

HYDRANAL™ Technical Information Sheet T008 Rev. 1

Use of Additional Solvents in Karl Fischer Titration

In special cases the addition of solubilizer is required in order to enable a direct titration of the sample and avoid complicated and error-prone pre-dissolution and pre-extraction steps. Fats, oils and long-chained hydrocarbons have limited solubility in methanol, which 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 in methanol. An addition of formamide improves the dissolution, dispersion and the extraction of water from these samples.

If the working conditions of the titration are modified, the requirements of the KF reagents must also be considered. The solvent used with the Hydranal-Composite one-component reagent can be extensively modified. However, the basic prerequisites for the KF titration must be maintained. Only a limited modification of the solvent component of the two-component system (Hydranal-Titrant/Solvent) is possible since the solvent contains substrates for the KF reaction system. The coulometric KF reagents, Hydranal-Coulomat A/AD/E/AG/AG-H, 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. Anolytes which contain a co-solvent in addition to methanol show increased recoveries when used with a diaphragmless generator electrode. Therefore, we recommend using a diaphragm generator electrode when working with a co-solvent containing anolyte. This will require the use of the appropriate catholyte.

Long-chain alcohols

Methanol does not satisfactorily dissolve long-chained hydrocarbons, so 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 measured during the titration. However, indication problems can occur if the indicator 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 long-chain alcohols, such as 1-propanol, to the working medium. 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, we offer Hydranal-Coulomat AG-H as a ready-to-use reagent that contains the long-chain alcohol 1-pentanol. For the cathodic compartment Hydranal-Coulomat CG should be used.

Chloroform

Fats, long-chained hydrocarbons and other lipophilic substances have limited solubility in alcohols. Addition of Hydranal-Chloroform greatly improves their solubility. For an exact determination of water, the methanol content should not be less than 35% by volume, although a 25% Hydranal-Methanol dry/75% Hydranal-Chloroform solvent mixture is acceptable for trace analyses, in spite of the possibility of a slight change in the stoichiometry of the KF reaction (the factor for the titrating agent apparently increases). An addition of Hydranal-Chloroform also accelerates the KF reaction.

The coulometric reagent, Hydranal-Coulomat A, 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.

Formamide

Hydranal-Formamide dry 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 also accelerates the extraction of moisture from solids and is used in the titration of starch, other foodstuffs and naturally occurring substances, as well as in titrations at elevated temperature. Hydranal-Formamide dry accelerates the speed of KF reaction. Because it can also influence the stoichiometry of the reaction, formamide should not be used at concentrations >50% by volume.

We have tried the use of formamide in the coulometric titration with diaphragm. Side reactions blacken the cathode, and after one day the anolyte and the catholyte had to be discarded. Coulometric titration without diaphragm can be applied in that case. In the coulometric titration without diaphragm 10-20% Hydranal-Formamide dry can be added to the anolyte. After 2 days, the reagent should be replaced.

Our recommendations for the use of additional solvents are summarized in the table below.

Max. volume of co-solvent	Volumetry	Coulometry with diaphragm (frit)	Coulometry without diaphragm (fritless)
Long-chain alcohol	Max. 50%	Max. 30%, but "pre-mixed reagent" is recommended ¹	Not recommended ²
Chloroform	Max. 70%	Max. 30%, but "pre-mixed reagent" is recommended ¹	Not recommended ²
Formamide	Max. 50%	No	Max. 20% ³
Toluene	Max. 70%	Max. 30%, but "pre-mixed reagent" is recommended ¹	Not recommended ²
Xylene	Max. 70%	Max. 30%, but "pre-mixed reagent" is recommended ¹	Not recommended ²
Acetonitrile	Max. 50%	Max. 30%	Max. 30%
N-Methyl pyrrolidone	Max. 50%	Not recommended ⁴	Not recommended ⁴
Dimethyl formamide	Max. 70% ⁵	Max. 20%	Max. 20%
Dimethyl sulfoxide	Not recommended ⁶		
Secondary alcohols	Not recommended ⁷		
Tertiary alcohols	Not recommended ⁷		

¹ possible problem with conductivity

² expect higher water recovery

³ recommended to dissolve sample externally and use standard reagent. If formamide was introduced, then the replacement of the reagent after 2 days is highly recommended.

⁴ side effects can occur (see Lab Report L549)

⁵ DMF with low quality delays KF reaction (see Lab Report L424). High quality DMF (>99%) like e.g. Honeywell Riedel-de Haën™ N,N-Dimethylformamide CHROMASOLV™ Plus is suited for KF titration. A mixture of DMF with Hydranal-Solvent gave good performance (see suitability test S073).

⁶ in presence of DMSO recovery rates are too low (see Lab Report L141)

⁷ may cause increase in titer values

Below pre-mixed Hydranal reagents are available:

Hydranal pre-mixed reagents	Volumetric one-component	Volumetric two-component	Coulometric with diaphragm (frit)	Coulometric without diaphragm (fritless)
Long-chain alcohol	LipoSolver MH	Solvent Oil	Coulomat AG-H	Not recommended
Chloroform	LipoSolver CM Solver (Crude) Oil	Solvent CM Solver (Crude) Oil	Coulomat A Coulomat Oil	Not recommended
Xylene	Solver (Crude) Oil	Solver (Crude) Oil	Coulomat Oil	Not recommended
Acetonitrile	-	-	Coulomat A-FA	Not recommended

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