Water determination in nitrogen bases

HYDRANAL™ Laboratory Report L 288

For water determination in nitrogen bases, the existing literature states:

1. Weak bases can be titrated directly.
2. Strong bases must be neutralized using benzoic acid.
3. There are some exceptions, where side reactions occur and result in no end point.

In general, these statements are correct. However, they appear rather vague; therefore we tried to make more precise statements and develop more exact titration methods.

We examined over 100 separate amines using the 3 common titration techniques:

- Volumetric titration with one-component reagents
- Volumetric titration with two-component reagents
- Coulometric determination

We followed this basic procedure for each technique:

1. Titrate the cell to dryness
2. Add water standard and titrate the recovery rate
3. Add sample and titrate the water content
4. Add water standard and titrate the recovery rate again

Parameters measured were the following:

- Time for titration
- End point stability (e. g. drift at the end of the titration)
- Recovery rate of water added (in the presence of the sample being investigated)

Honeywell

HONEYWELL RESEARCH CHEMICALS PORTFOLIO
Riedel-de Haën™ Burdick & Jackson™ Fluka™

Greyhound CHROMATOGRAPHY AND ALLIED CHEMICALS

The titration medium was acidified by:

- Addition of benzoic acid
- Addition of salicylic acid
- Addition of sulfite buffer (3 mol/L: introduce 54 g SO_2 into a mixture of 150 g methanol + 3 g imidazole)

The following reagent combinations were tested:

1. Volumetric one-component technique

Hydranal™-Composite 5, in combination with the following working media:

- 30 mL Hydranal-Methanol dry
- 30 mL Hydranal-Methanol dry + 5–7 g benzoic acid
- 30 mL Hydranal-Methanol dry + 5–7 g salicylic acid
- 20 mL Hydranal-Methanol dry + 15 mL sulfite buffer

2. Volumetric two-component technique

Hydranal-Titrant 5, in combination with the following working media:

- 30 mL Hydranal-Solvent
- 30 mL Hydranal-Solvent + 5–7 g benzoic acid
- 30 mL Hydranal-Solvent + 5–7 g salicylic acid
- 20 mL Hydranal-Solvent + 15 mL sulfite buffer

3. Coulometric determination

5 mL Hydranal-Coulomat CG as catholyte, in combination with the following anolyte solutions:

- 100 mL Hydranal-Coulomat AG
- 100 mL Hydranal-Coulomat AG + 20 g benzoic acid
- 100 mL Hydranal-Coulomat AG + 20 g salicylic acid
- 80 mL Hydranal-Coulomat AG + 20 mL sulfite buffer

The titration curves were evaluated; the results can be found in the table at the end of this report.

1. Aliphatic amines

Aliphatic amines are strongly basic and must be titrated in the presence of benzoic acid. According to the literature, the amount of sample added should be limited in order to ensure that the neutralizing capacity of the added acid is not exceeded.

n-Propylamine

When testing the recommendations with n-propylamine, the statement seems to be confirmed. After more exact investigation it shows that the recovery of 5 mg added water is slightly too high (about 102%). With the setting of more stringent end point conditions and an end point drift of 10 µL/min, an end point is no longer obtained with this standard determination.

Hence, it must be concluded that a slight side reaction occurs during the analysis of n-propylamine.

Coulometric determination in the presence of benzoic acid (5 × 0.5 g n-propylamine) shows a drift increase after each sample addition. It must, therefore, be concluded that the same side reaction occurs with n-propylamine.

2-Aminoethanol

When titrating 2-aminoethanol volumetrically, no end point is found with addition of benzoic acid. Only with the addition of salicylic acid a 2 g sample can be titrated as usual. Therefore, salicylic acid is recommended rather than benzoic acid.

The same is valid basically for the coulometric determination. The titration of small samples in the presence of benzoic acid results in a small increasing drift and a slightly higher recovery rate of water.

This increasing drift generally affects the limitations of coulometry in different ways:

1. If the drift after a determination is higher than that before a determination, the result obtained is incorrect. The coulometer calculates the drift correction using the drift value measured before the determination was started. The drift increase due to the sample is, therefore, not compensated for in the calculation of the result.
2. If the drift increase from sample to sample becomes too large, the titration no longer shuts off at all. Small samples have to be applied.
3. If the start drift is higher than 100 µg/min, the machine cannot be started. This threshold value varies from manufacturer to manufacturer, but is always given.

The addition of salicylic acid would also improve the titration characteristics for coulometry. The drift increase is smaller, and thus the amount of sample which can be titrated is larger. However, there is another much higher risk in this case.

Salicylic acid is oxidized by the anode under certain conditions and, therefore, poisons the electrode of the coulometer. This always takes place if the salicylic acid is to a large extent neutralized and the pH rises above 5 again. Because of this, ***we do not recommend the use of salicylic acid for coulometry.***

For aliphatic amines our investigation resulted in a few different titration methods, which are listed in the table at the end.

Most amines were titrated with the addition of benzoic acid. For the two-component reagents, salicylic acid is preferred in some cases. For coulometry, small samples are applied to avoid a too high drift increase between samples. Secondary and tertiary amines clearly behave differently. They cause far fewer problems than primary amines. This means that for coulometry also the amount of sample used depends only on the neutralizing capacity of the benzoic acid.

2. Aliphatic diamines

The titration of 1 mL 1,2-diaminoethane (ethylenediamine) as a free base and in the presence of benzoic acid or salicylic acid shows many more problems than with monoamines. Also, the difference between benzoic acid and salicylic acid is greater. Even salicylic acid suppresses the side reaction insufficiently, so that only relatively small sample weights can be titrated in this group of compounds.

The table at the end shows examples of diamines that were investigated.

With the two-component reagents it is only possible to titrate small quantities of sample, only with the strongly acidic sulfite buffer. Actually, these titrations should be classified as non-recommendable. Coulometry is generally not possible for this group of compounds, with the exception of hexamethylene diamine, which can perhaps be accepted as a compromise for water determination.

3. Cyclic amines

The table at the end shows some examples for cyclic amines. They behave like secondary amines except for a less pronounced side reaction and a slightly lower basicity. In this case, the addition of benzoic acid is sufficient.

For coulometry the addition of benzoic acid is not required. The neutralization capacity of the reagent is sufficient because the quantity of amine added is clearly limited by the increasing drift.

4. Aromatic amines

Aromatic amines only react as weak bases. It should therefore theoretically be possible to titrate them without problems. In practice there are clearly different findings. The titration of 5 g aniline in methanol gives no end point, due to a very strong side reaction. Addition of benzoic or salicylic acid reduces this side reaction, although still no end point is found. Reducing the sample weight to 2 g leads to an end point in the presence of salicylic acid, although it also depends on the instrument settings because the side reaction is only reduced, but not prevented.

This different behavior clearly contradicts our expectations. Obviously the side reaction is much more pronounced and not completely suppressed by addition of acid. From earlier investigations we know that aniline is methylated in the Karl Fischer (KF) medium, therefore it can produce N-methylaniline. This side reaction could be the cause for the problematic titration. We replaced the methanol with 2-chloroethanol and carried out the determination in Hydranal-Working Medium K. The side reaction was clearly weaker, and in the presence of salicylic acid a sufficiently stable end point could be obtained.

Since Hydranal-Working Medium K was declared as very toxic, in 2009 we made further investigations and found Hydranal-Buffer Base to be perfectly suited, as methanol is widely replaced by ethanol. 5 mL aniline can be determined with a very stable end point.

Amongst certain substance groups, the differences are very large. For substances that are easily oxidized, like 2-aminophenol, the sulfite buffer is preferred because it is more acidic than salicylic acid and the side reaction is even further suppressed. Using the two-component reagents, the addition of sulfite buffer is strongly recommended.

N-substituted aniline derivatives are less sensitive to the side reaction and may be analyzed using the volumetric standard procedure. All phenylenediamines are very sensitive to this reaction and have limited applicability even with the one-component reagents.

With coulometry all aromatic amines are very easily oxidized (or methylated), so methanolic reagents are generally not suitable. Even in the strongly acidic sulfite buffer, only small quantities can be analyzed and the recovery rates are also still too high. Only the methanol-free reagents Hydranal-Coulomat AK and Hydranal-Coulomat CG-K are suitable for this group of substances; additionally the sample size is limited to only 2 g. Also with coulometry the differences in chemical structure become noticeable. N-substituted aniline derivatives can be added in larger quantities, just as diphenylamine. Coating of the anode should not be overlooked, this often occurs sporadically with different aromatic amines. Also, recovery rates are observed to be too high; thus control of the recovery rate with Hydranal-Water Standard is strongly recommended.

5. Heterocycles

Heterocycles are weakly basic and chemically very similar, so most of them can be titrated according to the standard procedure (see table at the end).

But there are also exceptions. For benzimidazole or 1,2,4-triazole the sample weight is limited, since the substance has only limited solubility. For 2-aminopyridine or 2-aminobenzothiazole it is necessary to add benzoic acid for the volumetric titration in order to sufficiently suppress the side reaction.

Greater difficulties appear with coulometric determination in this group of compounds. For some condensed heterocycles it is advisable to add sulfite buffer, for others coulometry is generally less recommended.

Summary and chemical reasoning

After evaluation of all these results, the following conclusions can be made:

1. For titration of strong basic amines the KF working medium must be neutralized.
2. A few nitrogen bases cause problems even in acidic conditions. They give fading end points caused by side reactions.
3. The chemical nature of the side reactions is unknown. It could be oxidation of the amino group by iodine.
4. A further side reaction could be alkylation of the amino group with the formation of water. This could be possible with aromatic amines, since here the replacement of methanol by other alcohols reduces this side reaction.
5. Side reactions are often dependent on pH value. Lowering the pH using benzoic acid or salicylic acid or Hydranal-Buffer Base suppresses these side reactions.
6. The difficulties are more pronounced in coulometry. Occasionally the electrode is poisoned; it must therefore be assumed that amines may also be oxidized at the anode.
7. If side reactions are only partly suppressed, coulometry is only less recommended. The drift increase from sample to sample limits the size of each sample and the accuracy.
8. With the choice of a suitable method, most nitrogen bases can be titrated. Only water determination of aliphatic and aromatic diamines is unsatisfactory.

HYDRANAL™
HOTLINE

Europe and International
Thomas Wendt
HYDRANAL Center of Excellence
Tel: +49-5137 999-353
Fax: +49-5137 999-698
hydranal@honeywell.com

Europe and International
Agnieszka Kossakowska
HYDRANAL Technical Specialist
Tel: +48 512 355 628
hydranal@honeywell.com

USA and Canada
Doug Clark
HYDRANAL Technical Center
Tel: 1-800-Hydranal
(1-800-493-7262)
hydranal@honeywell.com

REAGENTS

34805	HYDRANAL-Composite 5	34801	HYDRANAL-Titrant 5
34741	HYDRANAL-Methanol dry	34800	HYDRANAL-Solvent
37817	HYDRANAL-Methanol Rapid	34836	HYDRANAL-Coulomat AG
37859	HYDRANAL-Buffer Base	34840	34840 HYDRANAL-Coulomat CG
32035	HYDRANAL-Benzoic acid	34820	HYDRANAL-Coulomat AK
37865	HYDRANAL-Salicylic acid	34821	HYDRANAL-Coulomat CG-K

WATER STANDARDS

34849	HYDRANAL-Water Standard 10.0	34426	HYDRANAL-CRM Water Standard 1.0
34425	HYDRANAL-CRM Water Standard 10.0	34446	HYDRANAL-Water Standard 0.1 PC
34828	HYDRANAL-Water Standard 1.0		

AUXILIARIES

34241	HYDRANAL-Molecular Sieve 0.3 nm	34788	HYDRANAL-Humidity Absorber

Legend for the table

Me:	30 mL Hydranal-Methanol dry	
So:	30 mL Hydranal-Solvent	
AG:	100 mL Hydranal-Coulomat AG	
Me + Be:	30 mL Hydranal-Methanol dry	+ 5 g benzoic acid or 30 mL Hydranal-Buffer Base
Me + Sa:	30 mL Hydranal-Methanol dry	+ 5 g benzoic acid or 30 mL Hydranal-Buffer Base
Me + Bu:	20 mL Hydranal-Methanol dry	+ 15 mL sulfite buffer
Wm + Sa	30 mL Hydranal-Working Medium K	+ 5 g salicylic acid
So + Bu:	30 mL Hydranal-Solvent	+ 5 g benzoic acid
So + Sa:	30 mL Hydranal-Solvent	+ 5 g salicylic acid
So + Bu:	15 mL Hydranal-Solvent	+ 15 mL sulfite buffer
A + Be:	100 mL Hydranal-Coulomat AG	+ 20 g benzoic acid
A + Bu:	100 mL Hydranal-Coulomat AG	+ 20 mL sulfite buffer
AK	100 mL Hydranal-Coulomat AK	
L:	Added as a solution in methanol	
(L):	Solubility on addition of the sample	
T:	Clouding on addition of the sample	
N:	Precipitation on addition of the sample	
...g:	Sample amount	

	HYDRANAL-Composite	HYDRANAL-Solvent/Titrant	HYDRANAL-Coulomat
Aliphatic amines			
n-Propylamine	Me + Be 1.5g	So + Sa 1g	AG + Be 10 × 0.2g
iso-Propylamine	Me + Be 2g	So + Sa 1.5g	AG + Be 15 × 0.2g
n-Butylamine	Me + Be 2g	So + Sa 1.5g	AG + Be 10 × 0.2g
1-Hexylamine	Me + Be 3g	So + Sa 3g	AG + Be 15 × 0.2g
3-Methoxypropylamine	Me + Sa 3g	So + Sa 2g	AG + Be 15 × 0.2g
Tris-(hydroxymethyl)-aminomethane	Me + Be 3g	So + Bu 3g	AG + Be 20 × 0.1g
2-Aminoethanol	Me + Sa 2g	So + Bu 2g	AG + Be 10 × 0.1g
Cyclohexylamine	Me + Be 2g	So + Be 2g	AG + Be 25 × 0.2g
Dipentylamine	Me + Be 3g	So + Be 4g	AG + Be 20 × 0.3g
Dicyclohexylamine	Me + Be 3g	So + Be 2g	AG + Be 15 × 1g
Diethanolamine	Me + Be 5g	So + Be 4g	AG + Be 15 × 0.5g
Triethylamine	Me + Be 4g	So + Be 4g	AG + Be 15 × 0.5g
N,N-Dimethylethanolamine	Me + Be 3g	So + Be 2g	AG + Be 15 × 0.5g
Triethanolamine	Me + Be 5g	So + Be 5g	AG + Be 15 × 0.5g
N,N-Dimethylcyclohexylamine	Me + Be 4g	So + Be 4g	AG + Be 20 × 0.5g
Diamines			
1,2-Diaminoethane (ethylenediamine) **Appl. L 027**	Me + Sa 0.5g	So + Bu 0.5g	not measurable
Diethylenetriamine **Appl. L 026**	Me + Sa 1g	So + Bu 0.5g	not measurable
Triethylenetetramine **Appl. L 026**	Me + Sa 0.5g	So + Bu 0.5g	not measurable
Tetraethylenepentamine **Appl. L 026**	Me + Sa 0.5g	So + Bu 0.5g	not measurable
3-(N,N-Dimethylamino)-propylamine	Me + Sa 1.5g	So +Bu 1g	not measurable
Hexamethylenediamine	Me + Sa 2g	So + Bu 0.5g	AG + Bu 20 × 0.2g
Cyclic amines			
Pyrrolidine	Me + Sa 1g	So + Be	AG 10 × 0.1g
Piperidine	Me + Be 3g	So + Be	AG 20 × 0.2g
1-Methylpiperidine	Me + Be 3g	So + Be	AG 20 × 0.5g
Piperazine	Me + Be 1.5g N	So + Be 1.5g N	AG 10 × 0.2g
Morpholine	Me + Be 3g	So + Be 3g	AG 20 × 0.5g

	HYDRANAL-Composite	HYDRANAL-Solvent/Titrant	HYDRANAL-Coulomat
Aromatic amines			
Aniline **Appl. L 030**	Wm + Sa 5g	So + Bu 1g	AK 15 × 0.1g
o-Toluidine	Wm + Sa 5g	So + Bu 1g	AK 10 × 0.2g
m-Toluidine	Wm + Sa 5g	So + Bu 1g	AK 10 × 0.1g
4-Anisidine	Wm + Sa 3g	So + Bu 1g	AK 10 × 0.1g L
2-Aminophenol	Me + Bu 2g	So + Bu 1g	not measurable
1-Naphthylamine	Wm + Sa 5g	So + Bu 2g	AK 20 × 0.2g L
N-Methylaniline	Me 5g	So 5g	AK 20 × 0.5g
N,N-Dimethylaniline	Me 5g	So 5g	AK 20 × 0.5g
N,N-Diethylaniline	Me 5g	So 5g	AK 40 × 0.5g
Diphenylamine	Me 5 g	So 5g	AK 10 × 0.5g L
1,2-Phenylenediamine	Wm + Sa 1g	not measurable	not measurable
1,3-Phenylenediamine	Wm + Sa 1g	not measurable	not measurable
4-Methyl-1,2-phenylenediamine	not measurable	not measurable	not measurable
Heterocycles			
Pyridine	Me 5g	So 5g	AG 20 × 1g
1-Picoline	Me 5g	So 5g	AG 20 × 1g
Quinoline	Me 5g	So 5g	AG 20 × 1g
Imidazole	Me 5g	So 5g	AG 20 × 1g L
1-Methylimidazole	Me 5g	So 5g	AG 25 × 1g L
Benzimidazole	Me 1g	So 1g	AG 10 × 1g L
1,3,5-Triazine	Me 5g	So 5g	AG 12 × 0.5g L
1,2,4-Triazole	Me 1g	So 1g	AG 10 × 0.5g L
Benzothiazole	Me 5g	So 5g	AG 40 × 0.5g
Pyrrole	Me 5g	So 5g	AG + Bu 30 × 0.2g
Indole	Me 5g	So 5g	not recommendable
Carbazole	Me 0.2g (L)	So 1g (L)	AG 10 × 0.05g (L)
Nicotine	Me 4g	So 3g	AG 10 × 0.2g
8-Hydroxyquinoline	Me 5g	So 5g	AG + Bu 10 × 0.5g L
2-Aminopyridine	Me 5g	So 5g	AG + Bu 15 × 0.5g L
3-Aminopyridine	Me + Sa 3g	So + Sa 2g	not recommendable
2-Aminobenzothiazole	Me + Sa 5g	So + Sa 2g	not recommendable

To order, please contact:

Greyhound Chromatography and Allied Chemicals
6 Kelvin Park
Birkenhead, Merseyside, CH41 1LT
Tel: 0151 649 4000
Email: info@greyhoundchrom.com
www.greyhoundchrom.com

Honeywell Specialty Chemicals Seelze GmbH
Wunstorferstrasse 40
30926 Seelze, Germany
Tel.: +49 (0)5137-999-353
Fax: +49 (0)5137-999-698
lab-honeywell.com

All statements and information provided herein are believed to be accurate and reliable, but are presented without guarantee, warranty or responsibility of any kind, express or implied. Statements or suggestions concerning possible use of our products are made without representation or warranty that any such use is free of patent infringement, and are not recommendations to infringe any patent. The user should not assume that all safety measures are indicated herein, or that other measures may not be required. User assumes all liability for use of the information and results obtained. WITHOUT LIMITING THE FOREGOING, HONEYWELL DISCLAIMS THE WARRANTY OF MERCHANTABILITY, FITNESS FOR USE AND NON-INFRINGEMENT. © 2018 Honeywell International Inc.

RESPONSIBLE CARE®
OUR COMMITMENT TO SUSTAINABILITY

Honeywell

Greyhound CHROMATOGRAPHY AND ALLIED CHEMICALS