Hydroxyl Number of Raw Polyols according to ASTM E1899-02

Polyols are basic raw materials used to produce different products like e.g. polyurethanes. To assure product constancy and quality of the final product, the hydroxyl number of the raw polyol has to be known. It is determined according to ASTM E1899-02.

Sample	Raw polyol, 0.5-1 g Pure octanol, $C_8H_{16}OH$, M = 130.23 g/mol
Compound	Hydroxyl end group, -OH
Chemicals	Tetrahydrofuran,THF p-Toluenesulfonyl isocyanate, TSI Water Acetonitrile, CH_3CN, 2-propanol
Titrant	Tetrabutylammonium hydroxide (TBAH) in 90% 2-propanol C(TBAH) = 0.1 mol/L
Standard	Potassium hydrogenphthalate, KHP n-octanol
Indication	DGi116-Solvent Electrolyte: Lithium nitrate saturated in acetonitrile
Chemistry	$ROH + CH_3\text{-}C_6H_4\text{-}SO_2\text{-}NCO \rightarrow CH_3\text{-}C_6H_6\text{-}SO_2\text{-}NH\text{-}COOR$ $CH_3\text{-}C_6H_4\text{-}SO_2\text{-}NCO + H_2O \rightarrow CH_3\text{-}C_6H_4\text{-}SO_2\text{-}NH_2 + CO_2$ $CH_3\text{-}C_6H_4\text{-}SO_2\text{-}NH\text{-}COOR + OH^- \rightarrow CH_3\text{-}C_6H_4\text{-}SO_2\text{-}N^-\text{-}COOR + H_2O$
Calculation	Hydroxyl number (mg KOH/g): R1 = Q2*C/m; C=56.1 Hydroxyl equivalent weight (g/equiv.) R2 = (56.1*1000) / R1 Pure subst.: Molecular weight (g/mol) R3 = (56.1*1000)*C / R1 C = 1 (nr. OH-group/molecule, e.g. 1 for n-octanol)
Waste disposal	Organic solvent waste
Author, Version	Chris Hynes / Ross C. Koile MT-NA, June 2009

Preparation and Procedures

- All reagents must be of high purity (e.g. HPLC grade) since the amount of water contained interferes with the analysis.
- Isocyanate solution (TSI):
  Add 25 g of p-toluenesulfonyl isocyanate to 450 mL of anhydrous acetonitrile.
- Titrant TBAH:
  100 mL 1M TBAH in methanol are added in a 1 L volumetric flask with 500 mL 2-propanol. Mix and fill up to the mark with 2-propanol.
- Special beaker 1 on Rondo Sample Changer is filled with acetonitrile to eliminate water traces.
- Method is best if run with two peristaltic pumps (THF, water) and a dosing unit (TSI) to automate the sample preparation (Step 1):
  - 10 mL THF are added with the 1st pump
  - 10 mL TSI solution are dispensed (dosing unit)
  - stir the solution
  - 2 mL water are added by the 2nd pump
  - Stir the sample solution.
- Subsequently, 40 mL THF are added and the titration is started (Step 2).

Remarks

- A blank value is dependent on the amount of alcohol in the THF. In fact, alcohol affects the chemical reaction. If a high quality, anhydrous THF supply is used, there should rarely show a detectable blank.
- The following points have to be performed to achieve a relative standard deviation below 1%:
  1. The titration tip needs to be cut above the sample line of step 1 (30 mL) but below it after final addition of THF (Step 2).
  2. All other sample tips should be cut high enough to never be below the sample line.
- Sample size is critical to this test method:
  - Use 0.5 g for 1000 g/equiv
  - Use 1 g for 2000 g/equiv

Great care should be taken not to get any sample on the sides of the beaker. This will not allow for reaction of polyol with isocyanate resulting in low hydroxyl numbers.

Instruments	- Titration Excellence T70 / T90 - 2 SP250 peristaltic pumps - Rondo 20 Sample Changer
Accessories	- 1 x Dosing Unit - 2 DV1020 glass burettes - Balance XS204 - LabX titration software

Results

OH-Number of pure n-octanol

Results

No.	Comment / ID	Start time	Sample size and results		
1/3	OCTANOL	2/25/2009 1:11:40 PM	0.1310	g	
			R1 = 431.633	mg KOH/g	Hydroxyl number
			R2 = 129.971	g/equiv	Equivalent weight
			R3 = 259.943	g/mol	Molecular weight
2/3	OCTANOL	2/25/2009 1:40:04 PM	0.1321	g	
			R1 = 429.911	mg KOH/g	Hydroxyl number
			R2 = 130.492	g/equiv	Equivalent weight
			R3 = 260.984	g/mol	Molecular weight
3/3	OCTANOL	2/25/2009 2:08.06 PM	0.1310	g	
			R1 = 426.361	mg KOH/g	Hydroxyl number
			R2 = 131.579	g/equiv	Equivalent weight
			R3 = 263.157	g/mol	Molecular weight

Statistics

Rx	Name	n	Mean value	unit	s	srel[%]
R1	Hydroxyl number	3	429.302	mg KOH/g	2.688	0.626
R2	Equivalent weight	3	130.681	g/equiv	0.820	0.628
R3	Molecular weight	3	261.361	g/mol	1.640	0.627

Additional results

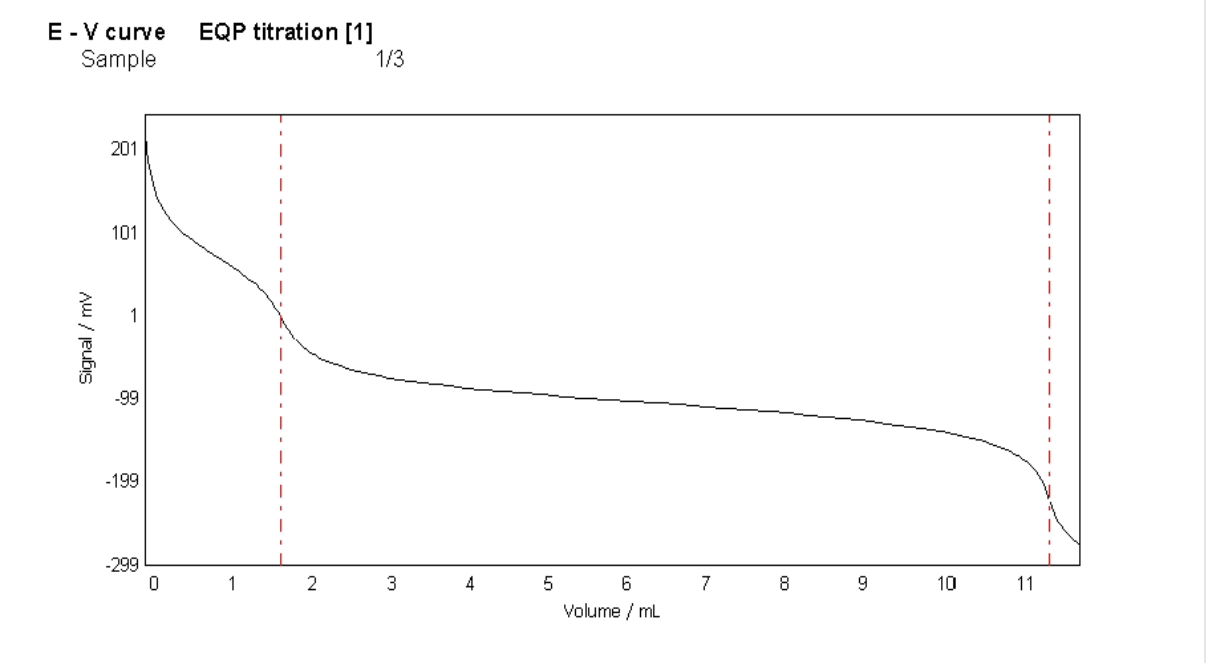
Statistics

Rx	Name	n	Mean value	unit	s	srel[%]
R1	Hydroxyl number	3	437.653	mg KOH/g	2.969	0.678
R2	Equivalent weight	3	128.188	g/equiv	0.873	0.681
R3	Molecular weight	3	256.376	g/mol	1.746	0.681

Remarks:

- The titration of OH end groups of polyols can be tested using pure n-octanol, $C_8H_{16}OH$.
- Note that n-Octanol has only **one** OH group at the end of its aliphatic chain. For this reason, the equivalent weight corresponds to the molecular weight, i.e. R2 = R3 = 130.681 g/mol.
- However, method m453A has been developed to be performed with any polyol, and therefore both end groups have to be taken into account into calculation R3.
- For this reason, calculation R3 is exactly two times R2 in the case of octanol. Obviously, calculation R3 is not valid for n-octanol and does not have to be considered.

Titration curve



Sample 1/3, series 2/25/2009, 1:11:38 PM

Table of measured values

	Volume mL	Increment mL	Signal mV	Change mV	1st deriv. mV/mL	Time s	Temperature °C
	0.000	NaN	217.8	NaN	NaN	0	25.0
	0.040	0.040	186.4	-31.4	NaN	6	25.0
	0.080	0.040	166.5	-19.9	NaN	12	25.0
	0.120	0.040	152.7	-13.8	NaN	18	25.0
	0.160	0.040	142.0	-10.7	NaN	24	25.0
	0.200	0.040	133.8	-8.2	-174.32	30	25.0
	0.240	0.040	127.0	-6.8	-150.74	36	25.0
	...	...	...	...	...	...	...
	1.641	0.040	10.2	-6.2	-155.22	250	25.0
	1.681	0.040	4.2	-6.0	-164.36	256	25.0
EQP1	1.711412	NaN	-1.4	NaN	-166.84	NaN	NaN
	1.721	0.040	-3.2	-7.4	-166.71	262	25.0
	1.761	0.040	-9.4	-6.2	-161.43	268	25.0
	1.801	0.040	-15.8	-6.4	-150.08	274	25.0
	1.841	0.040	-21.6	-5.8	-135.19	280	25.0
	1.881	0.040	-26.6	-5.0	-118.36	286	25.0
	...	...	...	...	...	...	...
	11.375	0.040	-197.8	-6.3	-196.06	737	25.0
	11.415	0.040	-206.0	-8.2	-234.50	744	25.0
	11.455	0.040	-216.5	-10.5	-255.80	751	25.0
EQP2	11.468579	NaN	-220.5	NaN	-256.63	NaN	NaN
	11.495	0.040	-228.2	-11.7	-253.28	760	25.0
	11.535	0.040	-238.1	-9.9	-227.90	767	25.0
	11.575	0.040	-246.1	-8.0	-187.95	775	25.0
	11.615	0.040	-252.0	-5.9	-146.99	781	25.0
	11.655	0.040	-257.1	-5.1	-116.57	787	25.0
	11.695	0.040	-261.4	-4.3	NaN	793	25.0
	11.735	0.040	-265.2	-3.8	NaN	799	25.0
	11.775	0.040	-268.6	-3.1	NaN	805	25.0
	11.815	0.040	-271.7	-3.1	NaN	812	25.0
	11.855	0.040	-274.5	-2.8	NaN	818	25.0

Sample 1/3, series 2/25/2009, 1:11:38 PM

Comments

Chemistry and Calculations

1) The acid carbamate is titrated with TBAH yielding two inflection points. The first equivalence point is the total amount of acid in the system, whereas the *second equivalence point* represents the amount of acid carbamate formed during the sample preparation portion of the method.

2) The Hydroxyl Number is given as the milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g sample:

$$OH-Number = \frac{(Q2 - B[OH-number]) * 56.1}{m}$$

where

m	=	Sample mass (g)
Q2	=	Titrant consumption between first and second equivalence point (mmoL)
B[OH-number]	=	Titrant consumption of the blank value (mmoL)
56.1	=	Molar mass of KOH

3) For a ***pure compound***, the OH-number is inversely proportional to the hydroxyl equivalent weight

Hydroxyl equivalent weight (g/equivalent) = 56100 / Hydroxyl Number

and the molecular weight

Molecular weight (g/mol) = (56100 x Number of OH-group per molecule) / Hydroxyl Number

4) The average molecular weight (g/mol) of the polyol can be calculated as follows:

$$MW = \frac{m \cdot 1000 \cdot 2}{Q2 - B[OH\_number]}$$

where

m	=	Sample mass (g)
Q2	=	Titrant consumption between first and second equivalence point (mmoL)
B[OH-number]	=	Titrant consumption of the blank value (mmoL)
1000	=	Conversion factor that converts grams to milligrams
2	=	Two end groups per polyol chain

If we combine equations 1) with equation 3) we find that the product of the Molecular Weight and the Hydroxyl Number is always 112200:

$$MW * OH-Number = 122200$$

This relationship can be used to calculate the average molecular weight of the polyols.

Tips and hints for the titration

- This test works best with an anhydrous, stabilized with anti-oxidant 2,6-Di-tert-butylphenol (BHT) and alcohol free tetrahydrofuran.
- Acetonitrile used for the preparation of the isocyanate solution (TSI) must also be anhydrous and alcohol free.
- Special care must be taken in order to minimize the amount of water that is introduced during the sample preparation portion of the test method. Thus, appropriate conditioning is required.
- A molecular sieve trap must be placed above the isocyanate solution since TSI is very sensitive to moisture. The titrant TBAH must be protected against the intake of CO_2 from air.
- The electrode will be removed from the 50:50 water:2-propanol conditioning beaker and placed in a beaker with anhydrous, alcohol free THF or acetonitrile to remove all water from the system. The electrode will then move to the sample beaker for the titration.
- Adding too much water for the neutralization of remaining isocyanate will change the matrix of the titration. This is not recommended for maximum repeatability.

Results

Raw Polyol No. 1

Results

No.	Comment / ID	Start time	Sample size and results		
1/8	Polyol No. 1	10/22/2008 12:12:08 PM	0.2239	g	
			R1 = 539.4	mg KOH/g	Hydroxyl number
			R2 = 203	g/equiv	Equivalent weight
2/8	Polyol No. 1	10/22/2008 12:41:34 PM	0.2151	g	
			R1 = 547.3	mg KOH/g	Hydroxyl number
			R2 = 205	g/equiv	Equivalent weight
3/8	Polyol No. 1	10/22/2008 1:11:16 PM	0.2183	g	
			R1 = 558.2	mg KOH/g	Hydroxyl number
			R2 = 201	g/equiv	Equivalent weight
4/8	Polyol No. 1	10/22/2008 1:40:49 PM	0.1821	g	
			R1 = 558.2	mg KOH/g	Hydroxyl number
			R2 = 201	g/equiv	Equivalent weight
5/8	Polyol No. 1	10/22/2008 2:09:54 PM	0.2283	g	
			R1 = 547.3	mg KOH/g	Hydroxyl number
			R2 = 205	g/equiv	Equivalent weight
6/8	Polyol No. 1	10/22/2008 2:38:33 PM	0.2013	g	
			R1 = 563.8	mg KOH/g	Hydroxyl number
			R2 = 199	g/equiv	Equivalent weight
7/8	Polyol No. 1	10/22/2008 3:07:38 PM	0.1935	g	
			R1 = 561.0	mg KOH/g	Hydroxyl number
			R2 = 200	g/equiv	Equivalent weight
8/8	Polyol No. 1	10/22/2008 3:37:18 PM	0.2494	g	
			R1 = 550.0	mg KOH/g	Hydroxyl number
			R2 = 204	g/equiv	Equivalent weight

Statistics

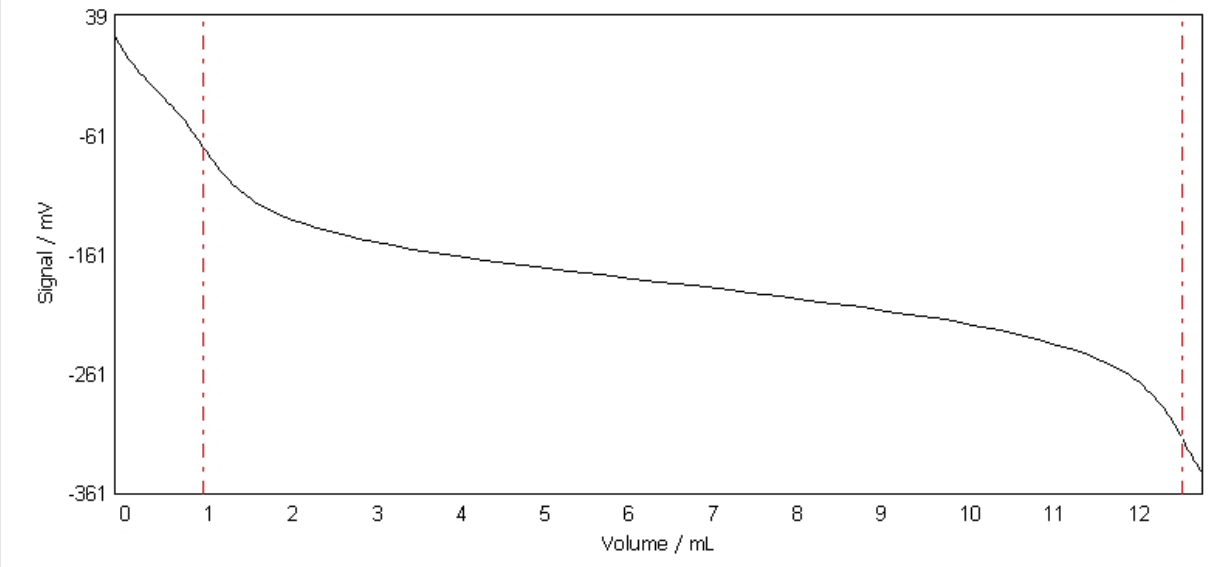
Rx	Name	n	Mean value	unit	s	srel[%]
R1	Hydroxyl number	8	553.2	mg KOH/g	8.4	1.518
R2	Equivalent weight	8	203	g/equiv	3	1.524

Additional results

Statistics

Rx	Name	n	Mean value	unit	s	srel[%]
Polyol No. 2						
R1	Hydroxyl number	18	271.9	mg KOH/g	4.3	1.585
R2	Equivalent weight	18	206	g/equiv	3	1.568
3 decimal digits:						
Polyol No. 3						
R1	Hydroxyl number	4	56.898	mg KOH/g	0.460	0.808
R2	Equivalent weight	4	986.024	g/equiv	7.976	0.809
Polyol No. 4						
R1	Hydroxyl number	3	57.821	mg KOH/g	0.268	0.463
R2	Equivalent weight	3	970.257	g/equiv	4.490	0.463
Polyol No. 5						
R1	Hydroxyl number	3	461.388	mg KOH/g	4.155	0.901
R2	Equivalent weight	3	121.596	g/equiv	1.101	0.902
Polyol No. 6						
R1	Hydroxyl number	3	59.947	mg KOH/g	0.285	0.476
R2	Equivalent weight	3	935.834	g/equiv	4.454	0.476
Polyol No. 7						
R1	Hydroxyl number	3	116.002	mg KOH/g	0.884	0.762
R2	Equivalent weight	3	483.630	g/equiv	3.688	0.763

Titration curve



Polyol No. 1, sample series 10/22/2008 12:12:07, sample 8/8

Table of measured values

	Volume mL	Increment mL	Signal mV	Change mV	1st deriv. mV/mL	Time s	Temperature °C
	0.000	NaN	22.7	NaN	NaN	0	25.0
	0.114	0.114	10.1	-12.6	NaN	5	25.0
	0.171	0.057	4.0	-6.1	NaN	12	25.0
	0.200	0.029	1.2	-2.8	NaN	18	25.0
	0.234	0.034	-2.1	-3.3	NaN	44	25.0
	0.264	0.030	-4.3	-2.2	-85.24	51	25.0
	0.321	0.057	-9.0	-4.7	-77.44	57	25.0
	...	...	...	...	...	...	...
	1.012	0.031	-65.2	-3.1	-102.72	173	25.0
	1.041	0.029	-68.9	-3.1	-103.03	179	25.0
EQP1	1.048733	NaN	-69.7	NaN	-103.29	NaN	NaN
	1.068	0.027	-71.6	-2.7	-103.51	185	25.0
	1.099	0.031	-74.8	-3.2	-102.88	191	25.0
	1.127	0.028	-77.8	-3.0	-101.59	197	25.0
	1.155	0.028	-80.4	-2.6	-99.19	203	25.0
	1.191	0.036	-84.1	-3.7	-96.44	209	25.0
	...	...	...	...	...	...	...
	12.653	0.024	-306.9	-2.8	-125.22	662	25.0
	12.679	0.026	-310.1	-3.4	-129.25	669	25.0
	12.700	0.021	-313.0	-2.9	-132.64	675	25.0
EQP2	12.717160	NaN	-315.1	NaN	-133.07	NaN	NaN
	12.721	0.021	-315.6	-2.6	-132.55	681	25.0
	12.747	0.026	-319.1	-3.5	-131.58	687	25.0
	12.768	0.021	-322.0	-2.9	-129.55	693	25.0
	12.790	0.022	-324.7	-2.7	-127.59	699	25.0
	12.816	0.026	-327.8	-3.1	-124.80	705	25.0
	12.842	0.026	-331.2	-3.4	NaN	713	25.0
	12.863	0.021	-333.7	-2.5	NaN	719	25.0
	12.890	0.027	-336.7	-3.0	NaN	725	25.0
	12.919	0.029	-339.8	-3.1	NaN	732	25.0
	12.948	0.029	-342.6	-2.8	NaN	738	25.0

Polyol No. 1, sample series 10/22/2008 12:12:07, sample 8/8

Method

001 Title

Type	General titration
Compatible with	T70 / T90
ID	m453A
Title	Hydroxyl number
Author	Administrator
Date/Time	11.02.2009 13:20:04
Modified at	11.02.2009 14:25:58
Modified by	admin
Protect	No
SOP	None

002 Sample

Number of IDs	1
ID 1	Polyol No. 1
Entry type	Weight
Lower limit	0.2 g
Upper limit	0.3 g
Density	1.0 g/mL
Correction factor	1.0
Temperature	25.0°C
Entry	Arbitrary

003 Titration stand (Rondo/Tower A)

Type	Rondo/Tower A
Titration stand	Rondo60/1A
Lid handling	No

004 Conditioning

Type	Fix
Interval	1
Position	Special beaker 1
Time	10 s
Speed	30%
Condition	No

005 Pump

Auxiliary reagent	THF
Volume	10.0 mL
Condition	No

006 Dispense (normal) [1]

Titrant	Isocyanate
Concentration	1.0 mol/L
Volume	10.0 mL
Dosing rate	60.0 mL/min
Condition	No

007 Stir

Speed	30%
Duration	600 s
Condition	No

008 Pump

Auxiliary reagent	H_2O
Volume	2.0 mL
Condition	No

009 Stir

Speed	30%
Duration	120 s
Condition	No

010 Pump

Auxiliary reagent	THF
Volume	40.0 mL
Condition	No

011 Stir

Speed	30%
Duration	30 s
Condition	No

012 Titration (EQP) [1]

Titrant

Titrant	TBAH
Concentration	0.1 mol/L

Sensor

Type	pH
Sensor	DGi116-Solvent
Unit	mV

Temperature acquisition

Temperature acquisition	No

Stir

Speed	30%

Predispense

Mode	None
Waiting time	0 s

Control

Control	User
Titrant addition	Dynamic
dE (set value)	6.0 mV
dV (min)	0.02 mL
dV (max)	0.5 mL
Mode	Equilibrium controlled
dE	0.5 mV
dt	3 s
t (min)	6 s
t (max)	30 s

Evaluation and recognition

Procedure	Standard
Threshold	50
Tendency	Negative
Ranges	0
Add. EQP criteria	No

Termination

At Vmax	25 mL
At potential	No
At slope	No
After number of recognized EQPs	Yes
Number of EQPs	2
Combined termination criteria	No
Accompanying stating	
Accompanying stating	No
Condition	
Condition	No

013 Calculation R1

Result	Hydroxyl number
Result unit	mg KOH/g
Formula	R1=(Q2-B[OH number])*C/m
Constant	M/z
M	M[KOH]
z	z[KOH]
Decimal places	1
Result limits	No
Record statistics	Yes
Extra statistical func.	No
Send to buffer	No
Condition	No

014 Calculation R2

Result	Equivalent weight
Result unit	g/equiv.
Formula	R2=(56.1*1000)/R1
Constant	0
M	M[None]
z	z[None]
Decimal places	1
Result limits	No
Record statistics	Yes
Extra statistical func.	No
Send to buffer	No
Condition	No

015 Conditioning

Type	Fix
Interval	1
Position	Conditioning beaker
Time	30 s
Speed	30%
Condition	No

016 End of sample

Conditioning beaker:	50:50 water:2-propanol
Special rinse beaker 1:	anhydrous, alcohol free THF or acetonitrile to remove all water from the electrode

Blank value determination

001 Title

Type	General titration
Compatible with	T70 / T90
ID	m453B
Title	Blank Hydroxyl number
Author	Administrator
Date/Time	11.02.2009 13:15:34
Modified at	11.02.2009 14:18:03
Modified by	admin
Protect	No
SOP	None

002 Sample

Number of IDs	1
ID 1	Blank value OH-No.
Entry type	Fixed volume
Volume	60 mL
Density	1.0 g/mL
Correction factor	1.0
Temperature	25.0°C
Entry	Arbitrary

003 Titration stand (Rondo/Tower A)

Type	Rondo/Tower A
Titration stand	Rondo60/1A
Lid handling	No

004 Conditioning

Type	Fix
Interval	1
Position	Special beaker 1
Time	10 s
Speed	30%
Condition	No

005 Pump

Auxiliary reagent	THF
Volume	10.0 mL
Condition	No

006 Dispense (normal) [1]

Titrant	Isocyanate
Concentration	1.0 mol/L
Volume	10.0 mL
Dosing rate	60.0 mL/min
Condition	No

007 Stir

Speed	30%
Duration	600 s
Condition	No

008 Pump

Auxiliary reagent	H_2O
Volume	2.0 mL
Condition	No

009 Stir

Speed	30%
Duration	120 s
Condition	No

010 Pump

Auxiliary reagent	THF
Volume	40.0 mL
Condition	No

011 Stir

Speed	30%
Duration	30 s
Condition	No

012 Titration (EQP) [1]

Titrant

Titrant	TBAH
Concentration	0.1 mol/L

Sensor

Type	pH
Sensor	DGi116-Solvent
Unit	mV

Temperature acquisition

Temperature acquisition	No

Stir

Speed	30%

Predispense

Mode	None
Waiting time	0 s

Control

Control	User
Titrant addition	Dynamic
dE (set value)	2.0 mV
dV (min)	0.005 mL
dV (max)	0.1 mL
Mode	Equilibrium controlled
dE	0.5 mV
dt	3 s
t (min)	6 s
t (max)	30 s

Evaluation and recognition

Procedure	Standard
Threshold	50
Tendency	Negative
Ranges	0
Add. EQP criteria	No

Termination

At Vmax	5 mL
At potential	No
At slope	No
After number of recognized EQPs	Yes
Number of EQPs	1
Combined termination criteria	No
Accompanying stating	
Accompanying stating	No
Condition	
Condition	No

013 Calculation R1

Result	Blank value
Result unit	mmol
Formula	R1=Q
Constant	1
M	M[none]
z	z[none]
Decimal places	1
Result limits	No
Record statistics	Yes
Extra statistical func.	No
Send to buffer	No
Condition	No

014 Conditioning

Type	Fix
Interval	1
Position	Conditioning beaker
Time	30 s
Speed	30%
Condition	No

015 End of sample

016 Blank

Name	OH number
Value B =	Mean[R1]
Unit	mmol
Limits	No
Condition	No

Conditioning beaker:	50:50 water:2-propanol
Special rinse beaker 1:	anhydrous, alcohol free THF or acetonitrile to remove all water from the electrode