyridine is a commonly used base for this purpose. More suitable, however, are buffering systems that not only neutralize but stabilize the pH of the system. HYDRANAL<sup>®</sup>-Solvent<sup>8</sup> fulfills this role; it has buffering capacity that can be utilized when titrating with the HYDRANAL<sup>®</sup> two-component reagent system. A 1 mL volume of HYDRANAL<sup>®</sup>-Solvent<sup>8</sup> can buffer approximately 0.6 mmol of acid, i.e. a maximum amount of 12 mmol of acid can be added to the titration if the usual quantity of 20 mL HYDRANAL<sup>®</sup>-Solvent<sup>8</sup> is used. We recommend the use of imidazole or, preferably, HYDRANAL<sup>®</sup>-

Buffer Acid<sup>9</sup> for larger quantities of acidic samples. Certain carboxylic acids that tend to esterify [1] are neutralized without esterification by using HYDRANAL<sup>®</sup>-Buffer Acid<sup>9</sup>.

Concentrated sulfuric acid and gaseous hydrochloric acid esterify very easily with methanol and therefore cannot be analyzed using this procedure (see section 10.2).

#### Procedure 8.6 O Acids, one-component, volumetric titration

10 mL HYDRANAL<sup>®</sup>-Methanol dry<sup>10</sup> and 20 mL HYDRANAL<sup>®</sup>-Buffer Acid<sup>9</sup> (buffering capacity 5 mmol/mL) or 10 mL HYDRANAL<sup>®</sup>-CompoSolver E<sup>11</sup> and 20 mL HYDRANAL<sup>®</sup>-Buffer Acid<sup>9</sup> are added to the titration vessel and titrated to dryness with HYDRANAL<sup>®</sup>-Composite. The acid being investigated (<100 mmol) is then added and titrated in a similar manner with HYDRANAL<sup>®</sup>-Composite.

#### Procedure 8.6 T Acids, two-component, volumetric titration

30 mL HYDRANAL<sup>®</sup>-Solvent<sup>8</sup> or HYDRANAL<sup>®</sup>-Solvent E<sup>12</sup> and 7 g HYDRANAL<sup>®</sup>-Imidazole<sup>13</sup> (=100 mmol) or 20 mL HYDRANAL<sup>®</sup>-Buffer Acid<sup>9</sup>

<sup>1</sup> 32035<sup>2</sup> 34807<sup>3</sup> 34810<sup>4</sup> 34726<sup>5</sup> 34836<sup>6</sup> 34843<sup>7</sup> 34830<sup>8</sup> 34800<sup>9</sup> 34804<sup>10</sup> 34741<sup>11</sup> 34734<sup>12</sup> 34730<sup>13</sup> 37864

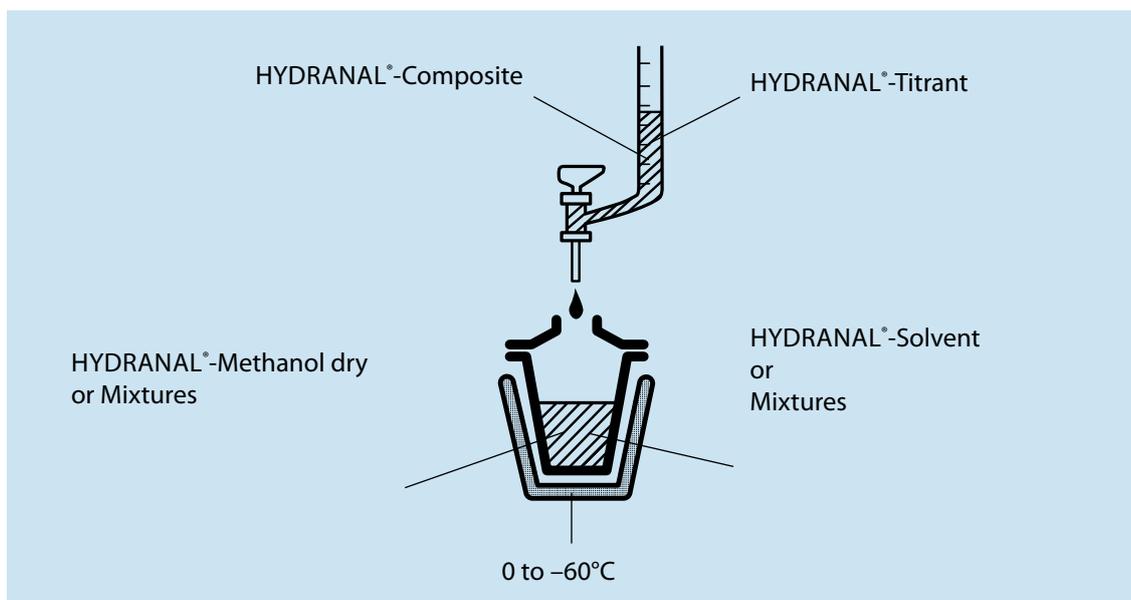


Diagram 8.7

are added to the titration cell and titrated to dryness with HYDRANAL®-Titrant or HYDRANAL®-Titrant E. The acid being measured (<120 mmol) is then added and titrated in a similar manner with HYDRANAL®-Titrant or HYDRANAL®-Titrant E.

#### Procedure 8.6 C Acids, coulometric titration

100 mL HYDRANAL®-Coulomat A<sup>1</sup>/AG<sup>2</sup>/AG-H<sup>3</sup>/E<sup>4</sup> and 20 g HYDRANAL®-Imidazole<sup>5</sup> are added to the anodic compartment of the coulometric cell 5 mL of HYDRANAL®-Coulomat CG<sup>6</sup>/E<sup>4</sup> is added in the usual way to the cathodic compartment. The instrument is turned on and analysis performed as normal. This amount of reagent is sufficient for the analysis of approximately 300 mmol of a moderately strong acid.

### 8.7 Titrations at low temperatures

Slowly occurring side reactions can be the cause of a continual consumption of iodine and do not allow a stable end point to the KF titration. These side reactions can sometimes be suppressed by carrying out the titration at lower temperatures. The titration can be carried out at 0 °C by placing the titration vessel in an ice bath. Lower titration

temperatures can be achieved by the use of a salt-ice or a dry ice/methanol mixture. The titration cell can of course, be equipped with a thermal jacket and be cryostatically cooled to a pre-determined and controlled temperature.

The choice of the low temperature for the titration is primarily determined by the nature and extent of the side reaction. The rate of the titration reaction using HYDRANAL®-reagents is still sufficiently high even at low temperatures. Using the two-component reagent, HYDRANAL®-Solvent/Titrant, titrations can still be carried out at -60 °C with satisfactory speed. At temperatures below -20 °C, HYDRANAL®-Composite is not recommended because of increasing viscosity.

Low temperature titrations can be carried out according to the standard procedures in section 5, or modified according to the titration variants given in sections 8.1 through 8.6. However, a few special points should be considered. At low temperatures the end point indication can shift. Therefore the polarization current and voltage must be adapted appropriately. Also, the sample should be in liquid form to allow injection via a septum if possible. Cells cooled to a low temperature absorb atmospheric moisture very easily and should not be opened to allow introduction of solid samples.

In principle, the coulometric determination of water at low temperatures is also possible. This does not appear useful in practice as the side reactions cannot be completely suppressed.

<sup>1</sup> 34807

<sup>2</sup> 34836

<sup>3</sup> 34843

<sup>4</sup> 34726

<sup>5</sup> 37864

<sup>6</sup> 34840

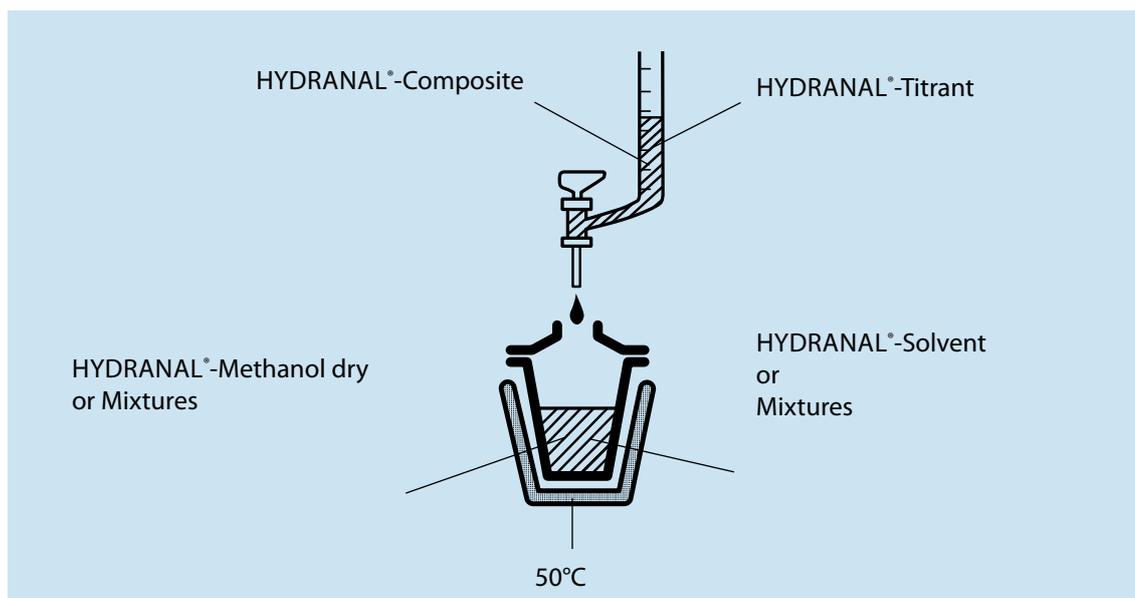


Diagram 8.8

The interferences accumulate with successive sample additions and the total effect of the side reaction increases. When the titration vessel is not cooled, for example during overnight storage, the side reaction is re-activated and consumes the reagent in a short time.

### 8.8 Titrations at elevated temperatures

Substances that dissolve slowly in methanol or the KF working medium can give slow titrations. This also applies to solids that release the retained water very slowly, as is the case with many foodstuffs and cellular substances [1]. A volumetric titration at an elevated temperature of 50-60 °C enables both the dissolution of the sample and an acceleration of the extraction of the moisture from the sample. A volumetric titration at 50 °C does not require any modifications to the standard procedure or instrument. The simplest form of equipment can be a controlled hotplate and a magnetic stirrer. Also, the titration cell can be placed in an oil bath and the temperature can be controlled by monitoring the working medium with a thermometer. If titrations at elevated temperatures are carried out frequently, a titration cell equipped with a thermostatically controlled jacket is recommended. Titration temperatures above 50 °C can lead to difficulties when using a standard titration cell. The boiling methanol condenses at the top of the vessel and causes an uncontrollable reflow of moisture into the titration system.

The standard techniques described in sections 5.1 and 5.2 are applicable to volumetric titrations at elevated temperatures. Basically, all of the titration variations described in sections 8.1 through 8.6 can be applied to titrations at elevated temperatures. HYDRANAL®-Formamide dry<sup>1</sup> is often added for the titration of foodstuffs, as discussed in section 8.3, in order to combine the extraction properties of this solvent with the advantages of the higher titration temperature.

An elevated temperature titration is carried out by adding the appropriate working medium to the titration cell and heating the system to the prescribed temperature. The working medium is then titrated to dryness and the sample is added and titrated in the usual manner. Because coulometry is not recommended for insoluble substances, we have not investigated coulometric titration at elevated temperatures.

### 8.9 Titrations in boiling methanol

For certain difficult samples, methods to more rigorously extract moisture are required. For example, a direct KF titration at 50 °C of coarsely ground coffee beans is not possible because the water is released from the sample too slowly.

<sup>1</sup> 34724

The moisture can be extracted by refluxing the sample and titrating the extract. We have combined the extraction by boiling methanol with a direct KF titration. The principle of this titration technique is depicted in the diagram 8.9.

We used a three-necked round bottom flask equipped with a magnetic stirrer. One end of the reflux column was connected to one of the three flask openings and the other end was sealed against moisture by the attachment of a large drying tube containing molecular sieves. The indicator electrode and the burette were connected to the remaining two openings of the titration flask (diagram 8.9).

A determination of water in this sample is carried out by first titrating the apparatus to dryness. To do this, 50 mL of HYDRANAL<sup>®</sup>-Methanol dry<sup>1</sup> are added to the flask, heated while stirring until boiling and titrated to dryness to a stable end point with HYDRANAL<sup>®</sup>-Composite. At this point, the methanol and the equipment are sufficiently pre-dried. The heater is then removed from the flask to allow a slight cooling of the HYDRANAL<sup>®</sup>-Methanol dry<sup>1</sup>. The sample (1-2 g) is added, the heater adjusted and the contents of the flask stirred.

The titration is then started. The titration takes approximately 20-25 minutes. We have tested this titration method in boiling HYDRANAL<sup>®</sup>-Methanol dry<sup>1</sup> with samples such as starch and flour. We believe that this technique can be employed in the investigation of numerous natural products and substances that release water very slowly. For example, caramels melt and release retained water easily at elevated temperatures, allowing a rapid determination of their water content. We believe that a titration in boiling HYDRANAL<sup>®</sup>-Methanol dry<sup>1</sup> is advantageous in other cases where a direct KF titration of the water content is otherwise not possible.

We also measured the recovery rate of water for the above describe method and concluded that a stoichiometric reaction for the titration is assured when HYDRANAL<sup>®</sup>-Composite is used.

### 8.10 The determination of water in gases

Moisture in gaseous samples must first be transferred into the liquid phase of the KF system. This can be achieved by bubbling the gas sample through an appropriate

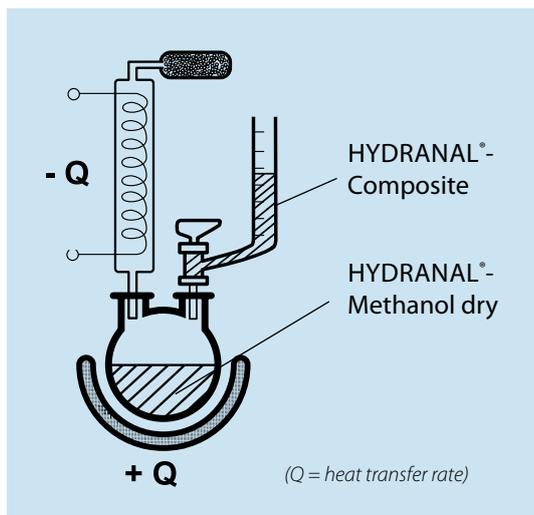


Diagram 8.9

sorption medium that absorbs the water from the sample. Liquids recommended for the absorption of water from gases are high boiling point alcohols like 1-propanol and ethylene glycol. The sorption medium containing the moisture from the gas sample is then titrated in the normal manner. A preferred method, however, is to pump the gas sample directly into the KF titration cell. This eliminates a number of potential sources of error, like the inherent water content of the sorption medium, changes in volume of the gas or the intrusion of extraneous moisture from handling.

Capillary tubes inserted deeply in the KF solution are used to transfer gaseous samples. Fritted glass filters are also recommended to improve the distribution of the gas. We consider the use of capillary tubes to be adequate, provided the flow rate of the gas does not exceed 250 mL/minute (15 liters/hour).

The system to introduce the gas into the titration cell should be well-designed and as compact as possible to minimize the loss or gain of moisture from surfaces. The system should also permit heating of tubing and supply lines to prevent the condensation of water from the gaseous sample.

<sup>1</sup> 34741

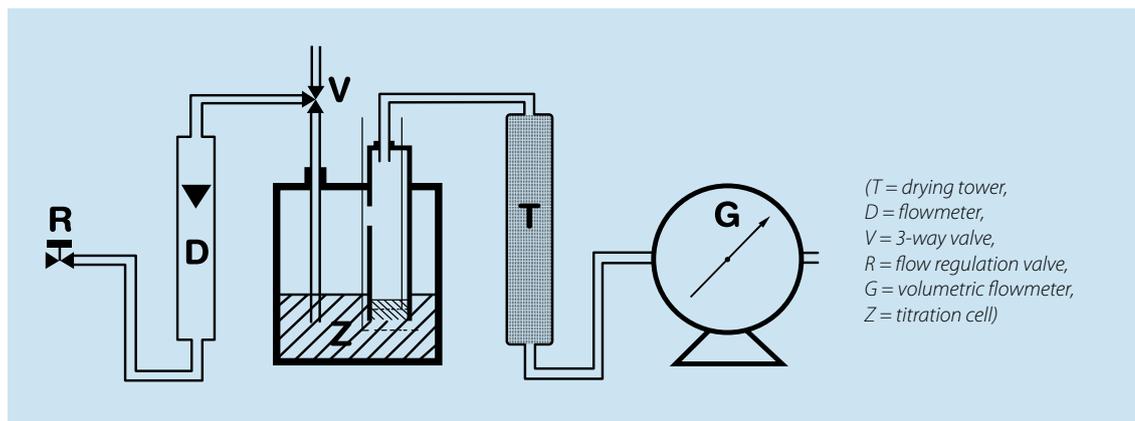


Diagram 8.10.1

A suitable arrangement for the titration of gases is depicted in figure 8.10.1. A flowmeter (D) is installed in the tubing. The flow rate of the gas is regulated by a valve (R). The system must be thoroughly purged in order to achieve stable and homogeneous conditions prior to introducing the gaseous sample into the KF titration cell. The installation of a three-way valve (V) enables the flow of gas to bypass the titration cell. Before starting the analysis, the flow of gas is bypassed through valve (V) and the flow rate regulated by valve (R), as monitored by the flow meter (D), to a constant flow of 100-500 mL/min. When the system has stabilized (after 10-30 minutes), the flow of gas is directed into the titration cell by valve (V). The volume of gas is determined either by calculation from the flow rate and time, or by the volumetric flow meter (G). A drying tower (T) is installed between the titration cell (Z) and the flow meter (G) to prevent back diffusion of moisture from the flow meter into the titration cell.

The sample size is determined by the water content of the gas being investigated, the instrumentation and the desired accuracy of the analysis. When the appropriate amount of gaseous sample has been directed through the titration cell, valve V is turned to bypass the remainder of the sample. The water content of a known amount of gaseous sample in the cell is thus titrated.

If water determination using this method is carried out frequently or if the reproducibility of the analysis and stability of the introductory system is to be verified, it is advantageous to install a titration arrangement directly to the sample source.

If the sample is taken from a container, the same titration arrangement can be used provided the gas in the container has not liquefied. Liquid samples must always be added as liquids to the titration cell (section 7.3.5).

Both volumetric and coulometric titration methods can be used for the determination of moisture in gases. Volumetric titrations require larger sample sizes containing mg amounts of water. Coulometric titrations are preferred for the determination of water in "dry" gases where the samples contain only a few  $\mu\text{g H}_2\text{O/liter}$ .

#### Procedure 8.10 O Gases, one-component, volumetric titration

50-100 mL HYDRANAL<sup>®</sup>-Methanol dry<sup>1</sup> are added to the titration vessel in the usual manner. Should larger amounts of gaseous sample be foreseen, mixtures of solvents can be used that have a higher boiling point and therefore will not evaporate easily while the sample is being introduced. A mixture of methanol and ethylene glycol or propanol is suitable. Pure ethylene glycol is highly viscous and problems can be encountered in the subsequent titration. The use of pure propanol can cause problems with the indication of the end point.

The solvent is titrated to dryness in the usual manner. HYDRANAL<sup>®</sup>-Composite 2<sup>2</sup> (titer approximately 2 mg  $\text{H}_2\text{O/ml}$ ) is the preferred reagent system. The desired volume of gas is

<sup>1</sup> 34741

<sup>2</sup> 34806

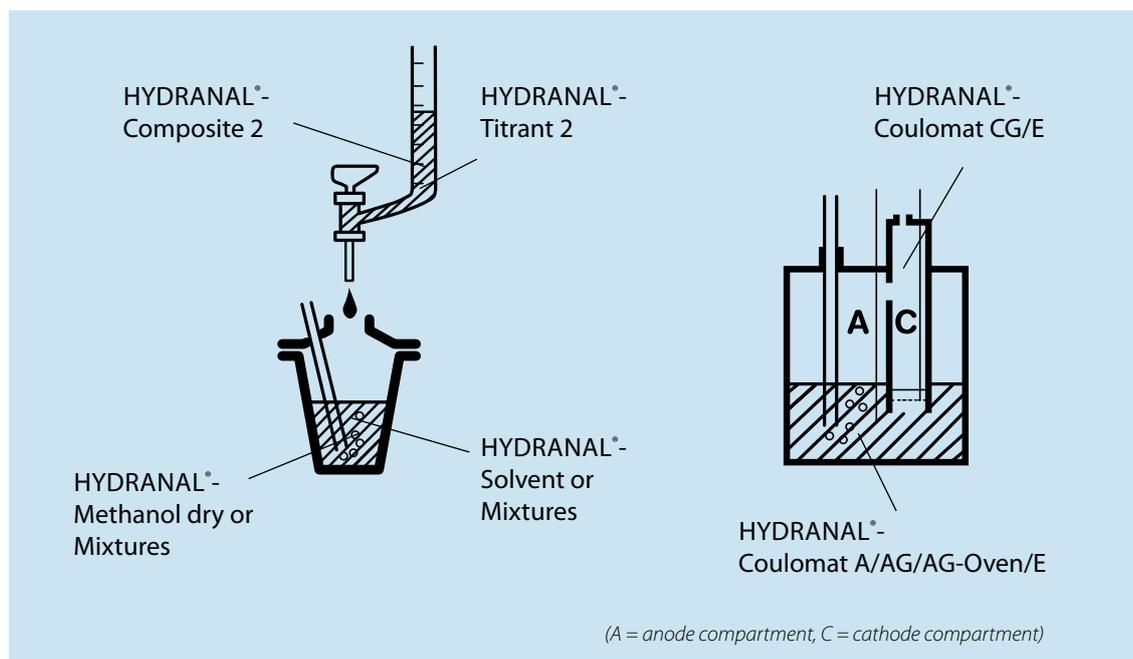


Diagram 8.10.2

introduced into the titration cell and the water adsorbed by the working medium from the sample is titrated with HYDRANAL®-Composite 2<sup>1</sup> in the same manner.

#### Procedure 8.10 T Gases, two-component, volumetric titration

A mixture of 20 mL HYDRANAL®-Solvent<sup>2</sup> and 40 mL 1-propanol are added to the titration cell and titrated to dryness with HYDRANAL®-Titrant 2<sup>3</sup>. The use of HYDRANAL®-Titrant 2<sup>3</sup> is preferred because of its lower titer. The desired amount of gaseous sample is then introduced into the titration cell and the water adsorbed is subsequently titrated using HYDRANAL®-Titrant 2<sup>3</sup> in the same manner.

#### Procedure 8.10 C Gases, coulometric titration

The titration cell of the coulometer is filled with HYDRANAL®-Coulomat AG Oven<sup>4</sup> and HYDRANAL®-Coulomat CG<sup>5</sup>, respectively and titrated to dryness in the usual manner. Then, a pre-determined quantity of gas is bubbled through the titration cell. The titration is started and the water content determined in the usual manner. In principle it is also possible to carry out the titration while the gas is bubbling through and thereby obtain the result very quickly. Consecutive determinations cause methanol to evaporate from the anode chamber of the titration cell. Evaporated methanol can be replaced using HYDRANAL®-Methanol dry<sup>6</sup> to maintain the original volume.

### 8.11 The use of ovens

Many substances release their water only at high temperatures making them unsuitable for direct KF titration. Examples of such substances are plastics and a number of inorganic salts.

The moisture in such substances can be driven off and collected in a tube furnace at 100 °C to 300 °C, depending on the sample, and transferred to the KF titration cell by purging the tube with a dry, inert gas. An example of such a system appears in diagram 8.11.1. A constant flow of gas is achieved by regulating valve (R) and monitoring the gas flow using the flow meter (D). The gas is then dried in the drying tower (T) before being passed over the heated sample into the titration cell (Z).

<sup>1</sup> 34806

<sup>2</sup> 34800

<sup>3</sup> 34811

<sup>4</sup> 34739

<sup>5</sup> 34840

<sup>6</sup> 34741

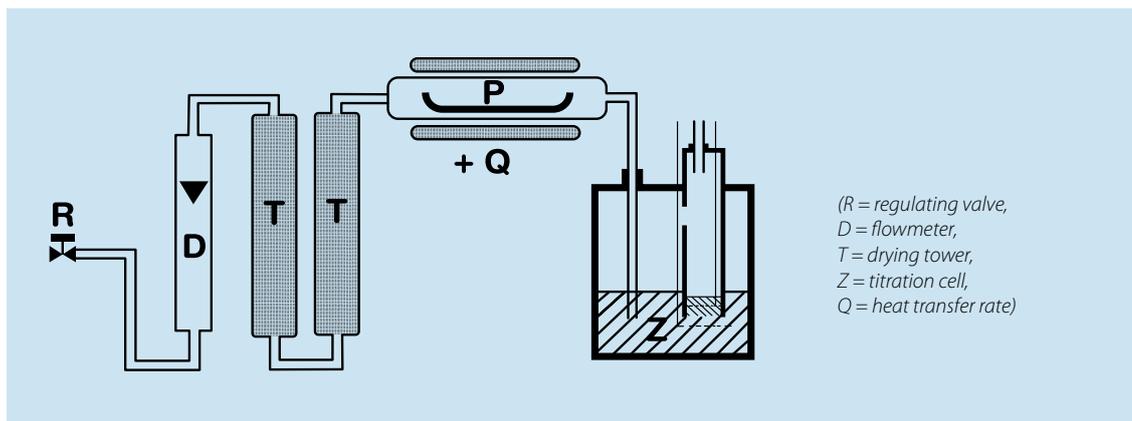


Diagram 8.11.1

This method of moisture determination can be applied to substances such as:

- Insoluble solids that only release their inherent water at temperatures above 60 °C (plastics, salts)
- Solids and liquids that undergo side reactions with conventional KF titration reagents (ascorbic acid, mineral oils), assuming that the matrix is not vaporized at these temperatures and that none of the substances disassociate or degrade to products that can interfere with the subsequent KF titration of water and lead to falsely high or low levels.

Suitable carrier gases are air or nitrogen, with nitrogen preferred when the sample is sensitive to oxidization at process temperatures of 100-300 °C. Commercially available pumps can be used for air and are available already equipped with dryers. Nitrogen is supplied from a pressurized container.

We recommend the use of molecular sieves to dry the carrier gas. A residual water content of less than 10 µg H<sub>2</sub>O/liter is thereby assured. This amount does not present a potential problem in the subsequent water determination. Carrier gases containing high amounts of water should be pre-dried using silica gel. KF reagents are not intended as drying agents as the solvents evaporate in the drying tube and can cause side reactions through dissociation of the components at higher temperatures.

The flow of carrier gas is set to 100 to 500 mL/min. Using smaller amounts of gas reduces the amount of extraneous moisture contributed by the carrier gas, which is usually eliminated by the drift correction of the instrumentation, and improves the absorption of extracted water by

the KF reagent in the vessel. Larger amounts of gas reduce the risk of water condensing in the tubing when large quantities of moisture are being transferred.

Commercially available KF ovens can be set to drying temperatures of 50-300 °C. Higher temperatures are necessary for drying inorganic salts. The temperature chosen depends on the properties of the substance being investigated. The moisture driven off from the sample in the drying oven is transferred into the titration cell by the carrier gas. The same fundamental rules for the investigation of gases (section 8.10) also apply here, and the same reagents can also be used. Since the samples often contain only trace amounts of moisture, it is preferred to combine the drying oven with a coulometer.

The sample size depends on the water content of the sample and the type of equipment used for KF titration. Generally, the size of the sample should be chosen to ensure that an adequate amount of water is present in the KF system. We recommend 500-3000 µg water for coulometric titrations, and 1-10 mg of water for volumetric titrations. Smaller amounts of water increase the standard deviation of the determinations; larger amounts of water can lead to condensation in the tubing.

A KF titration is carried out by first assembling the apparatus, switching on the instrumentation and preconditioning the system. The flow of gas is set to the desired rate and passed through the KF cell. The system must be brought to a stable condition before adding the sample. The drift must remain constant for a long period of time, at least 10 minutes, since this drift is later required for the automatic correction of the subsequent water determination. The

automatic correction for the drift is based on the assumption that the residual drift of the system does not change throughout the total duration of the determination, which is typically 20 minutes. Drift that increases from 6  $\mu\text{g}/\text{min}$  to 10  $\mu\text{g}/\text{min}$ , for example, could cause an error of as much as 80  $\mu\text{g}$  of water. This is why the baseline conditions should remain constant throughout the total conditioning of the system and subsequent determinations. The gas flow must not be altered under any circumstances as this will change the drift values as well.

Once the drift has stabilized, the previously weighed sample is added. The oven is opened and the combustion boat is quickly placed in the cold zone of the tubular oven. The oven is then immediately closed. The addition of the sample is a critical step because atmospheric moisture can enter the system while the oven door is open. This critical step should be practiced on blank samples to ensure smooth operation. It may be necessary to take this step into consideration in the calculations. Newer instruments use vials in a heating block, which is an improvement for the determination of very low water contents. The specific procedures for each instrument differ and the manufacturer's recommendations should be followed. The titrator is set so that it does not automatically shut off prematurely. It should be programmed to run for at least 10 minutes. This is necessary because the sample first has to be heated and only a small amount of water, if any, is initially released.

The working conditions must be optimized for each product analyzed. Of particular importance is the determination of the optimum oven temperature to remove the

water. The temperature must be high enough to drive off the moisture in the sample within 10-15 minutes. But it must be kept low enough to prevent vaporization of the sample matrix, which could interfere in the KF titration, and, at the same time, high enough to prevent condensation in the transfer tubing.

We determine the optimum temperature for a substance empirically by graphically evaluating the course of the titration against time (diagram 8.11.2). Water in the titration cell is not detected in the first minute (initial phase). The steepness of the curve increases as the water is released from the sample. The curve levels off after about 10-20 minutes as the last traces of moisture are driven off and the carrier gas purges the oven dry again.

The end of the titration should be reached after a further 3-10 minutes. Curve A in diagram 8.11.2 depicts the ideal course of drying sodium tartrate-2-hydrate at 160 °C. Curve B depicts a sluggish release of water as the oven temperature of 120 °C is too low.

### 8.12 Titration curves

We find valuable to record the course of a titration in terms of consumption of reagent vs. time during our investigations and in our development work. The titration curves give insight into the course of the titration, indicate potential sources of interference and enable a graphical elimination of interferences and an evaluation of the actual water content.

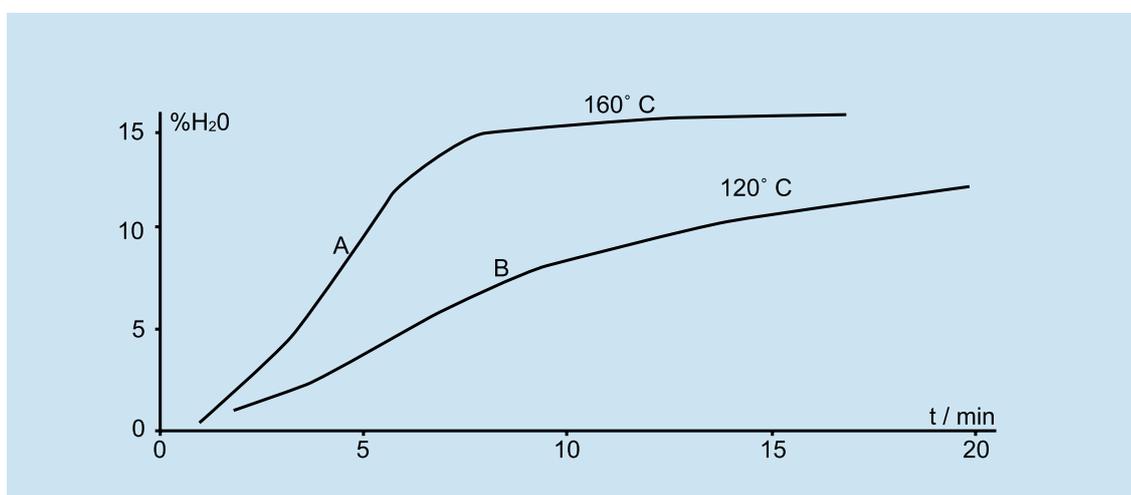


Diagram 8.11.2

Titration curves are obtained using commercially available titration instrument with an analog output fitted to the burette. An x-y recorder is connected to this output. The total titration is thus recorded. Many titrators offer the opportunity to connect a PC or display the titration curve on a monitor. Furthermore, we often titrate beyond the established end point in order to monitor any slow side reactions that might have influenced the titration. This can be clearly seen by the following examples.

Diagram 8.12.1 shows the regular course of the titration of 40 mg water with HYDRANAL®-Composite using HYDRANAL®-Methanol<sup>1</sup> as the working medium. The efficiency of the reagent is demonstrated by the rapid titration of the free water, as seen from the "a" region of the curve. The gradient of this portion of the titration curve is dependent upon the rate of addition of reagent from the burette. After reaching the sustained 20-second end point, point "b" (the excess of reagent) shows that the subsequent consumption of the reagent is virtually zero. This is an indication of how tightly sealed the cell is and the working technique of the titration.

Diagram 8.12.2 depicts the titration of 40 mg water in the presence of 5 mL acetone. Portion "b" of the curve is no longer vertical and indicates a continual consumption of the excess reagent and is caused by the ketal formation. The "b" portion of the graph is in fact a straight line. The rate of this side reaction is constant. The initial water content of the sample can therefore be evaluated by extrapolation of the "b" portion of the curve to  $t = 0$ . The origin of the curve,  $t = 0$ , should therefore be carefully determined. The titration must start immediately after the sample is added or, even better, shortly before the sample is added. This latter technique is called a "flying start."

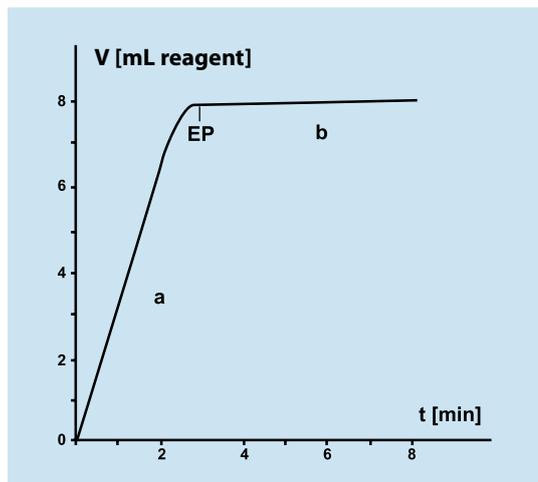


Diagram 8.12.1

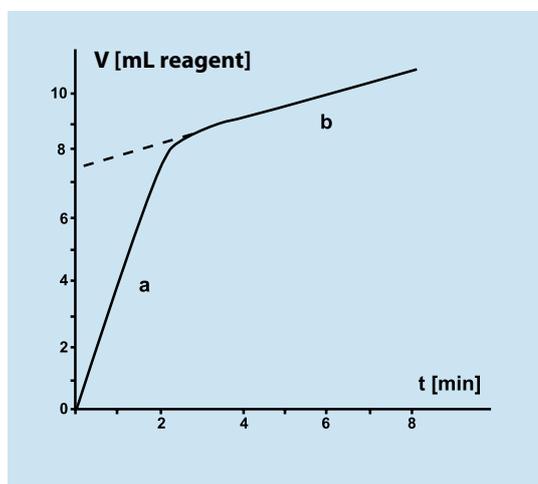


Diagram 8.12.2

<sup>1</sup> 34741 or 37817

The graphical evaluation of the course of a titration enables the real water content of individual samples to be determined more accurately, in spite of a slow side reaction taking place. Such a method should always be used when the side reaction cannot be suppressed by suitable means.

In many cases, the titration curves can give an indication of the source of error, and making it possible to reduce or even eliminate such interference. Diagram 8.12.3 depicts the attempt to titrate the water content of dimethylpolysiloxane in a methanolic working medium.

A strong side reaction, the etherification of the silanol groups, is the cause of a continuous consumption of reagent. A low water content could be inferred from the beginning of the titration curve. If the same titration is carried out in a methanol-free working medium according to the procedure 9.10.1, a definite end point is obtained, as shown in diagram 8.12.4. The subsequently low consumption of reagent is a clear indication that the side reaction has been suppressed sufficiently using the methanol-free medium, and that the end point given corresponds to the actual water content of the sample.

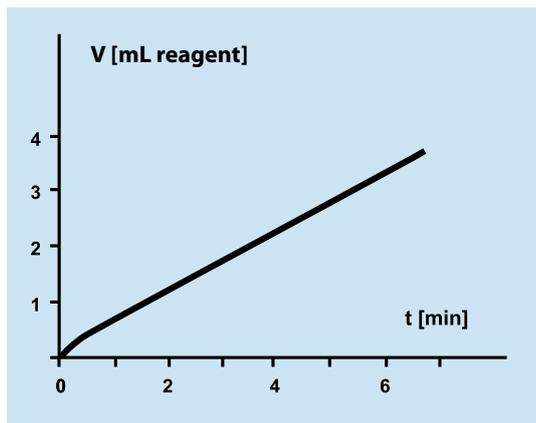


Diagram 8.12.3

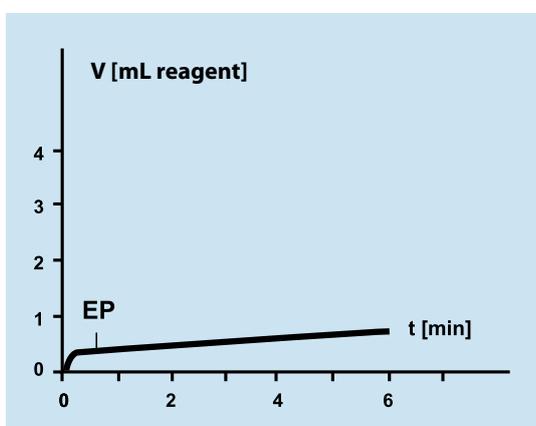


Diagram 8.12.4

## 9. Organic compounds

The moisture analysis by KF titration is frequently applied to organic compounds. It is important to adjust the titration conditions to accommodate the variety of matrices and functional groups of the compounds of interest.

### 9.1 Hydrocarbons

The determination of water in hydrocarbons is relatively straightforward and can usually be performed following the standard procedure

described in section 5.3. Solubility in the working medium may be an issue. Lower molecular weight hydrocarbons usually dissolve in methanol. Even if the dissolution is incomplete, the water is still titrated completely. Lipophilic hydrocarbons require the addition of 1-propanol, long-chain alcohols or HYDRANAL®-Chloroform<sup>1</sup> (sections 8.1 and

<sup>1</sup> 37863

Compound	Titration procedure
n-Pentane n-Hexane 2,2-Dimethylbutane 3-Methylpentene 2-Methylbutadiene	Standard titration procedures (sections 5.1, 5.2 or 5.3)
Benzene Toluene o-Xylene 2-Ethyltoluene 2,6-Dimethylstyrene	
iso-Octane Dodecane 1-Tetradecene Eicosane Octacosane Petroleum ether Gasoline	Addition of 1-propanol or chloroform to the working medium is recommended (sections 8.1 or 8.2)
Cyclohexane Methylcyclohexane Cycloheptane 4-Vinylcyclohexane Cyclododecane Decylcyclohexane Cyclopentadiene	
1,2-Dimethylnaphtalene 2,4,6-Trimethylstyrene Biphenyl Acenaphthene Fluorene 4,5-Methylenephenanthrene	
Allocymene Norbornadiene-(2.5)	Titration procedure as described in section 8.2 O

Table 9.1

Compound	Titration procedure
Allyl chloride Bromoform 1,2-Dibromomethane Dichloromethane Iodomethane 1,1,2,2-Tetrabromomethane 1,1,2,2-Tetrachloroethane	Standard titration procedures (sections 5.1, 5.2 or 5.3)
Benzyl chloride Benzyl bromide 2-Chloro-6-fluorobenzyl chloride 2-Chloro-6-fluorobenzotrithloride 4-Chlorotoluene Cyclohexyl chloride 1,2-Dichlorobenzene 1,2-Difluorobenzene 1-Iodonaphthalene	
1-Bromodecane 1-Bromohexadecane 1-Bromotetradecane 1-Chlorooctane	Addition of alcohol or chloroform to the working medium is recommended (sections 8.1 or 8.2)
4-Chlorobenzhydryl chloride	

Table 9.2

8.2), which not only improves the solubility but also accelerates the titration rate. Double bonds seldom interfere with the KF reaction, but can produce a slow or vanishing end point. We recommend the HYDRANAL<sup>®</sup>-Composite for compounds possessing double bonds because the interferences are less apparent using this reagent.

Because the water content of hydrocarbons is usually very low, the coulometric titration method is recommended. If the water content is determined volumetrically, a titrating reagent of low titer should be used, like HYDRANAL<sup>®</sup>-Composite 2<sup>1</sup> or HYDRANAL<sup>®</sup>-Titrant 2<sup>2</sup>.

A summary of the titration method we recommend for many common hydrocarbons is presented in Table 9.1.

## 9.2 Halogenated hydrocarbons

The determination of water in halogenated hydrocarbons is also straightforward. Typically, the solubility of these compounds in methanol is not a concern. The addition of HYDRANAL<sup>®</sup>-

Chloroform<sup>3</sup> may be necessary for more lipophilic compounds. Coulometry is also the recommended technique. The halogenated hydrocarbons we have investigated and the recommended titration procedures are summarized in Table 9.2.

Halogenated hydrocarbons can contain free chlorine as a result of the manufacturing processes. The chlorine oxidizes the iodide in the KF solution to iodine, which then "titrates" the water in the sample. This causes the measured water content to be erroneously low by a factor corresponding to the amount of free chlorine. To remove its interference on the titration, the free chlorine can be reduced prior to the KF titration or it can be added across a double bond. We give examples of both of these techniques. Free chlorine was bonded to 1-tetradecene for a determination of water in carbon tetrachloride (L 001).

<sup>1</sup> 34806

<sup>2</sup> 34811

<sup>3</sup> 37863

Compound	Titration procedure
Ethanol	Standard titration procedures (sections 5.1, 5.2 or 5.3)
Ethylene glycol	
1-Propanol	
2-Propanol	
Glycerin	
t-Butanol	
1,5-Pentanediol	
1-Hexanol	
3-Methyl-3-pentanol	
Cyclohexanol	
2-Methyl-2,4-pentanediol	
2-Heptanol	
1,2,6-Hexanetriol	
2,3-Dimethyl-3-pentanol	
1-Octanol	
2-Ethyl-1-hexanol	
2-Nonanol	
1-Geraniol	
1-Dodecanol	
Benzyl alcohol	
2-Phenoxyethanol	
2-Phenylpropanol	
Stearyl alcohol	Addition of alcohol or chloroform to the working medium is recommended (sections 8.1 or 8.2)

Table 9.3

**Procedure 9.2.1 Halogenated hydrocarbons**

A 2 mL aliquot of 1-tetradecene is mixed with 20 mL of the sample containing free chlorine. The solution turns colorless within several minutes and the chlorine odor disappears. The sample is chlorine-free with certainty after 10 minutes and can be titrated. Because the solubility of 1-tetradecene in methanol is poor, HYDRANAL<sup>®</sup>-Chloroform<sup>1</sup> is added as described in section 8.2. The water content of 1-tetradecene is determined separately and accounted for in the final calculations. We reduced the free chlorine in 1,2-dichloroethane using an imidazole-sulfite solution (L 003). Note: This solution must not contain any iodide!

**Procedure 9.2.2 Halogenated hydrocarbons**

A 10 g sample of HYDRANAL<sup>®</sup>-Imidazole<sup>2</sup> is dissolved in 100 mL HYDRANAL<sup>®</sup>-Methanol dry<sup>3</sup> prior to the addition of 5 g sulfur dioxide. A 2 mL aliquot of this imidazole-sulfite solution is mixed with 100 mL of the sample containing the free chlorine until the chlorine odor completely disappears. A portion of the treated sample is taken and titrated according to procedures 5.1-5.3.

The water content of the imidazole-sulfite solution is similarly determined (blank titration) and corrected for in the calculations. Instead of the imidazole-sulfite solution, HYDRANAL<sup>®</sup>-Solvent<sup>4</sup> can be added.

**9.3 Alcohols**

The KF determination of water in alcohols is straightforward. The solubility of alcohols in HYDRANAL<sup>®</sup>-Methanol dry<sup>3</sup> is usually better than their hydrocarbon counterparts. Addition of 1-propanol or hexanol proves necessary only for very lipophilic alcohols, like stearyl alcohol. Table 9.3 summarizes the recommended procedures for alcohols that we have investigated.

<sup>1</sup> 37863<sup>2</sup> 37864<sup>3</sup> 34741<sup>4</sup> 34800

Compound	HYDRANAL®- Composite	HYDRANAL®- Solvent + Titrant	HYDRANAL®- Coulomat
Phenol	Standard procedure	Standard procedure	Standard procedure
m-Cresol	5.1	5.2	5.3
p-Cresol			
2-Fluorophenol			
3-Fluorophenol			
4-Fluorophenol			
3-Chlorophenol			
4-Chlorophenol			
2,3-Dichlorophenol			
2,4-Dichlorophenol			
2,5-Dichlorophenol			
Salicylic acid			
Methyl salicylate			
Methyl-3-hydroxybenzoate			
Methyl-4-hydroxybenzoate			
2-Nitrophenol			
4-Nitrophenol			
Resorcinol dimethyl ether			
o-Cresol			Addition of salicylic acid procedure 8.5 C
2,3-Dimethylphenol			
2,3,5-Trimethylphenol			
2,3,6-Trimethylphenol			
2-Chlorophenol			
3-Bromophenol			
Pyrocatechol			
1-Naphthol		Addition of salicylic acid procedure 8.5 T	D, no end point
2-Naphthol			D, R = 130%
8-Hydroxyquinoline			R = 200%
Guaïacol			D
Hydroquinone		slugg. e.p.	R = 110%
Hydroquinone monomethyl ether		R = 110%	R = 103%
Resorcinol		R = 140%	R = 200%
Pyrogallol		no e.p.	no end point
2-Aminophenol	max. 1 g	no e.p.	brown solution
3-Aminophenol	max. 0.1 g	no e.p.	brown solution
4-Aminophenol	max. 0.1 g	no e.p.	brown solution
	max. 0.1 g		

*(D = deposition of material, R = recovery rate too high, slugg. e.p. = sluggish end-point)*

Table 9.4

The water content of alcohols can also be determined coulometrically. For samples with high water content the titration can take a relatively long time, so volumetric titration is preferred.

## 9.4 Phenols

We have investigated the KF titration of many phenolic compounds using both coulometric and volumetric titrations with one- and two-component reagents. We used the standard procedures described in sections 5.1, 5.2 and 5.3 and worked with a sample size of 10 g in each case. We also investigated the stability of the end point and the quantitative recovery rate of added water. Our results are presented in Table 9.4. The following general conclusions can be drawn from the results:

- The KF titration of most phenols is straightforward. Problems are mainly encountered with the higher molecular weight phenols and with amino-phenols.
- Volumetric titrations are less susceptible to interference than are coulometric titrations. The most suitable reagent is HYDRANAL<sup>®</sup>-Composite.
- An end point could not be reached when certain phenols were titrated, but rather a continual consumption of iodine was observed. This phenomenon is pH dependant. An addition of HYDRANAL<sup>®</sup>-Salicylic acid<sup>1</sup> suppressed this interference and enabled a normal titration. We presume that such phenols are oxidized by iodine and that the oxidation process is pH dependant.
- Interferences are encountered more frequently in coulometry. This behavior

can be explained by the higher oxidation potential of the anode in comparison to that of free iodine.

- In several cases a deposition of material onto the electrodes was noticed (designated "D" in Table 9.4). The electrodes were poisoned, i.e. the current yield was far too low and the electrodes had to be cleaned in a chromic/sulfuric acid or a nitric acid solution.
- We also found that the recovery rates of additionally added water were sometimes too high (designated "R" in Table 9.4). It could not be determined whether poisoned electrodes were the cause. We also found unexpected recovery rates for water using volumetry, which must be due to other causes.

A systematic evaluation of the analytical results awaits additional laboratory data. However, a number of conclusions pertinent to analogous phenols can be drawn from the data in Table 9.4. For reliable results when working with phenolic compounds, we recommend investigating the end point stability and determining the recovery rate of added water. The latter is easily accomplished by adding a known amount of water, e.g. 1 mL HYDRANAL<sup>®</sup>-Water Standard 1.0<sup>2</sup>, to the titrated phenol sample and continuing the titration.

## 9.5 Ethers

The KF determination of water in ethers is straightforward and similar in principle to hydrocarbons. Lipophilic ethers require the addition of alcohols or chloroform to the working medium (sections 8.1 and 8.2).

<sup>1</sup> 37865

<sup>2</sup> 34828

Compound	Titration procedure
Diethyl ether 1,4-Dioxane Diethylene glycol monomethyl ether Diethylene glycol diethyl ether Polyethylene glycol 200 Polyethylene glycol 1000	Standard titration procedures (sections 5.1, 5.2 or 5.3)
Anisole 4-Fluoranisole 2-Iodanisole Guaiacol Guaethol Resorcinol dimethyl ether	
Didecyl ether 1,3,5-Trioxane	Addition of alcohol or chloroform to the working medium is recommended (sections 8.1 or 8.2)

Table 9.5

Coulometry is suitable for the determination of short-chained and aromatic ethers. We found the titration end point of ethylene glycol derivatives to be sluggish. An end point could not be reached with vinylethyl ether. The ethers we investigated are summarized in Table 9.5.

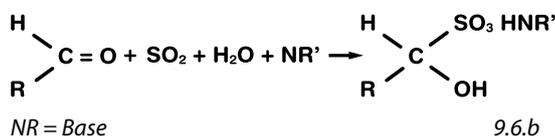
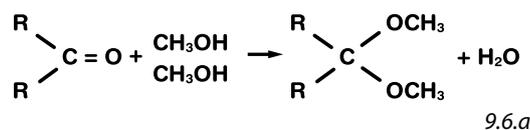
## 9.6 Aldehydes and ketones

Both aldehydes and ketones pose problems with KF titration because they form acetals and ketals respectively with conventional KF reagents (figure 9.6 a). The reaction forms water, which is also titrated, resulting in vanishing end points and erroneously high water content. With aldehydes a second side reaction, the bisulfite addition, can also occur (figure 9.6 b). This reaction consumes water and leads to erroneously low water content [1].

We have investigated the behavior of certain aldehydes and ketones toward the KF titration. The results have been published [1, 11]. The reactivity of aliphatic ketones decreases with increasing chain length. Aromatic ketones are less reactive than aliphatic ketones. Aldehydes are much more reactive than ketones and their tendency to undergo the bisulfite addition is particularly strong.

The formation of acetals and ketals can be suppressed by replacing methanol in the titrating agent with another solvent, typically pyridine and 2-methoxyethanol (methylglycol). However, we found both of these solvents to be unsatisfactory [1, 11]. Pure pyridine alters the stoichiometry of the KF reaction, enhances the bisulfite addition and leads to a falsely low water content. 2-Methoxyethanol does not sufficiently inhibit the formation of both ketals and acetal and results in a slow titration rate. The levels of water are too high and, because only small samples can be analyzed, the accuracy of the titration is negatively affected.

Our research identified suitable solvents that permit determination of water in aldehydes and ketones without adverse side reactions. These solvents are the basis of the HYDRANAL<sup>®</sup> K-type reagents.



### 9.6.1 Volumetric titration

As a result of the challenges with KF titration of aldehydes and ketones, we developed special reagents for their determination by volumetric titration:

HYDRANAL<sup>®</sup>-Composite 5 K<sup>1</sup>  
 HYDRANAL<sup>®</sup>-Working Medium K<sup>2</sup>  
 HYDRANAL<sup>®</sup>-Medium K<sup>3</sup>  
 HYDRANAL<sup>®</sup>-KetoSolver<sup>4</sup>

A detailed description of these reagents is presented in section 2.4. The following abbreviated working procedure provides an introduction to its usage:

#### Procedure 9.6.1.1 Aldehydes and Ketones

20-50 mL HYDRANAL<sup>®</sup>-Working Medium K<sup>2</sup> or HYDRANAL<sup>®</sup>-Medium K<sup>3</sup> or HYDRANAL<sup>®</sup>-KetoSolver<sup>4</sup> are added to the titration vessel and titrated to a stable end point with HYDRANAL<sup>®</sup>-Composite 5 K<sup>1</sup>. The sample is then added and immediately titrated to a stable end point.

By using these reagents and following the recommended titration procedures, the side reactions of acetal or ketal formation and the bisulfite addition are significantly suppressed. Consequently, interferences are not encountered in the titration of aldehydes and ketones. Other techniques can also reduce the influence of these negative side reactions in certain cases, as described in the following discussion.

<sup>1</sup> 34816

<sup>2</sup> 34817

<sup>3</sup> 34698

<sup>4</sup> 34738

Substance	Water content	Total amount	Restriction
<b>Aliphatic ketones</b>			
Acetone	0.064%	10 mL	
Methyl-n-propyl ketone	0.22%	10 mL	
Methyl-iso-butyl ketone	0.041%	10 mL	
Ethyl-iso-butyl ketone	0.39%	10 mL	
Allyl acetone	0.19%	10 mL	
3-Octanone	0.082%	10 mL	
2-Decanone	0.080%	10 mL	
Dihexyl-ketone	0.0086%	5 g	I
Cyclohexanone	0.032%	10 mL	
1,1,1-Trifluoroacetone	0.25%	10 mL	B
Hexachloroacetone	0.12%	5 mL	I
<b>Aromatic ketones</b>			
Acetophenone	0.029%	10 mL	
2-Fluoroacetophenone	0.21%	10 mL	
2,4-Dihydroxyacetophenone	0.021%	5 g	L
2-Aminoacetophenone	0.13 %	10 mL	
Benzylmethyl ketone	0.038%	10 mL	
Benzylacetone	0.64%	10 mL	
Benzophenone	0.0032%	5 g	I
Benzoin	0.043%	2 g	L
<b>Heterocyclic ketones</b>			
2-Acetylpyridine	0.39%	10 mL	B
2-Pyrrolidone	0.058%	10 mL	
N-Methyl-2-pyrrolidone	0.021%	10 mL	
2-Benzoylpyridine	0.016%	10 g	
3-Acetyllindol	0.34%	2 g	L
<b>Diketones</b>			
Diacetyl	0.10%	1 mL	B
Acetylacetone	0.043%	10 mL	
2,5-Hexandione	0.32%	10 mL	
1,2-Cyclohexandione	0.90%	1 g	B
Benzoylacetone	0.037%	10 g	
Benzil (Dibenzoyl)	0.032%	10 g	
Dibenzoylmethane	0.036%	10 g	
<b>Keto-carboxylic acids and derivates</b>			
2-Oxo-propionic acid	1.07%	10 mL	B, A
2-Oxo-butyric acid	0.95%	1 g	B, A
Levulinic acid	0.22%	10 mL	A
3-Phenyl propionic acid	0.020%	5 g	L
2-Acetylbenzoic acid	0.079%	5 g	L, A

(B = bisulfite addition, I = indication interferences, L = limited solubility, A = buffering of acid)

Table 9.6

Substance	Water content	Total amount	Restriction
2-Benzoyl benzoic acid	0.94%	10 mL	
Ethyl acetoacetate	0.52%	10 mL	
Ethyl levulinate	0.057%	10 mL	
Ethyl benzoylacetate	0.033%	10 g	
<b>Aliphatic aldehydes</b>			
Acetaldehyde	0.021%	2 mL	B
Propionaldehyde	0.15%	2 mL	B
n-Butyraldehyde	0.035%	5 mL	B
Crotonaldehyde	0.10%	5 mL	B
Octaldehyde	0.26%	5 mL	B
Glycolaldehyde	0.25%	1 g	B, L
Chloral	0.12%	10 mL	exothermic
Chloral hydrate	10.86%	0.5g	high water content
Bromal		0	I
Paraldehyde	0.018%	10 mL	
Cyclohexane carbaldehyde	0.027%	5 mL	
Diphenylacetaldehyde	0.11%	10 mL	B
Acetaldehyde diethylacetal	0.029%	10 mL	
Bromacetaldehyde diethylacetal	0.043%	10 mL	I
<b>Aromatic aldehydes</b>			
Benzaldehyde	0.13%	5 mL	B
2-Bromobenzaldehyde	0.10%	2 mL	B
Salicylaldehyde	0.027%	10 mL	
3-Hydroxybenzaldehyde	0.22%	5 g	B
2-Anisaldehyde	0.040%	10 mL	B
4-Dimethylaminobenzaldehyde	0.016%	10 g	
Phenylglyoxal	1.00%	0.5 g	B

(B = bisulfite addition, I = indication interferences, L = limited solubility, A = buffering of acid)

Table 9.6 (continued)

The bisulfite addition reaction begins upon addition of the sample to the sulfur dioxide-containing working medium. Therefore, the KF titration should be started immediately to prevent any water present in the titration vessel from undergoing the bisulfite addition. We utilize the "flying start" method whereby the sample is added within 20 seconds of start of the titration. The instrument initiates the titration as soon as the sample is added. Titrators should be programmed to add the reagent rapidly for the same reason. However, commercially available instruments vary greatly in this respect.

Despite such precautions, some of the water can still be bound as bisulfite adduct, especially when titrating aromatic aldehydes. The dissociation of the bisulfite adduct must first occur in order to run a reliable determination of

the water content in the sample. This is possible by using HYDRANAL<sup>®</sup>-K reagents since they sufficiently suppress the formation of acetals and ketals.

The amount of water to be titrated should be low enough so that titrations are not inordinately long. We found sample sizes that contain a total of 10-25 mg H<sub>2</sub>O are ideal. This amount of water consumes 2-5 mL of reagent.

We have investigated the moisture determination of a number of aldehydes and ketones during the development of the HYDRANAL<sup>®</sup>-K reagents. These compounds are listed in Table 9.6. The Table shows the name of the chemical and the water content (column 2). The water content given is for reference only and is not to be taken as a limit. Column 3 lists the size of the

sample that can be titrated in a 25 mL volume of HYDRANAL<sup>®</sup>-Working Medium K<sup>1</sup> or HYDRANAL<sup>®</sup>-Medium K<sup>2</sup>. The entry "10 mL/10 g" represents the largest sample size analyzed. Smaller sample sizes are indicated in column 4 with a designation for the reason of the limited sample size:

B = bisulfite addition

I = indication interferences

L = limited solubility

A = buffering of acid

The data in Table 9.6 shows that the determination of water in most ketones is straightforward. 10 mL samples of aliphatic ketones can be titrated without any interference, even with acetone and cyclohexanone which are particularly reactive. However, trifluoroacetone gives a noticeable bisulfite addition reaction so a "flying start" titration and a verification of end point are required for its reliable determination.

Aromatic ketones and long-chain aliphatic ketones are less reactive and can also be titrated with HYDRANAL<sup>®</sup>-Composite 5<sup>3</sup> and HYDRANAL<sup>®</sup>-Medium K<sup>2</sup> or HYDRANAL<sup>®</sup>-Working Medium K<sup>1</sup> or HYDRANAL<sup>®</sup>-KetoSolver<sup>4</sup> or HYDRANAL<sup>®</sup>-CompoSolver E<sup>5</sup> (the use of HYDRANAL<sup>®</sup>-Composite 5 K<sup>6</sup> is not necessary). Most heterocyclic ketones perform similarly to aromatic ketones. With acetyl pyridine the bisulfite addition is apparently activated by the pyridyl group, and therefore interferes with the water determination.

Diketones usually behave like normal ketones. Exceptions are diacetyl ketone and 1,2-cyclohexandione to a certain extent. The adjacent keto groups, particularly in diacetyl ketone, are very reactive and only small amounts of sample can be analyzed. This is not the case with benzyl ketone presumably due to the aromatic substituents present in this compound.

Keto-carboxylic acids shift the pH of the working medium and delay the course of the titration. Buffering the working medium slightly accelerates the titration and restores the pH.

#### Procedure 9.6.1.2 Keto-carboxylic acids

25 mL HYDRANAL<sup>®</sup>-Medium K<sup>2</sup> or HYDRANAL<sup>®</sup>-Working Medium K<sup>1</sup> or HYDRANAL<sup>®</sup>-KetoSolver<sup>4</sup> or HYDRANAL<sup>®</sup>-CompoSolver E<sup>5</sup> are added to the titration vessel, mixed with 0.1-0.5 g HYDRANAL<sup>®</sup>-Imidazole<sup>7</sup> and titrated to dryness with HYDRANAL<sup>®</sup>-Composite 5 K<sup>6</sup>. The keto-

carboxylic acid sample is then added and titrated in the usual manner.

Keto-carboxylic acids can be titrated according to procedure 9.6.1.2. Exceptions are 2-oxo-propionic acid and 2-oxobutyric acid (α-keto acids), which exhibit a strong tendency to undergo the bisulfite addition. The amounts of HYDRANAL<sup>®</sup>-Imidazole<sup>7</sup> added must be kept small since it enhances the bisulfite addition.

The pH of the working medium is not shifted by the esters of keto-carboxylic acids, and they can be titrated according to procedure 9.6.1.1.

Many aldehydes can be analyzed in a similar manner. The formation of acetals cannot be detected under these titration conditions. On the other hand, the bisulfite addition takes place very rapidly and the sample sizes usually have to be reduced. The "flying start" method is a good way of reducing the influence of the bisulfite addition.

Aromatic aldehydes are less reactive and consequently present fewer problems. Aliphatic aldehydes are more reactive. The formation of acetal with acetaldehyde is particularly strong, and a sample size of only 2 mL should be used for the titration. The reactivity decreases with increasing chain length and the sample size can be increased to 5 mL starting with butyraldehyde (see L 248).

Formaldehyde does not undergo acetal formation and can be titrated with methanolic reagents as in procedure 5.1 or 5.2. However, the total water content cannot be determined. Typically only 50% H<sub>2</sub>O is found in a 35% formaldehyde solution. Part of the water is bound as paraformaldehyde. The total water content can be determined by carrying out the titration at 50 °C according to procedure 8.7 E. Details can be found in Laboratory Reports L 006 and L 386.

A glyoxal solution (40%) behaves similarly to formamide and can be titrated at elevated temperatures (L 267). With a glutaraldehyde solution (50%) we titrated free water at room temperature and total water content at 50 °C.

<sup>1</sup> 34817

<sup>2</sup> 34698

<sup>3</sup> 34805

<sup>4</sup> 34738

<sup>5</sup> 34734

<sup>6</sup> 34816

<sup>7</sup> 37864

### 9.6.2 Coulometric titration

We have also developed reagents for the coulometric determination of water in ketones:

HYDRANAL<sup>®</sup>-Coulomat AK<sup>1</sup>  
HYDRANAL<sup>®</sup>-Coulomat CG-K<sup>2</sup>

The composition of both solutions is described in section 2.4. HYDRANAL<sup>®</sup>-Coulomat AK<sup>1</sup> is the anolyte and is added to the anodic compartment of the titration cell. HYDRANAL<sup>®</sup>-Coulomat CG-K<sup>2</sup> is the corresponding catholyte. Their use in determining water by coulometric titration was discussed in section 5.3. However, certain unique features of this reagent should be mentioned in further detail.

The solvent system of the reagent has been carefully made up to meet the demands of ketone analysis using modern KF instruments. The composition of the reagent has been optimized and should not be altered by the adding other solvents. For the same reason, no more than 20 mL of liquid sample per 100 mL of reagent should be used. The same restrictions apply to the analysis of solids dissolved in solvents. We recommend a 4:1 v/v solution of 2-methoxyethanol and HYDRANAL<sup>®</sup>-Chloroform<sup>3</sup>, or the solvents used individually, because they ensure minimal alteration to the electrolytic properties of the anolyte.

Use of methanol as the solvent is particularly detrimental because it enhances the formation of ketals. The coulometric titration cell must be thoroughly cleaned when replacing conventional methanol-containing coulometric reagents with HYDRANAL<sup>®</sup> K-type reagents. If ketones are analyzed on a regular basis, we recommend having a separate coulometric titration cell dedicated to this analysis to prevent the need for frequent cleaning or the possibility of methanol contamination.

Iodine solutions based on methanol must not be used to dry the reagents used in the ketone titration cell. We recommend the use of HYDRANAL<sup>®</sup>-Composite 5<sup>4</sup> or a solution of iodine in diethylene glycol monoethylether.

The reagent can be used in the usual way for the determination of water in ketones. The samples sizes should be relatively small, preferably 1 mL. The sample size of reactive ketones such as cyclohexanone should only be 0.2 mL or 0.5 mL. Larger samples can cause serious instrument drift and eventually an end point will not be reached. The instrument also influences the sample size.

After several ketone samples have been analyzed in the reagent, the instrument indicates a drift or a residual current. This drift corresponds to the amount of water that the instrument removes per minute. This also means that in a drifting cell there is a continual consumption of reagent. It is therefore understandable that a titration cell that has been used for a number of successive ketone titrations will have a permanent consumption of reagent. The reagent in the cell will be spent within a few days even if it has not been used for the titration of further samples.

Aldehydes can be analyzed with the same reagent but with some restrictions. Aldehydes undergo the same side reactions, but more rapidly than corresponding ketones. The water content of benzaldehyde, representative of aromatic aldehydes, can be determined with an acceptable degree of accuracy if the sample size is restricted to 0.5 mL. Aromatic aldehydes undergo the bisulfite addition and, like ketones, the dissociation of the bisulfite adduct must first occur in order to run a reliable determination of the water content in the sample. The acetal formation with n-butyraldehyde is particularly strong and the delay time of the instrument should not be set too high. This side reaction decreases with increasing chain length. Side reactions predominate in acetaldehyde to such an extent that it cannot be analyzed.

An accurate determination of water in aldehydes should be carried out using the volumetric titration with HYDRANAL<sup>®</sup>-Composite 5 K<sup>5</sup> and HYDRANAL<sup>®</sup>-Medium K<sup>6</sup> or HYDRANAL<sup>®</sup>-Working Medium K<sup>7</sup> or HYDRANAL<sup>®</sup>-KetoSolver<sup>8</sup>. HYDRANAL<sup>®</sup>-Coulomat AK<sup>1</sup> and HYDRANAL<sup>®</sup>-Coulomat CG-K<sup>2</sup> can also be used to investigate other compounds, like hydrocarbons, halogenated hydrocarbons or alcohols. They are not suitable for the analysis of acids and bases.

Using the same reagent for the determination of the water content of a mixture of ketones and other substances is possible if the substance does not chemically react with the ketone. Therefore, alcohols cannot be investigated in the presence of ketones.

<sup>1</sup> 34820

<sup>2</sup> 34821

<sup>3</sup> 37863

<sup>4</sup> 34805

<sup>5</sup> 34816

<sup>6</sup> 34698

<sup>7</sup> 34817

<sup>8</sup> 34738

Compound	Titration procedure
Acetic acid Propionic acid Butyric acid 2-Ethylhexanoic acid Mandelic acid Cinnamic acid Malonic acid Fumaric acid Tartaric acid Citric acid Benzoic acid Salicylic acid Naphthalenecarboxylic acid Indolecarboxylic acid Nicotinic acid	Standard titration procedures (sections 5.1, 5.2 or 5.3)
Dichloroacetic acid Bromoacetic acid Trichloroacetic acid	Neutralization according to procedure 8.6
Formic acid	See discussion in section 9.7 below

Table 9.7

We have found it economical and practical to titrate aldehydes/ketones and other compounds in separate, dedicated cells. The standard reagents for coulometry, HYDRANAL<sup>®</sup>-Coulomat A<sup>1</sup>/AG<sup>2</sup>/AG-H<sup>3</sup>/E<sup>4</sup> and HYDRANAL<sup>®</sup>-Coulomat CG<sup>5</sup>/E<sup>4</sup>, have a significantly higher water capacity than the HYDRANAL<sup>®</sup>-K reagents.

### 9.7 Carboxylic acids, esters and salts

The determination of water in carboxylic acids is usually straightforward provided the acids are soluble. Stronger acids have to be neutralized prior to the titration in order to maintain the pH of the KF system. Certain carboxylic acids (formic acid, acetic acid), tend to undergo side reactions and require special treatment [1]. The esters of carboxylic acids can be analyzed without any difficulty. More problematic are the salts of carboxylic acids since they do not dissolve readily (see section 10.1).

The determination of water can be conducted either volumetrically or coulometrically. We have investigated both methods in detail, and the results have been published [7, 9]. Some of the acids investigated are shown in Table 9.7. Interferences in the determination of carboxylic acids are primarily due to the formation of water during the esterification reaction. This is more

evident when the sensitive coulometric titration is used. Propionic acid is an example. The Water content can be successfully determined volumetrically whereas the interference due to esterification is noticeable when coulometric methods are used.

Dichloroacetic acid exhibits a slight tendency to esterify and must therefore be neutralized. The titration is conducted according to procedure 8.6.

This procedure also applies to other acids [7]. A buffered working medium accelerates the dissolution of citric acid and enables a rapid titration according to procedure 8.6.

The tendency of a carboxylic acid to esterify decreases with increasing chain length. Butyric acid, malonic acid, salicylic acid and many other carboxylic acids do not esterify and can be analyzed according to the standard procedures presented in sections 5.1, 5.2 and 5.3. The

<sup>1</sup> 34807

<sup>2</sup> 34836

<sup>3</sup> 34843

<sup>4</sup> 34726

<sup>5</sup> 34840

solubility of lipophilic (longer chain length) carboxylic acids can be improved by addition of 1-propanol or HYDRANAL®-Chloroform<sup>1</sup> to the working medium (procedures 8.1 and 8.2). Titration at elevated temperatures can also be carried out, and is advantageous for compounds such as stearic acid.

Formic acid is difficult because it is prone to esterification and iodometric oxidation (L 171). The esterification can be suppressed by using a non-methanolic solvent. A 2 mL sample of formic acid can be titrated in HYDRANAL®-Working Medium K<sup>2</sup> according to procedure 8.4 E. The side reaction, presumably oxidation by iodine, is enhanced by attempts to neutralize formic acid (L 171).

Terephthalic acid and similar carboxylic acids are difficult to dissolve. If titrated as a suspension, only the adherent moisture is determined. We dry a 2 g sample at 200 °C in the KF oven and set the instrument for a 30 second delay time. Amino acids are similar in that only the adherent moisture is determined by a titration of the suspension. Amino acids can be analyzed using the oven technique, the drying temperature being optimized for the particular compound.

A titration of esters of carboxylic acids is usually straightforward, as they remain neutral. The solubility in methanol decreases with increasing chain length, and the addition of 1-propanol or HYDRANAL®-Chloroform<sup>1</sup> according to procedures 8.1 and 8.2 respectively, proves helpful.

A coulometric analysis of ethyl acrylate is straightforward. We added HYDRANAL®-Chloroform<sup>1</sup> according to procedure 8.2 for the volumetric determination. Dimethyl terephthalate dissolves only slowly in mixtures of HYDRANAL®-Chloroform<sup>1</sup> and HYDRANAL®-Methanol dry<sup>3</sup>. Since the titration takes a long time, atmospheric moisture can affect the results of the determination of the low water content of the sample. We therefore used a KF coulometer and a drying oven with an oven temperature of 120 °C and a delay time of 30 seconds.

The salts of carboxylic acids can be determined without any difficulty if they are sufficiently soluble. Sodium benzoate is a prime example (L 339). We often carry out such titrations at elevated temperatures (procedure 8.8) and add HYDRANAL®-Formamide dry<sup>4</sup> (procedure 8.3) in order to dissolve the sample as rapidly as possible. We have used these techniques for investigating tripotassium citrate (L 241), diammonium hydrogen citrate, trisodium citrate dihydrate, potassium sodium tartrate-4-hydrate and sodium glutamate.

The water is released at room temperature so slowly from the magnesium salts of aspartic acid and aspartic acid hydrochloride that a titration

<sup>1</sup> 37863

<sup>2</sup> 34817

<sup>3</sup> 34741

<sup>4</sup> 34724

Substance of investigation	HYDRANAL®-Composite		HYDRANAL®-Solv. +Titr.		HYDRANAL®-Coulomat	
	Method	Sample mass	Method	Sample mass	Method	Sample mass
<b>Aliphatic Amines</b>						
n-Propylamine	8.5.0	1.5 g	9.8.T	1.0 g	8.5.C	2.0 g
iso-Propylamine	8.5.0	2.0 g	9.8.T	1.5 g	8.5.C	3.0 g
n-Butylamine	8.5.0	2.0 g	9.8.T	1.5 g	8.5..C	2.0 g
n-Hexylamine	8.5.0	3.0 g	9.8.T	3.0 g	8.5.C	3.0 g
3-Methoxypropylamine	8.5.0	3.0 g	9.8.T	2.0 g	8.5.C	3.0 g
tris-Hydroxymethylaminomethane	8.5.0	3.0 g	9.8.S	3.0 g	8.5.C	2.0 g
2-Aminoethanol	8.5.0	2.0 g	9.8.S	2.0 g	8.5.C	1.0 g
Cyclohexylamine	8.5.0	2.0 g	8.5.T	2.0 g	8.5.C	5.0 g
Dipentylamine	8.5.0	3.0 g	8.5.T	4.0 g	8.5.C	6.0 g
Dicyclohexylamine	8.5.0	3.0 g	8.5.T	2.0 g	8.5.C	15.0 g
Diethanolamine	8.5.0	5.0 g	8.5.T	4.0 g	8.5.C	7.0 g
Triethylamine	8.5.0	4.0 g	8.5.T	4.0 g	8.5.C	7.0 g
N,N-Dimethylethanolamine	8.5.0	3.0 g	8.5.T	2.0 g	8.5.C	7.0 g
Triethanolamine	8.5.0	5.0 g	8.5.T	5.0 g	8.5.C	7.0 g
N,N-Dimethylcyclohexylamine	8.5.0	4.0 g	8.5.T	4.0 g	8.5.C	10.0 g

Substance of investigation	HYDRANAL <sup>®</sup> -Composite		HYDRANAL <sup>®</sup> -Solv. +Titr.		HYDRANAL <sup>®</sup> -Coulomat	
	Method	Sample mass	Method	Sample mass	Method	Sample mass
<b>Aliphatic Amines</b>						
n-Propylamine	8.5.0	1.5 g	9.8.T	1.0 g	8.5.C	2.0 g
iso-Propylamine	8.5.0	2.0 g	9.8.T	1.5 g	8.5.C	3.0 g
n-Butylamine	8.5.0	2.0 g	9.8.T	1.5 g	8.5..C	2.0 g
n-Hexylamine	8.5.0	3.0 g	9.8.T	3.0 g	8.5.C	3.0 g
3-Methoxypropylamine	8.5.0	3.0 g	9.8.T	2.0 g	8.5.C	3.0 g
tris-Hydroxymethylaminomethane	8.5.0	3.0 g	9.8.S	3.0 g	8.5.C	2.0 g
2-Aminoethanol	8.5.0	2.0 g	9.8.S	2.0 g	8.5.C	1.0 g
Cyclohexylamine	8.5.0	2.0 g	8.5.T	2.0 g	8.5.C	5.0 g
Dipentylamine	8.5.0	3.0 g	8.5.T	4.0 g	8.5.C	6.0 g
Dicyclohexylamine	8.5.0	3.0 g	8.5.T	2.0 g	8.5.C	15.0 g
Diethanolamine	8.5.0	5.0 g	8.5.T	4.0 g	8.5.C	7.0 g
Triethylamine	8.5.0	4.0 g	8.5.T	4.0 g	8.5.C	7.0 g
N,N-Dimethylethanolamine	8.5.0	3.0 g	8.5.T	2.0 g	8.5.C	7.0 g
Triethanolamine	8.5.0	5.0 g	8.5.T	5.0 g	8.5.C	7.0 g
N,N-Dimethylcyclohexylamine	8.5.0	4.0 g	8.5.T	4.0 g	8.5.C	10.0 g

is not possible. However, the titration at 50 °C in the presence of HYDRANAL<sup>®</sup>-Formamide dry<sup>1</sup> takes 3-5 minutes.

The disodium salt of ethylenediaminetetraacetic acid (Na<sub>2</sub>EDTA · 2 H<sub>2</sub>O) is similar and also requires the addition of HYDRANAL<sup>®</sup>-Formamide dry<sup>1</sup> and a titration at elevated temperatures (L 012).

### 9.8 Compounds containing nitrogen

The amine bases represent the most important group of compounds that contain nitrogen. This group consists of aliphatic, aromatic and heterocyclic amines. The amines act very differently toward the KF titration but can be classified into 3 groups:

- Weakly basic compounds
- Strongly basic compounds
- Compounds that undergo side reactions

We have investigated a large number of nitrogenous bases and summarized them in Table 9.8.1. The investigation techniques and results are summarized in an extensive

Laboratory Report (L 288). Additional nitrogen compounds can be found in the Index of Laboratory Reports in section 14.2.

Weak basic amines of the first category with pK<sub>b</sub> values above 8 (mainly heterocyclic amines) resemble hydrocarbons and can be analyzed according to the standard procedures given in sections 5.1 and 5.2. A coulometric determination according to procedure 5.3 is also possible.

The second group comprises strongly basic amines, mainly aliphatic amines, which alter the pH of the KF system and cause fading end points. They must be neutralized by the addition of an excess of HYDRANAL<sup>®</sup>-Benzoic acid<sup>2</sup> or HYDRANAL<sup>®</sup>-Salicylic acid<sup>3</sup> to the working medium or by the use of HYDRANAL<sup>®</sup>-Buffer Base<sup>4</sup>, in accordance with procedure 8.5. The sample size must be such that it will be completely neutralized by the benzoic acid or by the HYDRANAL<sup>®</sup>-Buffer Base<sup>4</sup>.

The third group of amines is irregular [1]. A stable end point cannot be achieved with aniline, toluidine, aminophenol and certain diamines, even when they have been neutralized before titration. We presume the presence of a side reaction, although its chemical nature has not been confirmed. It is possibly an N-methylation reaction of the aromatic amine. An oxidation reaction with excess iodine is also conceivable as well as anodic oxidation in coulometry. These side reactions are partly pH dependent and can

<sup>1</sup> 34724

<sup>2</sup> 32035

<sup>3</sup> 37865

<sup>4</sup> 37859

Substance of investigation (continued)	HYDRANAL®- Composite		HYDRANAL®- Solv. +Titr.		HYDRANAL®- Coulomat	
	Method	Sample mass	Method	Sample mass	Method	Sample mass
<b>Diamines</b>						
1,2-Diaminoethane	9.8.0	0.5 g	9.8.S	0.5 g	n.d.	
Diethylenetriamine	9.8.0	1.0 g	9.8.S	0.5 g	n.d.	
Triethylenetetramine	9.8.0	0.5 g	9.8.S	0.5 g	n.d.	
Tetraethylenepentamine	9.8.0	0.5 g	9.8.S	0.5 g	n.d.	
3-(N,N-dimethylamino)-propylamine	9.8.0	1.5 g	9.8.S	1.0 g	n.d.	
Hexamethylenediamine	9.8.0	2.0 g	9.8.S	0.5 g	n.d.	
<b>Cyclic amines</b>						
Pyrrolidine	9.8.0	1.0 g	8.5.T	1.5 g	5.3	1.0 g
Piperidine	8.5.0	3.0 g	8.5.T	3.0 g	5.3	4.0 g
1-Methylpiperidine	8.5.0	3.0 g	8.5.T	3.0 g	5.3	10.0 g
Piperazine	8.5.0	1.5 g	8.5.T	1.5 g	5.3	2.0 g
Morpholine	8.5.0	3.0 g	8.5.T	3.0 g	5.3	10.0 g
<b>Aromatic Amines</b>						
Aniline	9.8.K	5.0 g	9.8.S	1.0 g	8.4.C	1.5 g
o-Toluidine	9.8.K	5.0g	9.8.S	1.0 g	8.4.C	2.0 g
m-Toluidine	9.8.K	5.0 g	9.8.S	1.0 g	8.4.C	1.0 g
4-Anisidine	9.8.K	3.0 g	9.8.S	1.0 g	8.4.C	1.0 g
2-Aminophenol	9.8.K	1.0 g	9.8.S	1.0 g	n.d.	
1-Naphthylamine	9.8.K	5.0 g	9.8.S	2.0 g	8.4.C	2.0 g
N-Methyl aniline	5.1	5.0 g	5.2	5.0 g	8.4.C	10.0 g
N,N-Dimethylaniline	5.1	5.0 g	5.2	5.0 g	8.4.C	10.0 g
N,N-Diethylaniline	5.1	5.0 g	5.2	5.0 g	8.4.C	20.0 g
Diphenylamine	5.1	5.0 g	5.2	5.0 g	8.4.C	5.0 g
1,2-Phenylenediamine	9.8.K	1.0 g	n.d.		n.d.	
1,3-Phenylenediamine	9.8.K	1.0 g	n.d.		n.d.	
4-Methyl-1,2-phenylenediamine	n.d.		n.d.		n.d.	
<b>Heterocyclic amines</b>						
Pyridine	5.1	5.0 g	5.2	5.0 g	5.3	2.0 g
2-Picoline	5.1	5.0 g	5.2	5.0 g	5.3	2.0 g
Chinoline	5.1	5.0 g	5.2	5.0 g	5.3	2.0 g
Imidazole	5.1	5.0 g	5.2	5.0 g	5.3	2.0 g
1-Methylimidazole	5.1	5.0 g	5.2	5.0 g	5.3	2.5 g
Benzimidazole	5.1	1.0 g	5.2	1.0 g	5.3	1.0 g
1,3,5-Triazine	5.1	5.0 g	5.2	5.0 g	5.3	6.0 g
1,2,4-Triazole	5.1	1.0 g	5.2	1.0 g	5.3	5.0 g
Benzothiazole	5.1	5.0 g	5.2	5.0 g	5.3	20.0 g
Pyrrole	5.1	5.0 g	5.2	5.0 g	n.r.	
Indole	5.1	5.0 g	5.2	5.0 g	n.r.	
Carbazole	5.1	0.2 g	5.2	1.0 g	5.3	0.5 g
Nicotine	5.1	4.0 g	5.2	3.0 g	5.3	2.0 g
8-Hydroxychinoline	5.1	5.0 g	5.2	5.0 g	n.r.	
2-Aminopyridine	5.1	5.0 g	5.2	5.0 g	n.r.	
3-Aminopyridine	9.8.0	3.0 g	9.8.T	2.0 g	n.r.	
2-Aminobenzothiazole	9.8.0	5.0 g	9.8.T	2.0 g	n.r.	
n.d. = not determinable , n.r. = not recommended						

Table 9.8.1: Columns 2-4 list the section in this manual where further details of the titration are found, and the mass of the compound investigated.

be suppressed by making the conditions strongly acidic. HYDRANAL<sup>®</sup>-Salicylic acid<sup>1</sup>, and in some cases sulfur dioxide, can be used for this purpose. We recommend the following procedures.

**Procedure 9.8 O Nitrogenous compounds, one-component, volumetric titration**

30 mL HYDRANAL<sup>®</sup>-Buffer Base<sup>2</sup> or 30 mL HYDRANAL<sup>®</sup>-Methanol dry<sup>3</sup> and 5 g HYDRANAL<sup>®</sup>-Salicylic acid<sup>1</sup> are added to the titration vessel. The HYDRANAL<sup>®</sup>-Salicylic acid<sup>1</sup> is added to a funnel, placed in the lid of the titration vessel and washed into the vessel with HYDRANAL<sup>®</sup>-Methanol dry<sup>3</sup>. The solution is titrated to dryness with HYDRANAL<sup>®</sup>-Composite. Then the base under investigation is weighed into the cell and titrated with HYDRANAL<sup>®</sup>-Composite.

**Procedure 9.8 T Nitrogenous compounds, two-component, volumetric titration**

30 mL HYDRANAL<sup>®</sup>-Solvent<sup>4</sup> and 6 g HYDRANAL<sup>®</sup>-Salicylic acid<sup>1</sup> are added to the titration vessel. The HYDRANAL<sup>®</sup>-Salicylic acid<sup>1</sup> is added to a funnel, placed in the lid of the titration vessel and washed into the vessel with HYDRANAL<sup>®</sup>-Solvent<sup>4</sup>. The solution is titrated to dryness with HYDRANAL<sup>®</sup>-Titrant. Then the base under investigation is weighed into the vessel by difference and titrated with HYDRANAL<sup>®</sup>-Titrant in the same way.

**Procedure 9.8 S Nitrogenous compounds, volumetric titration**

15 mL HYDRANAL<sup>®</sup>-Solvent<sup>4</sup> and 15 mL of a methanolic sulfur dioxide solution (3 mol SO<sub>2</sub>/liter) are added to the titration vessel and titrated to dryness using HYDRANAL<sup>®</sup>-Titrant. The base under investigation is weighed into the vessel and titrated in the same way with HYDRANAL<sup>®</sup>-Titrant.

The interferences are more pronounced in coulometric titrations and occasionally cause poisoned electrodes. Coulometry is therefore only marginally suitable. Salicylic acid can also be used for acidification in coulometry, although salicylate anions (if the acid is fully neutralized) can also cause poisoning of electrodes. Therefore, we do not recommend the use of salicylic acid. In certain cases, especially aromatics, a methanol-free working medium is advisable. In these cases, procedure 8.4 is followed. In Table 9.8.1 working methods tested by us and recommended sample sizes are given. For coulometry the given sample weight is the sum of approximately 10 to 20 equally sized samples.

Certain compounds give more reliable titrations in a methanol-free and acidified working medium, for example aniline (L 030), ethylenediamine (L 027) or diethylenetriamine and homologous molecules (L 026). Procedure 9.8 K can be used for these compounds. The sample size is limited with these compounds because the side reaction cannot be fully suppressed.

**Procedure 9.8 K Reactive nitrogenous compounds**

25 mL HYDRANAL<sup>®</sup>-Working Medium K<sup>5</sup> and 5 g HYDRANAL<sup>®</sup>-Salicylic acid<sup>1</sup> are added to the titration vessel and titrated to dryness using HYDRANAL<sup>®</sup>-Composite 5<sup>6</sup>. Then a maximum of 30 mmol amine base is added. The water content is titrated with HYDRANAL<sup>®</sup>-Composite 5<sup>6</sup>. The determination of water in acid amides does not present any difficulties. They can be analyzed according to the standard procedures 5.1, 5.2 and 5.3.

Compound	Titration procedure
Formamide N,N-Dimethylformamide Chloroacetamide N,N-Dimethylacetamide Urea	Standard titration procedures (sections 5.1, 5.2 or 5.3)

Table 9.8.2

<sup>1</sup> 37865

<sup>2</sup> 37859

<sup>3</sup> 34741

<sup>4</sup> 34800

<sup>5</sup> 34817

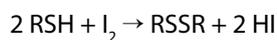
<sup>6</sup> 34805

The titration of nitro-compounds is equally straightforward. They can be analyzed according to the standard procedures 5.1, 5.2 and 5.3. However, nitrocompounds are chemically reduced in coulometry without a diaphragm and cannot be titrated with this method.

Determination of the water content of hydroxylamine and hydrazine salts is difficult since both compounds are oxidized by iodine in neutral solutions and a titration is only possible in strongly acidic conditions. A water determination with HYDRANAL<sup>®</sup>-Composite does not allow a pH adjustment in the solvent and, therefore, hydroxyammonium salts give erroneously high water content. Indication irregularities occur with hydrazine.

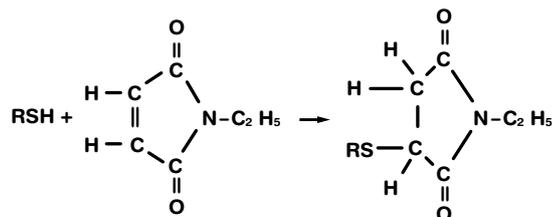
## 9.9 Compounds containing sulfur

Most sulfur-containing compounds, like sulfides, disulfides and sulfonic acids do not present any difficulty in the determination of their water content. The mercaptans (thiols) are an exception because they are oxidized by the iodine and the water content is erroneously high. This oxidation is rapid and quantitative and can thus be utilized for the removal of thiols.



We investigated this technique with cysteine hydrochloride monohydrate [3]. The sulfide group is first iodometrically oxidized in the titration vessel with HYDRANAL<sup>®</sup>-Titrant using HYDRANAL<sup>®</sup>-Formamide<sup>1</sup> as the solvent (i.e. in the absence of sulfur dioxide). HYDRANAL<sup>®</sup>-Solvent<sup>2</sup> is then added and titrated with HYDRANAL<sup>®</sup>-Titrant. The water is thereby determined.

Details of this analysis can be found in the literature [3]. The water content of all solvents used must be determined by a blank titration and corrected for in the calculations. This method appears to be applicable only to samples with relatively high water content. The coupling of thiols of low water content to N-ethylmaleimide, according to Francis and Pershing, appears to be more suitable. This method can also be used for cysteine. We have investigated N-acetylcysteine (L 315), L-cysteine hydrochloride (L 316, 317), S-carboxymethyl-L-cysteine (L 318).



We also verified this method with 1-octanethiol (L 032), thioglycolic acid (L 256), ethylthioglycolate (L 280) and glycerinemonothioglycolate (L 173).

### Procedure 9.9 Sulfur-containing compounds

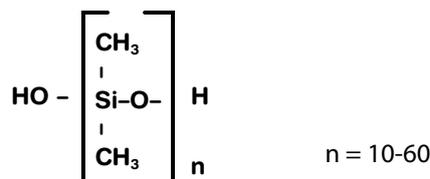
20 mL HYDRANAL<sup>®</sup>-Methanol dry<sup>3</sup>, 5 mL HYDRANAL<sup>®</sup>-Buffer Acid<sup>4</sup> and 1 g N-ethylmaleimide (8 mmol) are added to the titration vessel and titrated to dryness with HYDRANAL<sup>®</sup>-Composite, after which 0.5 g (approximately 3.3 mmol) 1-octanethiol are added. The conversion is complete after about 5 minutes and the free water can then be determined using HYDRANAL<sup>®</sup>-Composite.

We could determine water content <0.1% using this method. This analytical technique can also be applied to other mercaptans if the above referenced (and optimized) ratios can be maintained.

The behavior of dimethylsulfoxide is very unusual (L 141). Although stable end points are obtained in the presence of dimethylsulfoxide, the recovery rates for water are erroneously low. The recovery rate is reduced to 95% by 5% DMSO by volume and to 80% by 25% DMSO in methanolic solutions. The use of DMSO as a solvent is questionable and should be closely scrutinized.

## 9.10 Siloxanes, silanols

Difficulties are encountered in the determination of water in dimethylpolysiloxanediol having the following structure:



<sup>1</sup> 34724

<sup>2</sup> 34800

<sup>3</sup> 34741

<sup>4</sup> 34804

The outer silanol groups etherify with the methanol in the reagent and the end point of the KF titration fades. A titration using a methanol-free reagent is possible (L 057). A comparison of both titrations is given by diagrams 8.12.3 and 8.12.4.

#### Procedure 9.10.1 Siloxanes

30 mL HYDRANAL<sup>®</sup>-Working Medium K<sup>1</sup> are added to the titration vessel and titrated to dryness with HYDRANAL<sup>®</sup>-Composite 5<sup>2</sup>. 5 g siloxane are then weighed and added. The water content is titrated with HYDRANAL<sup>®</sup>-Composite 5<sup>2</sup>. Stop time: 10 seconds.

The water content of methyl hydrogenpolysiloxane can be determined using the same procedure.

It is also possible to accelerate the etherification of the silanol groups catalytically to an extent that the water thereby formed can be titrated. This is an indirect analysis of silanol groups using KF reagents. Boron trifluoride is used as the catalyst and its amount is chosen to maintain a pH of 2.5-3. HYDRANAL<sup>®</sup>-Chloroform<sup>3</sup> is added to improve the solubility. The etherification is further enhanced by a temperature of 50 °C.

#### Procedure 9.10.2 Siloxanes, elevated temperatures

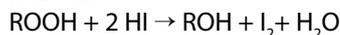
20 mL HYDRANAL<sup>®</sup>-Solvent<sup>4</sup>, 30 mL HYDRANAL<sup>®</sup>-Chloroform<sup>3</sup> and 4 mL boron trifluoride-diethyl ether complex are added to the titration vessel, heated to 50 °C and titrated to dryness with HYDRANAL<sup>®</sup>-Titrant. Approximately 0.5 g siloxane are then added and titrated.

## 9.11 Peroxides

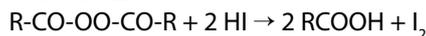
We have investigated the water determination of some peroxides (L 279).

Iodine is formed with the Karl Fischer reagent according to two possible reactions.

Reaction 1:



Reaction 2:



For one side, the hydroperoxides produce equimolar amounts iodine and water, which can be reacted with a sufficient excess of sulfite so that the KF titration is not disturbed (Reaction 1). All other peroxides react according to Reaction 2, although with different reaction rates. The water determination is carried out at lower temperatures in order to suppress side reactions. An overview is given in the following table.

For details, refer to titration methods in section 8.7, literature publication [15] and Laboratory Report L 279.

Hydroperoxide ROOH	$\text{I}_2 + \text{H}_2\text{O}$	immediate	$\text{SO}_2$ excess
Perester R-CO-OO-R'	$\text{I}_2$	slow	0 °C
Diacylperoxide R-CO-OO-CO-R'	$\text{I}_2$	fast	-20 °C
Percarbonate R-O-CO-OO-CO-O-R'	$\text{I}_2$	very fast	-40 °C

Table 9.11

<sup>1</sup> 34817

<sup>2</sup> 34805

<sup>3</sup> 37863

<sup>4</sup> 34800

## 10. Inorganic compounds

The chemical structures of inorganic compounds differ very greatly, and substances must be differentiated and treated individually if necessary [1]. A number of common fundamental rules are given in this section, together with recommendations of working procedures.

### 10.1 Salts

Salts of inorganic and organic acids as well as other crystalline compounds can comprise water in various ways:

- Water of crystallization
- Included water
- Adherent moisture

The method used to determine the water content can sometimes differentiate between adherent moisture and water of crystallization or included water.

#### 10.1.1 Water of crystallization

The water of crystallization can only be determined quantitatively when the sample can be dissolved in a suitable solvent. Suitable solvents are methanol and HYDRANAL®-Solvent<sup>1</sup> in accordance with procedures 5.1 and 5.2. The addition of HYDRANAL®-Formamide dry<sup>2</sup> according to procedure 8.3 or a titration at elevated temperatures according to procedure 8.8 can also be utilized. Usually the working conditions should ensure that the sample dissolves within 3-5 minutes. We have analyzed a number of hydrates as summarized in Table 10.1.1.

<sup>1</sup> 34800

<sup>2</sup> 34724

Compound	Titration procedure
Aluminum sulfate octadecahydrate	Titration according to standard procedures (sections 5.1, 5.2) or addition of formamide (section 8.3)
Ammonium iron (II) sulfate hexahydrate	
Ammonium oxalate monohydrate	
Barium acetate monohydrate	
Barium chloride dihydrate	
Cadmium acetate dihydrate	
Calcium chloride dihydrate	
Iron (II) chloride tetrahydrate	
Iron (II) sulfate heptahydrate	
Potassium sodium tartrate tetrahydrate	
Potassium oxalate monohydrate	
Copper sulfate pentahydrate	
Magnesium acetate tetrahydrate	
Magnesium chloride hexahydrate	
Magnesium sulfate hexahydrate	
Manganese (II) chloride tetrahydrate	
Disodium hydrogenphosphate-12-hydrate	
Sodium hypophosphite monohydrate	
Sodium tartrate dihydrate	
Nickel sulfate hexahydrate	
Zinc sulfate heptahydrate	
Zinc sulfate monohydrate	

Table 10.1.1

Compound	Titration procedure
Ammonium chloride	Titration according to standard procedures (sections 5.1, 5.2) or addition of formamide (section 8.3)
Ammonium nitrate	
Potassium chloride	
Potassium fluoride (L 244)	
Potassium hexafluorophosphate (L 247)	
Potassium hydrogen fluoride	
Potassium iodide	
Potassium nitrate	
Sodium dihydrogen phosphate	
Sodium iodide	

Table 10.1.2

The solubility of the different salts varies greatly. Zinc sulfate heptahydrate dissolves very quickly and the titration of the water content is straightforward. Zinc sulfate mono-hydrate dissolves slowly and incompletely and not all of the water is titrated. The water of crystallization in manganese sulfate monohydrate cannot be titrated because this substance is insoluble.

Problems can be encountered with the salts of copper. When the two-component reagent is used, the instrumental indication shows an immediate end point. Cupric ions apparently depolarize the indicator electrodes. This interference is not observed when HYDRANAL®-Composite is used. The water contents found are 0.5 mol too low as the cupric copper has an oxidizing effect in the KF solution [1].

Iron (III) salts behave similarly. Titration of iron (III) chloride-6-hydrate was possible with HYDRANAL®-Composite (L 023). With sodium molybdates (L 231) the water content found is far too high. Potassium hexacyanoferrate (II)-3-hydrate can only be titrated with the one component reagent HYDRANAL®-Composite (L 334).

When substances dissolve slowly, as is the case with barium chloride dihydrate or cadmium acetate dihydrate, finely grinding the sample can help.

With certain hydrates, the water of crystallization can be titrated without the sample actually dissolving. An example of such a hydrate is calcium hydrogen phosphate dihydrate,  $\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}$ , which can be titrated at 50 °C in the presence of HYDRANAL®-Formamide dry<sup>1</sup> within 20 minutes using the two-component reagent. Such substances can be titrated as suspensions, though care must be taken to ensure that the water content diffuses out of the

crystal lattice. The titration time can be reduced by grinding the sample.

The hydrates of calcium sulfate are somewhat unique. The water of crystallization in calcium sulfate dihydrate cannot be titrated, whereas the water of the hemihydrate (fired plaster) can be.

### 10.1.2 Entrapped moisture

Many anhydrous crystalline salts include approximately 0.1-0.3% water; this causes the product to harden during storage. The same is true of organic crystalline substances, e.g. sugar. This entrapped moisture can only be determined by volumetric analysis when the substance completely dissolves. A titration according to procedures 5.1 or 5.2 can then be conducted. The addition of HYDRANAL®-Formamide dry<sup>1</sup> can help in many cases (procedure 8.3). A number of substances investigated are given in Table 10.1.2.

Another method to determine the amount of entrapped water is by using of a drying oven. Some substances release entrapped moisture at temperatures around 300 °C, so that the combination of a drying oven and a KF instrument, as described in procedure 8.11, could be used. We have analyzed iron (III) salts (L 023), iron (III) pyrophosphate (L 252) and trimagnesium phosphate (L 250) with this method.

### 10.1.3 Adherent moisture

If only the adherent moisture on the surface of the sample is to be determined, the

<sup>1</sup> 34724

Compound	Titration procedure
Aluminum oxide Chromium dioxide Iron (III) oxide Bismuth oxide Tin (IV) oxide Calcium carbonate	Titration according to standard procedure 5.1 or 5.2
Antimony oxide Copper (II) oxide Manganese (IV) oxide	Buffer with HYDRANAL®-Buffer Acid according to 8.5
Lead (II) oxide Calcium oxide Calcium peroxide Magnesium oxide Mercury oxide Silver oxide Zinc oxide Zinc peroxide Sodium hydrogen carbonate Potassium hydrogen carbonate	React rapidly with KF reagents

Table 10.2

dissolution of the substance must be prevented. Furthermore, the titration should be conducted very swiftly in order to prevent the diffusion of water of crystallization or entrapped moisture into the titration. We use the following procedure that uses a high proportion of HYDRANAL®-Chloroform<sup>1</sup> to prevent dissolution:

#### Procedure 10.1.3 Inorganic salts, adherent moisture

5 mL HYDRANAL®-Solvent<sup>2</sup> and 20 mL chloroform are added to the titration vessel and titrated to a stable end point. A large sample, 2-5 g, is then added and immediately titrated with HYDRANAL®-Titrant to a 5 second end point. If a partial dissolution of the sample cannot be prevented, a graphical evaluation of the titration, as described in section 8.12, can be conducted to distinguish between adherent moisture and water of crystallization.

## 10.2 Acids, oxides and carbonates

Two important points must be made when determining the water content of acids. First, the acids must be neutralized to prevent a shift in the working pH of the KF solution. Second, certain acids tend to undergo esterification that forms water and gives falsely high results [1].

The working technique as described in section 8.6 is therefore employed for the titration of acids, i.e. the acids are neutralized in the titration vessel with HYDRANAL®-Imidazole<sup>3</sup> or HYDRANAL®-Buffer Acid<sup>4</sup>. This method only applies to aqueous acids.

Concentrated acids like gaseous hydrogen chloride or 96% sulfuric acid would undergo partial esterification with methanol and lead to erroneously high water contents. They must be neutralized in a methanol-free medium beforehand.

Procedure 10.2 Acids, oxides and carbonates  
A 100 mL measuring flask is filled with 50 mL dry (<0.01% H<sub>2</sub>O) pyridine. Approximately 5 g of the acid to be determined are then accurately weighed out and added to the flask. After cooling to room temperature, the pyridinium salt precipitate is brought into solution by filling

<sup>1</sup> 37863

<sup>2</sup> 34800

<sup>3</sup> 37864

<sup>4</sup> 34804

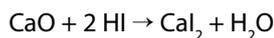
the flask to the 100 mL mark with HYDRANAL<sup>®</sup>-Methanol dry<sup>1</sup>. An aliquot of this is taken and its water content determined according to procedure 5.1 or 5.2.

The calculation of the water content of the acid must take the water content of the pyridine and the methanol into account. These values must be determined separately.

Sulfuric acid (L 049) and sulfuric acid/hydrofluoric acid mixtures (L 050) are analyzed according to this procedure. A special procedure has been established for anhydrous hydrofluoric acid. This acid is determined directly in a mixture of HYDRANAL<sup>®</sup>-Methanol<sup>1</sup> and HYDRANAL<sup>®</sup>-Imidazole<sup>2</sup>.

Dodecylbenzene sulfonic acid has to be neutralized with HYDRANAL<sup>®</sup>-Buffer Acid<sup>3</sup> (L 337).

KF solutions are always weakly acidic and can react with oxides, CaO for example:



The water formed in the reaction is also titrated. This reaction is quantitative with strongly basic oxides, and can occur so quickly that the amounts of water liberated actually correspond to the stoichiometry. Other oxides react sluggishly and the reaction can be sufficiently suppressed by buffering the medium to pH 7 to enable an accurate determination of the water content. A number of fired oxides are stable and no difficulties are encountered. Hydroxides, carbonates and certain salts of weak acids have titration behavior similar to the oxides.

Fired antimony oxide can be titrated directly; precipitated antimony oxide dissolves only slowly. When working with these compounds, we recommend benzyl alcohol as the working medium and titrating to a 5 second end point. Precipitated manganese dioxide is very reactive and requires an immediate titration in a buffered medium. Sodium hydrogen carbonate and potassium hydrogen carbonate react quantitatively with the KF reagent and the stoichiometrically formed water (1 mol/mol NaHCO<sub>3</sub>) can be subtracted in the calculations.

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<sup>1</sup> 34741

<sup>2</sup> 37864

<sup>3</sup> 34804

## 11. Foods and natural products

Food and other natural products are often subject to moisture analysis. Moisture affects shelf life, packaging properties and texture of foods and the careful control is necessary to maintain product quality. We have investigated the determination of water in food products extensively over the past years. Data on specific products [10] as well as a summary of techniques have been published [1]. We have found that KF titration is more reliable than determining the water content by the loss on drying method. We typically recommend volumetric titration for solid food products that are insoluble in usual KF working media.

Because foods often contain complex cellular structures that release water very slowly even if finely divided, we often combine titration at elevated temperatures (procedure 8.8) with an addition of HYDRANAL<sup>®</sup>-Formamide<sup>1</sup> (procedure 8.3). We have also carried out titrations in boiling HYDRANAL<sup>®</sup>-Methanol dry<sup>2</sup> (procedure 8.9), a method that proves very advantageous for a large number of food samples.

It is impossible to define one titration method that works for all compounds; each product requires an individual treatment because of the disparate solubility and chemical stability properties. Therefore, we have developed many product-specific procedures for commonly-analyzed food substances.

### 11.1 Carbohydrates

The adherent moisture of saccharose (sucrose) is of primary interest. It is determined in a working medium of high chloroform content (80% HYDRANAL<sup>®</sup>-Chloroform<sup>3</sup>, 20% HYDRANAL<sup>®</sup>-Methanol dry<sup>2</sup>, v/v) following procedure 8.2 (L 073). Saccharose (sucrose) must be completely dissolved in order to determine the total, i.e. entrapped as well as adherent water content. A

working medium containing 50% HYDRANAL<sup>®</sup>-Formamide<sup>1</sup> by volume (L 073) according to procedure 8.3 is preferred.

Glucose, maltose and honey (L 233) fully dissolve at room temperature, but can also be titrated at 50 °C [10]. Galactose, fructose, lactose and mannitol (L 210) require the addition of HYDRANAL<sup>®</sup>-Formamide<sup>1</sup> according to procedure 8.3. At 50 °C the standard procedure without HYDRANAL<sup>®</sup>-Formamide<sup>1</sup> can be employed (L 168).

Fondant (saccharose and glucose syrup) requires the addition of HYDRANAL<sup>®</sup>-Formamide<sup>1</sup> and titration at 50 °C (L 322).

Glucose-based molasses does not dissolve satisfactorily in methanol and adheres to the electrodes, requiring the addition of HYDRANAL<sup>®</sup>-Formamide dry<sup>1</sup> according to procedure 8.3 (L 105). The same applies to starch syrup (L 213), molasses (L 227), penetrose (L 071), and saccharose-based fruit gums (L 099, L 100).

Sugar replacements like sorbitol (L 320) or xylite (xylitol) (L 324) need HYDRANAL<sup>®</sup>-Formamide dry<sup>1</sup>.

The water content of potato starch must also be measured at elevated temperatures according to procedure 8.8 (L 072) because the water is released slowly and incompletely at room temperature. The same is true of wheat flour (L 068). Wheat grits are coarse and must be finely ground before a titration at 50 °C is possible (L 067). A titration in boiling HYDRANAL<sup>®</sup>-Methanol dry<sup>2</sup> according to procedure 8.9 is preferred.

### 11.2 Fats and fatty products

Fats present a problem because of their poor solubility in methanol. Chloroform or long chain alcohols are often used as a solvent agent [1, 10].

Sunflower oil can be titrated according to procedure 8.2 with an addition of HYDRANAL<sup>®</sup>-Chloroform<sup>3</sup> to the working medium. The sample is added using a plastic syringe without the needle due to its viscosity. A titration agent of low titer should be chosen for the titration (L 075) as the water content is very low (approximately 0.01%). The same is applicable to

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peanut oil and rape seed (canola) oil (L 319). We found a slight post-consumption of reagent with several oils that could be due to a side reaction (L 063). We therefore recommend a rapid titration and a 5 second end point.

The same chloroform-containing solvent is used for the moisture analysis of margarine. The sample is added using a Teflon® spatula or a syringe without the needle. The margarine should be homogenized before addition (L 083). The same considerations apply for the moisture analysis of butter (L 104).

The water content of lard and other hard fats is low and titration agents of low titer are preferred, like HYDRANAL®-Composite 2<sup>1</sup> or HYDRANAL®-Titrant 2<sup>2</sup> (L 098).

Mayonnaise is titrated in a HYDRANAL®-Methanol dry<sup>3</sup>-HYDRANAL®-Chloroform<sup>4</sup> medium according to procedure 8.2. A plastic syringe without a needle is used to add the sample (L 084). A titration agent with a high titer (HYDRANAL®-Composite 5<sup>5</sup> or HYDRANAL®-Titrant 5<sup>6</sup>) should be used because of the high water content.

### 11.3 Dairy and proteinaceous products

Because its water content is high, difficulties during the KF titration of milk are rarely encountered. Standard procedures in 5.1 or 5.2 are followed. The milk must be homogenized prior to taking the sample. For accuracy, the sample should be added to the titration vessel carefully using a plastic syringe with needle. The sample weight is calculated by the difference in weight technique (L 085).

The technique used for milk can be applied to coffee cream [10], yogurt (L 097) and curds (L 074). All samples must be thoroughly homogenized. Viscous samples should be added to the cell using a plastic syringe without the needle.

High and low fat milk powders (L 081, L 082) can be analyzed using standard titration techniques. Because the titrations can take as long as ten minutes, we prefer to conduct such titrations at elevated temperatures (procedure 8.8). The addition of HYDRANAL®-Chloroform<sup>4</sup> helps to distribute the fats of high-fat milk. We have found KF titration to be more reliable than determining the water content by the loss on drying method.

Dairy fat emulsions tend to deposit on the vessel walls and indicator electrodes. To avoid this, we recommend a 1:1:1 mixture of HYDRANAL®-Methanol dry<sup>3</sup>, HYDRANAL®-Formamide dry<sup>7</sup> and HYDRANAL®-Chloroform<sup>4</sup> by volume as the working medium (L 077).

Cheese presents a problem because water does not extract from it easily. To overcome this problem, we finely grate the sample beforehand, use a HYDRANAL®-Methanol dry<sup>3</sup>-HYDRANAL®-Formamide dry<sup>7</sup> mixture as the working medium (procedure 8.3), and titrate at elevated temperatures (L 095).

Dried egg powders are amenable to KF titration. A mixture of HYDRANAL®-Methanol dry<sup>3</sup> and HYDRANAL®-Formamide dry<sup>7</sup> according to procedure 8.3 is also used for the determination of water in dried egg white at elevated temperatures (L 163). We have also applied the same method to the determination of water in egg yolk (L 103).

### 11.4 Vegetable-based products

Vegetable-based products are often difficult to titrate using the KF method because the water is usually released slowly and incompletely from the sample matrix. As an example, extraction of soya grits for 24 hours at room temperature in methanol did not extract all of the water in the sample. As a result, titration at 50 °C is the preferable method for these samples. This method has been successfully used for the analysis of starches and flour (refer to section 11.1). Our investigations with roasted coffee show that titration in boiling HYDRANAL®-Methanol dry<sup>3</sup> can also improve the extraction. The coffee is finely ground and titrated using the apparatus described in procedure 8.9. The titrations are rapid and the results are reliable. We have used the same technique for the analysis of coffee beans. We previously used pre-extraction techniques for the determination of water in roasted coffee. The water content of the roasted coffee sample was extracted at 50-60 °C using HYDRANAL®-Methanol dry<sup>3</sup>. A part of the extract

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was subsequently titrated. Raw coffee can be titrated under same conditions (L 335).

Coffee extracts (instant coffee) should be titrated at room temperature in the presence of formamide. The water content is released too slowly using pure methanol. Certain differences exist between spray tower dried and freeze dried instant coffees (L 092). We also recommend the addition of HYDRANAL<sup>®</sup>-Salicylic acid<sup>1</sup> in order to suppress a side reaction caused by a by-product. The titration can be carried out according to procedure 8.3.

Cocoa powder is measured at elevated temperatures according to procedure 8.8 (L 094). The titration takes approximately 10 minutes. This is another example where we recommend titration in boiling methanol. The beans are finely milled in a laboratory grinder equipped with a cooling jacket. The titration is carried out in the presence of formamide at 50 °C (L 093).

Ginger also requires the addition of HYDRANAL<sup>®</sup>-Formamide dry<sup>2</sup> and titration at 50 °C (L 341).

Almonds should be finely ground prior to titration at 50 °C in the presence of HYDRANAL<sup>®</sup>-Formamide dry<sup>2</sup> (L 086 and L 295).

We have also carried out titrations of corn, wheat and other grains at 50 °C and confirmed their reproducibility and repeatability when using HYDRANAL<sup>®</sup>-Reagents.

With wheat flour (L 329), wheat semolina (L 331) and rusks (L 332) we also have applied the tube furnace combined with the KF titrator.

We have also studied the KF titration of snuff (finely pulverized tobacco) at 50 °C and found the addition of HYDRANAL<sup>®</sup>-Formamide dry<sup>2</sup> according to procedure 8.3 beneficial. The water content of tobacco stems, which contain very coarse particles, could only be measured by titration in boiling HYDRANAL<sup>®</sup>-Methanol dry<sup>3</sup>.

### 11.5 Chocolates, sweets, toffees

An analysis of chocolate requires an addition of HYDRANAL<sup>®</sup>-Chloroform<sup>4</sup> to dissolve the fats. We recommend the procedure outlined in section 8.2. If the chocolate sample is first cut into very small pieces, a suspension can be made within minutes. The water content of the suspension can then be easily titrated (L 071 and L 079).

The addition of HYDRANAL<sup>®</sup>-formamide dry<sup>2</sup> to the working medium (procedure 8.3) aids the extraction and titration of toffee at elevated temperatures and maltitol-based candies at room temperature (L 309). The sample added in the form of fine flakes dissolves in 3-5 minutes (L 069 and L 224). Mamba<sup>®</sup> brand toffees (chewy fruit-flavored toffees) are also titrated at 50 °C in the presence of HYDRANAL<sup>®</sup>-Formamide dry<sup>2</sup> according to procedure 8.3 (L 091). Thinly sliced wine gums are analyzed in a similar fashion (L 066). Marzipan is added to a HYDRANAL<sup>®</sup>-Methanol dry<sup>3</sup>/HYDRANAL<sup>®</sup>-Chloroform<sup>4</sup> mixture according to procedure 8.3 in the form of flakes and titrated at 50 °C (L 080 and L 232). Licorice also benefits by the addition of HYDRANAL<sup>®</sup>-Formamide dry<sup>2</sup>. The titration is carried out according to procedure 8.3 (L 088).

Chewing gum necessitates a separate extraction of water (L 308).

Usually the use of a homogenizer in the titration vessel shortens the time for dissolution, and in some cases can avoid the need for HYDRANAL<sup>®</sup>-Formamide dry<sup>2</sup> addition.

### 11.6 Bakery products, pastas

Light pastries, like biscuits (L 078) and rusks (L 064), must be finely milled using a laboratory grinder. They are then titrated at 50 °C in the presence of formamide. The same method is used for the analysis of noodles and pasta (L 076).

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## 12. Medicines and cosmetic products

Moisture content affects the shelf-life, tablet stability and efficacy of most drugs. Karl Fischer titration has been a standard method in the leading pharmacopoeias for the last forty years. The determination of the water content is obligatory for many chemicals used in the manufacture of medicines. The different pharmacopoeias prescribe differing analytical techniques. A direct titration of the water content is the preferred method, though back titrations are sometimes warranted. The end point is usually determined amperometrically, although visual end point determinations are possible. The solvents and sample sizes are prescribed in the individual methods.

The pharmacopoeias also describe the manufacture of the KF reagent solutions. The European Pharmacopoeia (Ph. Eur.) describes a reagent solution consisting of 700 mL ethylene glycol monomethyl ether, 700 mL pyridine, 200 g iodine and 190 g liquid sulfur dioxide. The United States Pharmacopoeia (USP) recommends a reagent solution comprising of 670 mL methanol, 270 mL pyridine, 125 g iodine and an indefinite amount of gaseous sulfur dioxide.

The reagents as described in these pharmacopoeial methods are not commercially available. Consequently, the use of HYDRANAL<sup>®</sup>-reagents for titration of drug substances is permitted by both pharmacopoeias and is much more convenient than preparing the individual reagent solutions. The USP states: "A commercially available, stabilized solution of Karl Fischer reagent may be used. Commercially available reagents containing amines other than pyridine and/or alcohols other than methanol may also be used." The same is true for the Ph. Eur. It permits the use of "other methods ... provided that the same results ... will be achieved." We have carried out a variety of comparison tests of the Ph. Eur. reagent versus HYDRANAL<sup>®</sup>-Composite 5<sup>1</sup>. These tests are available upon request.

In addition to defining the reagents, the pharmacopoeias prescribe the analytical procedures for the listed products. HYDRANAL<sup>®</sup>-Reagents can be used for all of these procedures. Besides the products specifically listed in the pharmacopoeia, the water content of many other drug and cosmetic products must be

measured. We have investigated a number of products and formulations using the methods described below.

Methanol is not a good solvent for herbs; neither extracts nor suspensions give reliable titrations. By adding HYDRANAL<sup>®</sup>-Chloroform<sup>2</sup> according to procedure 8.3, a rapid titration and a stable end point is assured (L 138).

The determination of the water content of suppository aids, which are waxed-based, involves dissolving the sample in a working medium containing HYDRANAL<sup>®</sup>-Chloroform<sup>2</sup> and titrating at elevated temperatures (procedure 8.2). A titrant of low titer should be used if the water content of the sample is low.

Amylase-containing samples benefit by the addition of HYDRANAL<sup>®</sup>-Formamide dry<sup>3</sup> (procedure 8.3), which improves the dispersion and enables a rapid titration (L 149).

Viscous lecithin samples benefit by the addition of both HYDRANAL<sup>®</sup>-Chloroform<sup>2</sup> and HYDRANAL<sup>®</sup>-Formamide dry<sup>3</sup> (L 333).

Penicillin can be difficult to analyze because it contains penicilloic acid and other hydrolysis products of penicillin that are also oxidized by iodine and lead to erroneously high results. This side reaction can be suppressed by titrating in weakly acidic conditions. We follow procedure 8.4 C for the coulometric determination of water, but first add 20 g HYDRANAL<sup>®</sup>-Salicylic acid<sup>4</sup> to acidify 100 mL HYDRANAL<sup>®</sup>-Coulomat A<sup>5</sup>. We have successfully analyzed penicillin G procaine, penicillin G Na, penicillin G K and tetracycline HCl using this method. The procedures 8.4 O and 8.4 T apply for volumetric methods of determining the water content (L 166). Benzyl penicillin procaine is described in Laboratory Report L 307.

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Erythromycin is titrated quite easy using HYDRANAL®-Reagents (L 242), whereas fading end points are found with the pyridine-containing reagents. Dobutamine hydrochloride monohydrate requires an addition of HYDRANAL®-Salicylic acid<sup>1</sup> (L 230) in order to suppress a side reaction. For adenosine-5'-triphosphoric acid disodium salt, increasing the pH with HYDRANAL®-Buffer is advisable (L 249). The mono-phosphate can be titrated with the standard method.

With many organic salts, the addition of HYDRANAL®-Formamide dry<sup>2</sup> in combination with titration at 50 °C improves the titrations. This is the case for magnesium aspartate (L 010 and L 268), magnesium lactate (L 225), calcium glycerophosphate (L 251), calcium gluconate (L 259) or caffeine (L 024). For arginine aspartate the addition of HYDRANAL®-Salicylic acid<sup>1</sup> is additionally advisable (L 298).

Glycerine monostearate requires the addition of HYDRANAL®-Chloroform<sup>3</sup> or titration at 50 °C to aid solubility (L 297).

Medicines for intravenous injections are sometimes supplied as dry substrates in order to prolong their shelf-life. The residual water content significantly affects shelf-life and can be specified to be as low as <100 µg H<sub>2</sub>O per ampoule. The determination of water as such low levels can be difficult, mostly because of the possible contamination by extraneous moisture once the ampoule seal has been broken. If the substance is dissolved by injecting HYDRANAL®-Methanol dry<sup>4</sup> into the ampoule through the lyophilization stopper, a correction factor for the water content of the methanol is necessary. We used a modified coulometric determination method and injected dry anolyte into the ampoule to dissolve the sample (L 135), as described in procedure 12.1 below. Newer models of KF-ovens allow vials to be heated and investigated directly.

#### Procedure 12.1 Lyophilized samples

The coulometric cell is dried in the usual manner. Anolyte is added and approximately 5 mL are then removed from the cell using a long-needed plastic syringe and immediately returned to the anodic compartment. The coulometer indicates the moisture adhering to the syringe. The moisture is removed from the syringe by repeated purging the syringe with anolyte until anhydrous.

Using the dry syringe, 5 mL of anolyte are removed from the cell and injected into the sample ampoule through the lyophilization stopper. The substance dissolves (or suspends) in the anolyte upon shaking (vibroshaking may be necessary). The dissolved sample is then injected into the anodic compartment of the coulometric cell using the same syringe. The water content is determined according to standard procedure 5.3.

Water-based cosmetic preparations such as facial tonics, hydro-active fluids, super-effect fluids, suntan oils, shower gels, chamomile and herbal shampoos as well as beeswax preparations are analyzed in methanolic media by following the standard titration procedures (L 172).

Emulsions such as suntan creams or night creams should be analyzed at elevated temperatures in the presence of HYDRANAL®-Chloroform<sup>3</sup>. The same applies for panthenol and liquid lanolin.

Waxes that contain citric acid distearylester or pentaerythrite-di-coconut ester (Dehymuls® E or F) dissolve very slowly at room temperature. We have successfully measured their water content by KF titration at 50 °C in the presence of trichloroethylene (L 132, L 133).

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## 13. Technical products

The term “technical products” applies to very disparate group of products that can be analyzed by KF titration methods. Procedures for analysis of technical gases, oils, plastics, ion exchangers, paper, paints, fertilizers and many other products are found in the literature [1]. We have investigated a number of these substances in our own laboratories, usually in reply to customer inquiries. All of the products reported here have been studied in our laboratory.

### 13.1 Mineral oils, crude oils and related products

Mineral oils and their derivatives mainly consist of long-chained hydrocarbons and have limited solubility in methanol. Addition of HYDRANAL<sup>®</sup>-Chloroform<sup>1</sup> improves solubility, although this is not always successful since the problems encountered are often more complex. Crude oil is basically a mixture of hydrocarbons containing tar. The water in crude oils is not homogeneously distributed. This requires special sample preparation techniques, such as addition of HYDRANAL<sup>®</sup>-Xylene<sup>2</sup> to the working medium. This proved particularly helpful in the analysis of crude oils like Iran Heavy and Bachaquero grades described in Laboratory Report L 108 and in procedure 13.1.1 below.

#### Procedure 13.1.1 Crude oil

30mL HYDRANAL<sup>®</sup>-Solver (Crude) Oil<sup>3</sup> or a 25 mL mixture of HYDRANAL<sup>®</sup>-Methanol dry<sup>4</sup>, HYDRANAL<sup>®</sup>-Chloroform<sup>1</sup> and HYDRANAL<sup>®</sup>-Xylene<sup>2</sup> (1:1:2 v/v/v) is added to the titration vessel and titrated to dryness with HYDRANAL<sup>®</sup>-Composite. A 1-5 g sample of crude oil is then accurately weighed and added using a syringe (weighing by difference). The water content of the crude oil sample is then determined by titrating with HYDRANAL<sup>®</sup>-Composite.

Most useful and reliable is the use of HYDRANAL<sup>®</sup>-Solver (Crude) Oil<sup>3</sup>. It fulfills the requirements of ASTM D 4377-00. The solubility and titration speed is improved in comparison to the solvent mixture.

Oil distillates vary greatly. Low boiling-point fractions necessitate an addition of chloroform followed by titration according to procedure 8.2. Coulometric methods of analysis can be used

since the water content of distillates is typically very low. The standard procedure 5.3 can be followed as HYDRANAL<sup>®</sup>-Coulomat A<sup>5</sup>/AG-H<sup>6</sup> contains solubilizing agents.

Kerosene behaves similarly, although the HYDRANAL<sup>®</sup>-Chloroform<sup>1</sup> content should be increased for the coulometric determination according to procedure 8.2 C (L 112).

Heavy heating oils tend to deposit onto the electrodes and vessel walls during KF titrations. We therefore recommend an addition of toluene to the working medium as given in the procedure 13.1.1 for fuel oil (L 111).

Lubrication oils (motor oils, hydraulic oils) consist primarily of hydrocarbons, but contain many additives. These additives improve the viscosity, lower the pour point, prevent oxidation, reduce friction, suppress the formation of foam, amalgamate or separate solids as well as having a number of other functions. They deserve particular attention when lubricants are analyzed since they can interfere in the KF titration. Modified mercaptans, thiophosphoric acid esters and higher phenols can be oxidized by the KF titration, thereby consuming iodine and introducing errors. Ketones and ketoacids can undergo the formation of ketals with methanol and produce water. The same is true of the free silanol groups in polysiloxane additives. Overbased earth alkaline sulfonates and phenolates contain metal oxides that can react with acids in the KF reagents to produce water.

We have investigated several motor oils and certain additives in greater depth. The water content of a basic oil containing no additives could be determined without any difficulty according to procedure 8.2. Polyols, like antifreeze, can be analyzed by following the standard procedure 5.1. A 4:1 mixture of HYDRANAL<sup>®</sup>-Medium K<sup>7</sup> and HYDRANAL<sup>®</sup>-Formamide dry<sup>8</sup> must be used for the

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dissolution of olefin copolymers. The water determination was straightforward under these conditions. A 3:1 HYDRANAL<sup>®</sup>-Chloroform<sup>1</sup>: HYDRANAL<sup>®</sup>-Methanol dry<sup>2</sup> mixture was used for the analysis of polybutene.

Two additives point out the problems associated with moisture determination of additive-containing oils. An incorrect water content of 8% was found when overbased calcium sulfonate underwent KF titration, presumably due to calcium oxide reacting with the KF reagent (see section 10.3). Like the overbased calcium sulfonate, zinc diethyl dithiophosphate also gave erroneous results (2.8% water), in this case from the oxidation of the sulfide groups by the iodine.

Consequently, it is not surprising that incorrect values for the water content of motor oils containing additives are obtained by direct KF titration methods. We found an apparent water content of 1700 ppm in ARAL Super Elastic Turbo SAE 15 W/40 by a volumetric titration according to procedure 8.2 E (L 201). We further determined water contents of 1400 ppm in Shell Rimula<sup>®</sup> Multigrade and 2000 ppm in a Texaco oil. We proved that this oil can be oxidized by iodine and that the reductive components can put the results in error. In summary, it can be said that a direct titration of the water content of motor oil is not particularly reliable.

To overcome these errors due to reactive additives, we use a KF oven to drive off the moisture directly into a coulometric cell (procedure 8.12). At oven temperatures of 120-140 °C, we found 32 ppm H<sub>2</sub>O in the ARAL oil, compared to 1700 ppm without the oven. Apparently, the additives disassociate at higher oven temperatures and cause errors. For these investigations we set the oven vertically and use it as an "oil vaporizer" (L 106). Newer KF ovens allow analysts to investigate oils in an oil sampler or vial.

Silicon oils present fewer problems. Their analysis requires an addition of HYDRANAL<sup>®</sup>-Chloroform<sup>1</sup> in order to improve the solubility. We follow procedure 8.2, modified by also using HYDRANAL<sup>®</sup>-Titrant 2<sup>3</sup> because of the low water content of the oils. For coulometric determinations, we use HYDRANAL<sup>®</sup>-Coulomat Oil<sup>4</sup> or a mixture of 60 mL HYDRANAL<sup>®</sup>-Coulomat A<sup>5</sup> and 40 mL chloroform as the anolyte. Insulating oils (transformer oils) resemble silicone oils and can be analyzed according to the same procedure.

## 13.2 Paints, lacquers, adhesives

Pigments are solids that normally do not dissolve in KF reagents. However, the adherent water can be determined without any difficulty. Procedure 5.1 or 5.2 is followed.

The determination of water in dispersion paints containing polyvinyl acetates and inter-mixed polymers of vinyl chloride and acetate is straightforward. We followed the standard procedure described in section 5.1 in most cases. The addition of HYDRANAL<sup>®</sup>-Formamide dry<sup>6</sup> according to procedure 8.3 O greatly improves the dispersion of acrylic paints. We use a plastic syringe without the needle to add the sample. The sample size (approximately 0.05-0.1 g) must be determined accurately since the water content is relatively high.

Epoxy styrene varnish has to be titrated in a mixture of methanol-toluene (L 323).

The influence of the organic solvent in lacquers must also be considered since it can interfere in the titration of the water content. Ketones (section 9.6) and reactive amines (section 9.8) are especially problematic. If a stable end point cannot be achieved in a methanolic medium, a methanol-free working medium should be used. In a number of cases, an unknown side reaction could be suppressed by the use of HYDRANAL<sup>®</sup>-Working Medium K<sup>7</sup> and following procedure 8.4.

The water content of the fungicide paste Mergal<sup>®</sup> is determined on a regular basis by our laboratories. Titration at 50 °C according to procedure 8.8 ensures a facile dispersion of the paste. Adhesives are analyzed using various methods. The titration of polyurethane adhesive in methanol according to procedure 5.1 is straightforward. An addition of HYDRANAL<sup>®</sup>-Chloroform<sup>1</sup> following procedure 8.2 was necessary for the determination of water in chlorinated polyurethane caoutchouc (L 124) in order to dissolve the sample. We also used the same procedure for the determination of water in cyanoacrylate adhesives (UHU<sup>®</sup> instant glue) (L 118).

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<sup>7</sup> 34817

### 13.3 Plastics

Water is usually very securely entrapped in plastics and difficult to titrate. The water content can only be determined volumetrically when the substance can be dissolved in a suitable solvent. For plastics, easy dissolution is the exception rather than the rule.

Phenol-urea-formaldehyde resins dissolve only slowly at room temperatures and the water determination can take as long as 30 minutes. Resulting values are often erroneously low. A titration at 50 °C in the presence of HYDRANAL<sup>®</sup>-Formamide dry<sup>1</sup> only takes 4-6 minutes (L 130) and gives more accurate results.

#### Procedure 13.3.1 Phenol-urea-formaldehyde resins

20 mL HYDRANAL<sup>®</sup>-Solvent<sup>2</sup> and 10 mL HYDRANAL<sup>®</sup>-Formamide dry<sup>1</sup> are added to the titration vessel, heated to 50 °C and titrated to dryness with HYDRANAL<sup>®</sup>-Titrant. The sample (0.1-0.2 g) is then added and titrated at 50 °C. Polyamide is insoluble in the KF working medium and is first dissolved in 2,2,2-trifluoroethanol (L 126). The time required to dissolve the sample depends primarily on the chip size. Stirring as well as heating to 50-70 °C reduces the time required.

#### Procedure 13.3.2 Polyamides

20 mL trifluoroethanol are added to a 50 mL measuring flask and a sample (<1 g) is added. The sample should dissolve within two hours when constantly stirred. 25 mL HYDRANAL<sup>®</sup>-Solvent<sup>2</sup> are added to the titration vessel and titrated to dryness with HYDRANAL<sup>®</sup>-Titrant. The total sample in the measuring flask is then added and immediately titrated according to standard procedure 5.2. The residual water

content of 2,2,2-trifluoroethanol is determined by a blank titration of 20 mL of the solvent.

The polyamide will precipitate during the course of the titration. The titration vessel must therefore be cleaned occasionally to remove scale from the electrodes and cell walls.

Polycarbonates dissolve in certain chlorinated hydrocarbons; we used the following procedure (described in L 129). In general the indirect method using a KF oven should be preferred.

#### Procedure 13.3.3 Polycarbonates

25 mL HYDRANAL<sup>®</sup>-Working Medium K<sup>3</sup> and 20 mL trichloroethylene are added to the titration cell and titrated to dryness with HYDRANAL<sup>®</sup>-Composite. The sample (approximately 2 g) of polycarbonate is then added and titrated when dissolved.

The time required to dissolve the sample depends on the size of the chips. This is true of all plastics. The chip size should therefore be as small as possible. If the dissolution time is long, the drift value of the titration cell should be determined and taken into account in the calculations. The cell drift is the residual consumption of reagent by the dry titration cell and is expressed in mL reagent per minute. It is best determined by titrating the cell to dryness as usual and then setting the instrumentation to continual titration for 5 minutes.

Procedures according to DIN (Deutsches Institut für Normung e.V.) 53715, "Determination of water content of plastics by the Karl Fischer

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Plastic	Temperature needed to release water
Acrylonitrile-Butadiene-Styrene Copolymer (ABS)	180 °C
Melamine resin	
Polyacrylamide-copolymerizate (L 246)	160 °C
Polyamide (L 167)	200 °C
Polycarbodiimide	160-200 °C
Polycarbonate (L 127)	150 °C
Polyethylene (L 128)	160-200 °C
Polymethylmethacrylate (L 215)	140 °C
Polypropylene	180 °C
Polyethyleneterephthalate	160-180 °C
Terephthalic acid	180-200 °C
Soft PVC (L 204)	200 °C
	140-160 °C

Table 13.3

method," recommended for the titration of suspensions of powdered plastics also apply. We conducted determinations on powdered polyethylene according to standard procedures 5.1 and 5.2 and found a reasonable correlation with results from determinations using a drying oven (section 8.11) (L 193). Plastic granulates do not release water completely and the results from volumetric titrations are often too low.

The water content of powdered polypropylene is only partially released during a volumetric titration. It is our experience that the drying tube method should be used for this determination. The drying oven combined with a KF coulometer is being used more frequently as the effectiveness of the combination in solving difficult titrations becomes apparent. Using this technique, the water is driven off at 120-200 °C and transferred into the KF cell by a dried carrier gas. The moisture determination is carried out according to procedure 8.11. Different oven temperatures are recommended for different types of plastics.

We have carried out the water determination in many different plastics. A comprehensive overview is given in Laboratory Report L 328.

### 13.4 Liquified gases

The water determination in liquid gases can be carried out by volumetric and coulometric titration if some sample peculiarities are taken into account. We have titrated liquified butane (L 338) and sulfur dioxide (L 340).

## 14. Appendix

### 14.1 Literature

- [1] Eugen Scholz "Karl-Fischer Titration"  
Springer-Verlag, Berlin, Heidelberg, New  
York, Tokyo (1984), 140 pages  
ISBN 3-540-12846-8 German Edition  
ISBN 3-540-13734-3 English Edition
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### 14.2 Index of Laboratory Reports

During the development of our HYDRANAL®-Reagents and throughout the years of assisting our customers, we studied the water determination in many different substances. The detailed and optimized procedures, special sample preparation or handling considerations and other relevant information are recorded in our HYDRANAL® Laboratory Reports. We provide these useful, detailed HYDRANAL® reports to our customers free of charge. These reports can be obtained from [hydranal@sial.com](mailto:hydranal@sial.com).

(-)-(1R,2S)-(1,2-Epoxypropyl)phosphonic acid disodium salt	L 571	3-Ethyl-3-methyl-2,5-pyrrolidindion (Ethosuximide)	L 510
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## 14.4 Reagent index

### Volumetric reagents

#### One-component reagents

Cat. No.	Product	Description
<b>HYDRANAL®-Composite</b>		
34805	HYDRANAL®-Composite 5	General one-component reagent, Water equivalent ~5 mg H <sub>2</sub> O/mL
34806	HYDRANAL®-Composite 2	One-component reagent, Water equivalent ~2 mg H <sub>2</sub> O/mL
34827	HYDRANAL®-Composite 1	One-component reagent, Water equivalent 0.7-1 mg H <sub>2</sub> O/mL
<b>HYDRANAL®-Working Medium / Dry</b>		
34734	HYDRANAL®-CompoSolver E	Ethanol-based working medium for general use
34741	HYDRANAL®-Methanol dry	Working medium for general use
37817	HYDRANAL®-Methanol Rapid	Working medium containing accelerators
<b>HYDRANAL®-One-component working mediums</b>		
37855	HYDRANAL®-LipoSolver CM	Chloroform-based working medium for water determination in non-polar samples
37856	HYDRANAL®-LipoSolver MH	Chloroform-free working medium for water determination in non-polar samples
34697	HYDRANAL®-Solver(Crude)Oil	Working medium containing xylene and chloroform for water determination of oils

#### Two-component reagents

<b>HYDRANAL®-Titrant</b>		
34801	HYDRANAL®-Titrant 5	General two-component reagent, Water equivalent 5.00 ± 0.05 mg H <sub>2</sub> O/mL
34811	HYDRANAL®-Titrant 2	Two-component reagent, Water equivalent 2.00 ± 0.02 mg H <sub>2</sub> O/mL
<b>HYDRANAL®-Solvent</b>		
34800	HYDRANAL®-Solvent	General solvent
34812	HYDRANAL®-Solvent CM	Solvent for water determination in oils
34749	HYDRANAL®-Solvent Oil	Solvent for water determination in oils free of halogenated solvents
<b>HYDRANAL®-Titrant</b>		
34732	HYDRANAL®-Titrant 5E	Ethanol-based titrant, Water equivalent 5.00 ± 0.05 mg H <sub>2</sub> O/mL
34723	HYDRANAL®-Titrant 2E	Ethanol-based titrant, Water equivalent 2.00 ± 0.02 mg H <sub>2</sub> O/mL
34730	HYDRANAL®-Solvent E	Ethanol-based solvent, To be used with HYDRANAL®-Titrant E

#### For water determination in ketones and aldehydes (HYDRANAL®-K Reagents)

34816	HYDRANAL®-Composite 5K	Titrant for water determination in ketones and aldehydes, Water equivalent ~5 mg H <sub>2</sub> O/mL
34698	HYDRANAL®-Medium K	Working medium for water determination in ketones and aldehydes. To be used with HYDRANAL®-Composite
34817	HYDRANAL®-Working Medium K	Working medium for water determination in ketones and aldehydes. To be used with HYDRANAL®-Composite.
34738	HYDRANAL®-KetoSolver	Working medium for water determination in ketones and aldehydes free of halogenated solvents. To be used with HYDRANAL®-Composite
34820	HYDRANAL®-Coulomat AK	Anolyte for the titration of ketones
34821	HYDRANAL®-Coulomat CG-K	Catholyte for the titration of ketones

## Coulometric reagents (HYDRANAL®-Coulomat)

### Reagents with Halogenated Hydrocarbons

Cat. No.	Product	Description
34807	HYDRANAL®-Coulomat A	Anolyte for general use
34868	HYDRANAL®-Coulomat Oil	Anolyte for the titration of oils

### Reagents without Halogenated Hydrocarbons

34726	HYDRANAL®-Coulomat E	Ethanol-based anode and cathode reagent
34836	HYDRANAL®-Coulomat AG	Reagent for general use For the anode chamber of cells with a diaphragm For cells without a diaphragm
34810	HYDRANAL®-Coulomat AD	Reagent for cells without diaphragm
34843	HYDRANAL®-Coulomat AG-H	Reagent for investigation of hydrocarbons For the anode chamber of cells with a diaphragm For cells without a diaphragm
34739	HYDRANAL®-Coulomat AG Oven	Reagent for the anode chamber of a coulometric cell connected to a Karl Fischer Oven
34829	HYDRANAL®-Coulomat AF 7	Anolyte suitable for coulometer AF 7
34840	HYDRANAL®-Coulomat CG	Catholyte for general use

### For coulometric water determination in ketones

34820	HYDRANAL®-Coulomat AK	Anolyte for water determination in ketones
34821	HYDRANAL®-Coulomat CG-K	Catholyte for water determination in ketones

## Standards and buffers for Karl Fischer Titration

### For standardization of titrants

34849	HYDRANAL®-Water-Standard 10.0	Certified non-hygroscopic standard Water content 10.0 mg/g (Exact value on Certificate of Analysis. Tested against NIST SRM 2890.)
34813	HYDRANAL®-Standard 5.0	Non-hygroscopic standard Water content = $5.00 \pm 0.02$ mg/mL (20 °C)

### Primary standard

34803	HYDRANAL®-Standard sodium tartrate-dihydrate	Water content = $15.66 \pm 0.05\%$
34696	HYDRANAL®-Standard sodium tartrate dihydrate	Standard for volumetric Karl Fischer titration (Exact value on Certificate of Analysis. Tested against NIST SRM 2890.)

### To check the coulometry

34847	HYDRANAL®-Water Standard 0.1	1 g contains $0.1 \text{ mg} \pm 0.01\%$ H <sub>2</sub> O (Exact value on Certificate of Analysis. Tested against NIST SRM 2890.)
34828	HYDRANAL®-Water Standard 1.0	1 g contains $1.0 \text{ mg} \pm 0.1\%$ H <sub>2</sub> O (Exact value on Certificate of Analysis. Tested against NIST SRM 2890.)

### To check the Karl Fischer Oven

34748	HYDRANAL®-Water Standard KF-Oven 220-230°C	Solid Standard with a water content of $5.55\% \pm 0.05\%$ (Exact value on Certificate of Analysis. Tested against NIST SRM 2890.)
34693	HYDRANAL®-Water Standard KF-Oven 140-160°C	Solid standard, water content: ~5% (Exact value on Certificate of Analysis. Tested against NIST SRM 2890.)

**Other Standards**

Cat. No.	Product	Description
34802	HYDRANAL®-Water-in-methanol 5.0	Water content 5.00 ± 0.02 mg/mL
34694	HYDRANAL® Water Standard Oil	Mineral-oil based matrix standard for KF titration in oils. (Exact value on Certificate of Analysis. Tested against NIST SRM 2890.)

**Solubilizing agents for Karl-Fischer titration**

34724	HYDRANAL®-Formamide dry	Max. 0.02 % H <sub>2</sub> O
37863	HYDRANAL®-Chloroform	Max. 0.01 % H <sub>2</sub> O
37866	HYDRANAL®-Xylene	Max. 0.01 % H <sub>2</sub> O

**For buffering**

34804	HYDRANAL®-Buffer Acid	Buffer capacity 5 mmol acid/mL reagent
37859	HYDRANAL®-Buffer Base	Buffer capacity 1 mmol base/mL reagent
37864	HYDRANAL®-Imidazole	Max. 0.1 % H <sub>2</sub> O
32035	HYDRANAL®-Benzoic acid	Buffer substance for KF titration.
37865	HYDRANAL®-Salicylic acid	Buffer substance for KF titration.

**Absorbent**

34788	HYDRANAL®-Humidity Absorber	≤25% capacity (water)
34241	HYDRANAL®-Molecular sieve 0.3 nm	beads

**Karl Fischer Titration without instruments**

37858	HYDRANAL®-Moisture Test kit	Test set for KF titration containing syringes, titration vessel and reagents. Contains 2 x 500 mL HYDRANAL®-Solvent E (34730); 100 mL HYDRANAL®-Standard 5.0 (34813); 100 mL HYDRANAL®-Titrating agent for test kit (34732).
34732	HYDRANAL®-Titrant 5 E	Refill pack for the HYDRANAL®-Moisture Test kit.

**Karl Fischer reagents containing pyridine**

36115	Reagent solution according to Karl Fischer	For titrimetric determination of water, Supplied in one solution, Iodine/sulfur dioxide/pyridine solution, 1 mL ~ 5 mg H <sub>2</sub> O
36116	Reagent solution according to Karl Fischer	Solution A: sulfur dioxide/pyridine, For titrimetric determination of water, Supplied in two separate solutions, 0.5 mL each of solutions A and B mixed are equivalent to ~ 3 mg H <sub>2</sub> O For use with Solution B (36117)
36117	Reagent solution according to Karl Fischer	Solution B: methanolic iodine For titrimetric determination of water, Supplied in two separate solutions, 0.5 mL each of solutions A and B mixed are equivalent to ~ 3 mg H <sub>2</sub> O For use with Solution A (36116)

Purchasers must determine the suitability of the product(s) for their particular use. Additional terms and conditions may apply.

## Karl Fischer Titration HYDRANAL® Literature

The comprehensive literature and application library on [sigma-aldrich.com/hydranal](http://sigma-aldrich.com/hydranal) makes daily work easier for HYDRANAL®-Users, and is always available anytime you need it.

### Brochures

HYDRANAL Composite (GXH)

HYDRANAL The Coulometric Cell (HYK)

HYDRANAL Water Standards (JJP)

HYDRANAL Product Line Overview (HMR)



## HYDRANAL-Multimedia Guide CD Version 4.0 (NVO)

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