HIRANUMA APPLICATION DATA	Karl Fischer Titrator	Data No.	KF6	Nov.29. 2018
Water contents	**Amines**			

1.Abstract

Water content of amines could be determined by Karl Fischer coulometric titrator. In coulometric titration, iodine of Karl Fischer reagent is generated by electrolysis and generated iodine quantitatively reacts with water. Reaction formula is described below.

$$H_2O + I_2 + SO_2 + 3RN + CH_3OH \rightarrow 2RN \cdot HI + RN \cdot HSO_4CH_3$$

$$2RN \cdot HI \rightarrow I_2 + 2RN + 2H^+ + 2e^-$$

The amines change anode solution pH to basic. In the case of an amine with stronger basicity than benzylamine (pKa = 9.34[1]) as a guideline, there are such effects as the end point becomes unclear. Therefore, when measuring a strongly basic amine, add a neutralizing agent to the anode solution beforehand to suppress the influence of undesirable effect caused by adding the sample. This application introduces an example for the water determination in cyclohexylamine(liquid), diethanolamine(liquid) and imidazole(solid). Reference
1) H. K. Hall, J. Am. Chem. Soc. (1957) 79 5441.

2. Apparatus and Reagents

(1) Apparatus

Titrator	:	HIRANUMA Karl Fischer Coulometric titrator AQ-series or MOICO-A19
Electrolytic cell	:	Standard Cell Fritless Cell (No cathode solution required)

(2)Reagents

Anode solution	:	HYDRANAL Coulomat AG (Honeywell)
Cathode solution	:	HYDRANAL Coulomat CG (Honeywell)
Neutralizing agent	:	Benzoic acid

3. Procedure

3.1. Measurement of liquid sample

(1) Add 10 g of benzoic acid and 100 mL of anode solution in anode compartment of titration cell as shown in Fig.3.1. Add one ampoule of cathode solution into the cathode compartment. When fritless cell is used, cathode solution is not necessary. Stir the anode solution to dissolve benzoic acid.
(2) Start blanking to attain stable background.
(3) Wash the syringe with sample.
(4) Draw the sample into syringe and then weigh the syringe.
(5) Inject sample from rubber septum of electrolytic cell as shown in Fig.3.2.

3.2. Measurement of solid sample

(1) Add 10 g of benzoic acid and 100 mL of anode solution in anode compartment of titration cell as shown in Fig.3.1. Add one ampoule of cathode solution into the cathode compartment. Stir the anode solution to dissolve benzoic acid.

(2) Start blanking to attain stable background.

(3) Put a sample container, powder funnel and spoon on the balance. Record its read (S_1 [g]).

(4) Open the glass stopper of titration cell lid to introduce the sample with powder funnel as shown in Fig.3.3.

(5) Start titration. Measurement parameter is shown in Table 4.1.

(6) Weigh the sample container, powder funnel and spoon again and record its read (S_2 [g]). The difference of (S_1-S_2 [g]) is set as sample size.

(7) Blank measurement is also performed with same procedure except for sample addition.

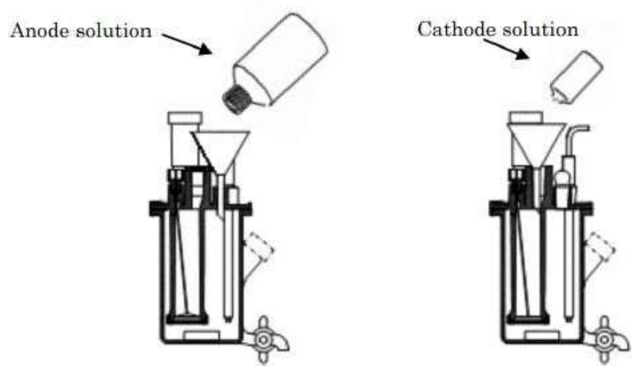

Fig.3.1. Preparation of the reagents. (Standard Cell)

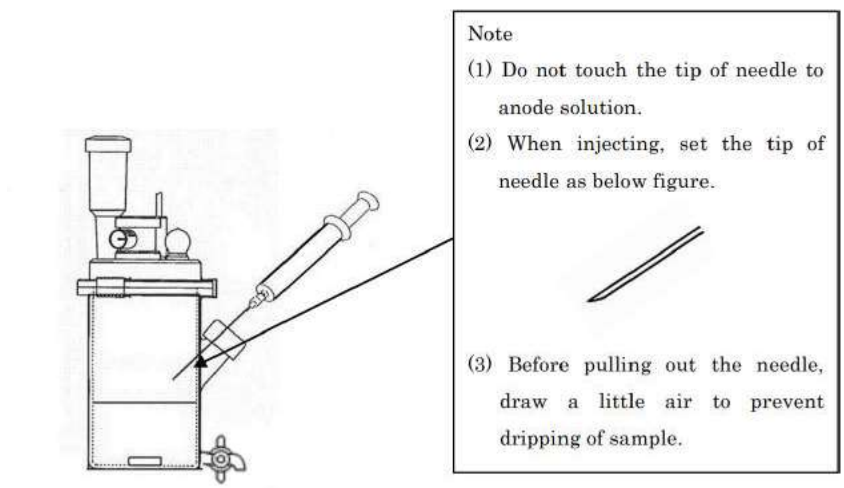

Fig.3.2. Injection of liquid sample.

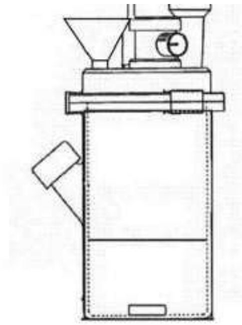

Fig.3.3. Addition of solid sample.

4. Parameters and results

Table 4.1. Parameters

Condition File		
Cal Mode	0:Sample weight(net)	
	X=(H_2O-BLANK)/SIZE	
Interval Time	20	sec
Current	SLOW	
S-Timer*	0	min
Blank Value	0	μg
Unit Mode	AUTO	
Auto Interval	0	g
Minimum Count	5	μg
Back Ground	ON	
Sample Size Input	Every Time	
Cell Type	Standard/Fritless	

* Dissolving time for solid sample set on S.Timer

Table 4.2. Results of water content measurement in amines

Sample	Reagent	Cell	Sample Size (g)	Water (μg)	Water Content (%)	Statistics Results	
Cyclohexylamine	AG	Standard	0.1742	235.5	0.1352	Avg.	0.1350 %
	+ Benzoic acid		0.1790	239.5	0.1338	SD	0.8 %
	/ CG		0.1941	263.8	0.1359	RSD	0.8 %
	AG	Fritless	0.2232	307.1	0.1376	Avg.	0.1367 %
	+ Benzoic acid		0.2694	366.1	0.1359	SD	0.0009 %

					0.1367	RSD	0.6 %
					0.1940	Avg.	0.1923 %
	/ CG		0.2877	557.8	0.1939	SD	0.0029 %
			0.2340	442.3	0.1890	RSD	1.5 %
	AG	Fritless	0.2361	476.8	0.2019	Avg.	0.2020 %
			0.2473	505.0	0.2042	SD	0.0022 %
			0.2696	538.9	0.1999	RSD	1.1 %
Imidazole	AG	Standard	0.4219	643.7	0.1526	Avg.	0.1524 %
	/ CG		0.6296	964.0	0.1531	SD	0.0008 %
			0.3946	597.7	0.1515	RSD	0.5 %
	AG	Fritless	0.2336	371.5	0.1590	Avg.	0.1586 %
			0.3491	547.7	0.1569	SD	0.0015 %
			0.2551	407.6	0.1598	RSD	0.9 %

5. Note

(1) When the side reaction of amine cannot be suppressed even though you use neutralizing agent, phenomena such as unstable blanking or undetectable endpoint can be obtained. In that case, it may be improved by reducing the amount of sample or replacing titration solvent with new one.

(2) Since aromatic amines react with methanol to form water, it is necessary to use reagent for ketone.

(3) The optimized electrolysis control for fritless cell of AQ series released after 2009 improves the measurement accuracy of fritless cell. It can be used with the evaporator as well. Suitable reagent for fritless cell is required. For example, Hydranal coulomat AG and AG-Oven are compatible with fritless cell.

Keywords: Karl Fischer, Coulometric titration, Amine

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