1. Abstract

Water content of cyclohexanone is 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.

$$H_2O \; + \; I_2 \; + \; SO_2 \; + \; 3RN \; + \; CH_3OH \rightarrow 2RN \cdot HI \; + \; RN \cdot HSO_4CH_3$$
$$2RN \cdot HI \rightarrow I_2 \; + \; 2RN \; + \; 2H^+ \; + \; 2e^-$$
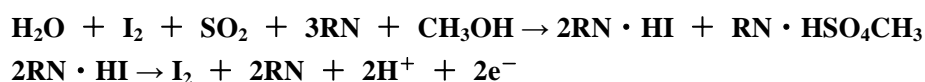
Ketones and aldehydes would interfere the Karl Fischer reaction by side-reaction with methanol (formula (1)).

$$R_2CO \; + \; 2CH_3OH \rightarrow \; R_2C(OCH_3)_2 \; + \; H_2O \quad \cdot \cdot \cdot (1)$$

Therefore it is necessary to use methanol-free anode and cathode solution. There are commercially available reagents with a special composition for ketones and aldehydes. However, cyclohexanone has particularly a strong side reaction activity, so it is difficult to measure by direct injection method at room temperature. In the measurement of cyclohexanone, it is effective to lower the activity of side reaction by cooling or to separate cyclohexanone and water by distillation.

This application introduces an example for the water determination in cyclohexanone with cooled direct injection method and azeotropic distillation method.

2. Apparatus and Reagents

(1) Apparatus for cooled direct injection method

Titrator	:	Hiranuma Karl Fischer Coulometric titrator	AQ-series
Electrolytic cell	:	Electrolytic cell w/cooling chamber	P/N : D327326-1

(2) Apparatus for azeotropic distillation method

Titrator	:	Hiranuma Karl Fischer Coulometric titrator	AQ-series
Evaporator	:	Hiranuma Oil Evaporator	EV-2000L
Electrolytic cell	:	Standard Cell	

(3) Reagents

Anode solution	:	HYDRANAL coulomat AK (for ketone, Honeywell)
Cathode solution	:	HYDRANAL coulomat CG-K (for ketone, Honeywell)
Distillation solvent	:	Dehydrated toluene
Carrier gas	:	Nitrogen gas

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3. Procedure

3.1. Cooled direct injection method

    (1) Fill 100 mL of anode solution and one ampoule of cathode solution into the electrolytic cell as shown in Fig.3.1.

    (2) Cool the inside of the cell by circulating 5 °C cold water in the cooling chamber and wait until the temperature stabilizes.

    (3) Start blanking to attain stable background.

    (4) Wash the syringe with sample.

    (5) Draw the sample into syringe and then weigh the syringe.

    (6) Inject sample from rubber septum of electrolytic cell as shown in Fig.3.2.

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

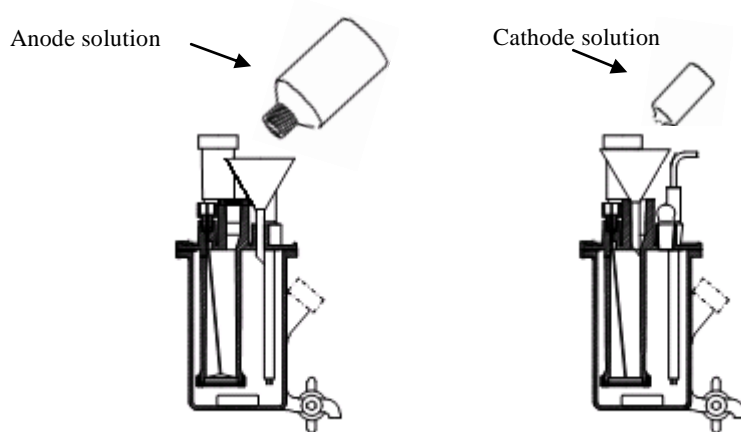   (8) Weigh the syringe again and then set the difference of weight to sample size.

Anode solution   Cathode solution

Fig.3.1. Preparation of the reagents.

Note

(1) Do not touch the tip of needle to anode solution.

(2) When injecting, set the tip of needle as below figure.

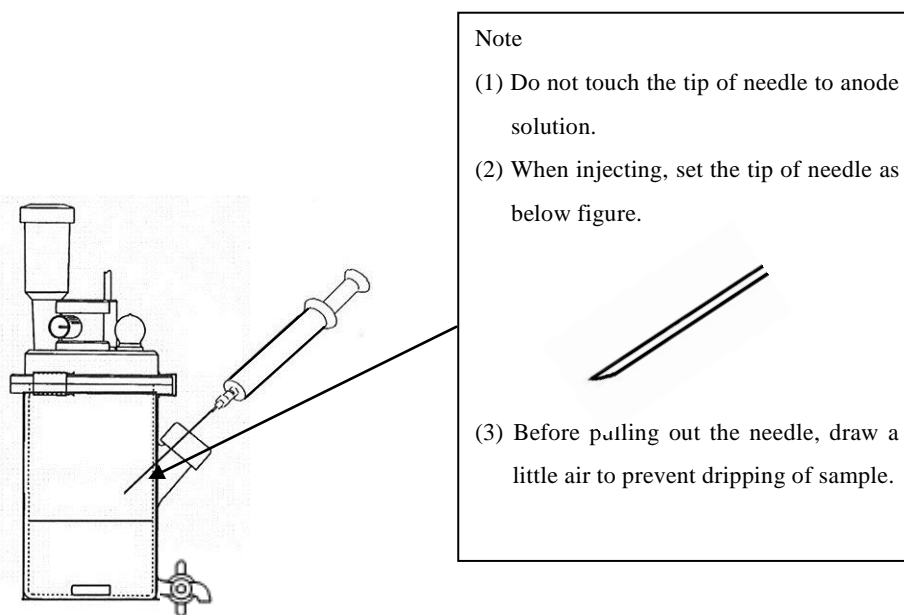(3) Before pulling out the needle, draw a little air to prevent dripping of sample.

Fig.3.2. Injection of sample.

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3.2. Azeotropic distillation method

(1) Fill 100 mL of anode solution and one ampoule of cathode solution into the electrolytic cell as shown in Fig.3.1.

(2) Start blanking to attain stable background.

(3) Connect electrolytic cell and evaporation chamber with tube. Flow carrier gas with 50 mL/min.

(4) Fill 5 mL of distillation solvent in evaporation chamber and heat the chamber at 120 °C.

(5) Keep blanking to attain stable background with carrier gas flowing into electrolytic cell.

(6) Wash the syringe with sample.

(7) Draw the sample into syringe and then weigh the syringe.

(8) Inject sample from rubber septum of distillation chamber as shown in Fig.3.3 and Fig.3.4.

(9) Start titration. Measurement parameter is shown in Table 4.2.

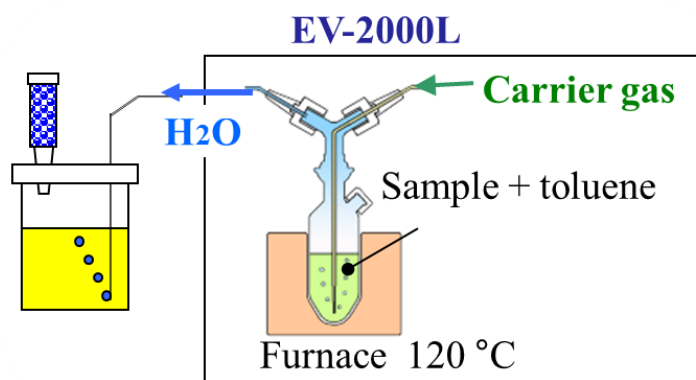(10) Weigh the syringe again and then set the difference of weight to sample size.

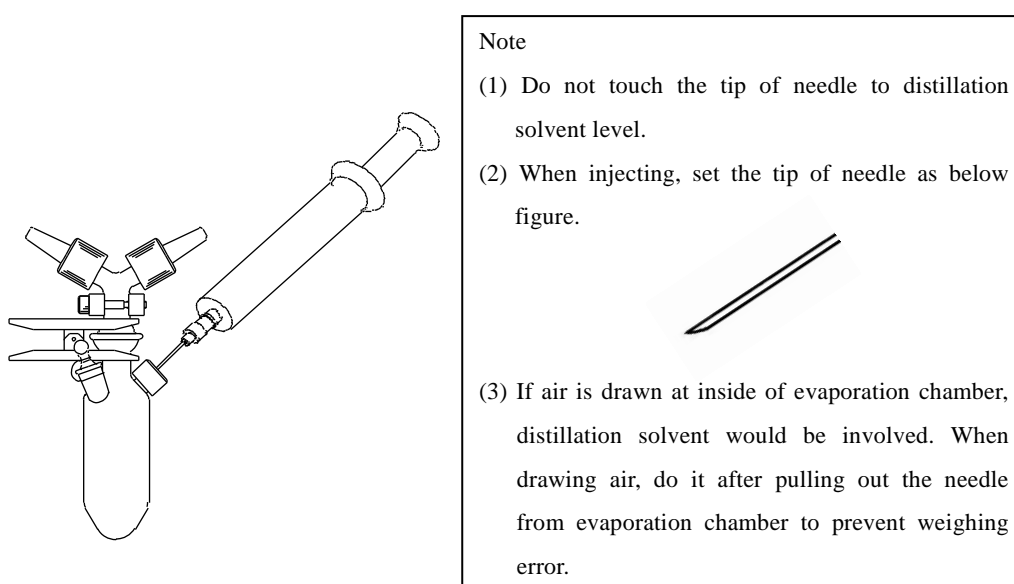Fig.3.3. Schematic diagram of azeotropic distillation method.

Note

(1) Do not touch the tip of needle to distillation solvent level.

(2) When injecting, set the tip of needle as below figure.

(3) If air is drawn at inside of evaporation chamber, distillation solvent would be involved. When drawing air, do it after pulling out the needle from evaporation chamber to prevent weighing error.

Fig.3.4. Sample injection into evaporation chamber.

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4. Parameters and results

Table 4.1 Parameters for cooled direct injection method

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

Table 4.2 Parameters for azeotropic distillation method

Condition File	
Cal Mode	0:Sample weight (net)
	X=(H_2O-BLANK)/SIZE
Interval Time	40 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

Table 4.3 Results of water content measurement in cyclohexanone

Method	Sample size (g)	Water (μg)	Water content (ppm)	Statistics result		
Cooled direct injection	0.2692	55.1	204.7	Avg.	224.8	ppm
	0.2581	62.6	242.5	SD	19.0	ppm
	0.2711	61.6	227.2	RSD	8.5	%
Azeotropic distillation	1.3661	300.2	219.7	Avg.	220.7	ppm
	1.5261	338.9	222.1	SD	1.2	ppm
	1.5824	348.6	220.3	RSD	0.5	%

5. Note

(1) Azeotropic distillation method achieved better results with repetition accuracy than the cooled direct injection method. Since the boiling point of cyclohexanone was 155 °C higher than water and toluene, it seems that water could be separated well from cyclohexanone by distillation. The distillation method can also be applied to paints containing resins and lubricants containing additives.

(2) When substances that cause side reactions flow out from the distillation chamber into the cell, the background gets unstable or high. In that case, it may be improved by reducing the amount of sample or replacing titration solvent with new one.

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