

HIRANUMA APPLICATION DATA	Karl Fischer Titrator	Data No.	KF4	Jun.6. 2017
Water contents	Oil products			

1. Abstract

Water content of Oil products are 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.



Kerosene and diesel oil do not interfere the Karl Fischer reaction and direct injection method could apply. Anode solution for Oil is selected to dissolve samples.

It is known that some of the oil additives interfere Karl Fischer reaction. In that case, azeotropic distillation method with Oil evaporator is appropriate. Water is separated from oil sample by distillation and introduced to electrolytic cell with carrier gas.

Mercaptanes and hydrogen sulfide in oil interfere Karl Fischer reaction. Since these side reactions occur quantitatively, water content result could be corrected with concentration of mercaptanes and hydrogen sulfide. 1 ppm of mercaptanes or hydrogen sulfide lead 0.3 ppm or 0.6 ppm higher water content respectively.

2. Apparatus and Reagents

(1) Apparatus

Titration	:	Karl Fischer Coulometric titrator	AQ-2200A
Evaporator	:	Oil Evaporator	EV-2000L
Electrolytic cell	:	Standard Cell Fritless Cell	

(2) Reagents for direct injection method

Anode solution	:	Hydranal coulomat AG-H (for Oil, nonhalogenated)
Cathode solution	:	Hydranal coulomat CG

(3) Reagents for azeotropic distillation method

Anode solution	:	Hydranal coulomat AG (for general use, nonhalogenated)
Cathode solution	:	Hydranal coulomat CG
Distillation solvent	:	Dehydrated toluene
Carrier gas	:	Nitrogen gas

3. Procedure

3.1. 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) 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.
- (6) Start titration. Measurement parameter is shown in Table 4.1.
- (7) Weigh the syringe again and then set the difference of weight to sample size.

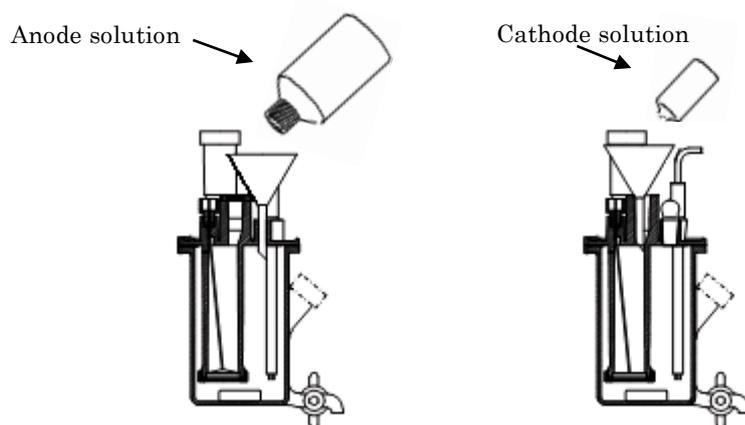
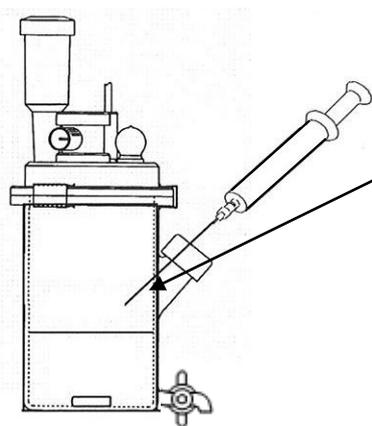


Fig.3.1. Preparation of the reagents.



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.

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 5mL 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.

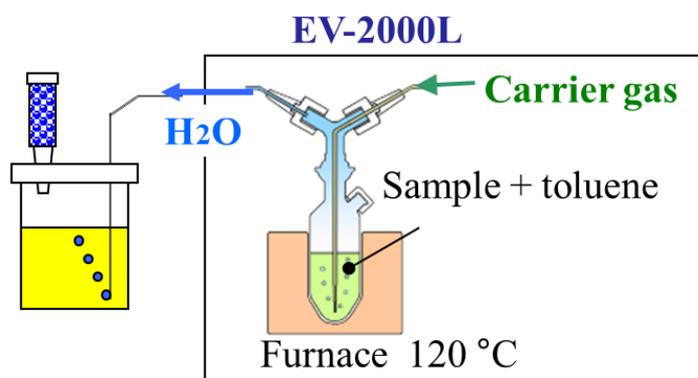


Fig.3.3. Schematic diagram of azeotropic distillation method.

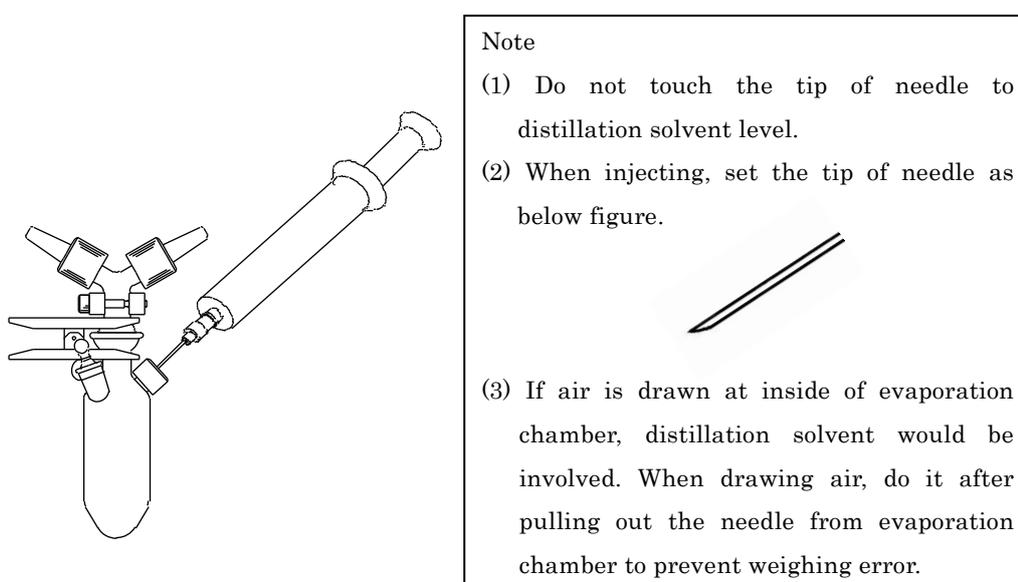


Fig.3.4. Sample injection into evaporation chamber.

4. Parameters and results

Table 4.1. Parameters for 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 ug
Unit Mode	AUTO
Auto Interval	0 g
Minimum Count	5 ug
Back Ground	ON
Sample Size Input	Every Time
Cell Type	Standard / Fritless

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
Min.Timer	5 min
Blank Value	0 ug
Unit Mode	AUTO
Auto Interval	0 g
Minimum Count	5 ug
Back Ground	ON
Sample Size Input	Every Time
Cell Type	Standard / Fritless

Table 4.3. Results of water content measurement in Oil products

Sample	Apparatus	Cell	Reagent	Sample Size (g)	water (μ g)	Water content
kerosene	AQ	Standard	AG-H	2.3483	65.5	27.9 ppm
			CG	2.3482	61.5	26.2
				2.4432	63.5	26.0
diesel oil	AQ	Standard	AG-H	2.0817	72.7	34.9 ppm
			CG	1.9804	68.4	34.5
				2.0600	70.4	34.2

Table 4.4. Results of water content measurement in Oil products

Sample	Apparatus	Cell	Reagent	Sample Size (g)	water (µg)	Water content
Biodiesel	AQ	Standard	AG-H	0.9719	977.9	0.1006 %
			CG	0.9108	914.9	0.1005
				0.8408	839.2	0.0998
Transmission fluid	AQ+EV-L	Standard	AG	0.7267	246.6	339.3 ppm
			CG	0.9484	329.1	347.0
				0.9051	311.9	344.6
		Fritless	AG	0.8201	300.4	366.3 ppm
				0.8152	289.4	355.0
				0.9452	330.4	349.6

5. Note

- (1) Use dried syringe and syringe vial for preventive of contamination by atmospheric water.
- (2) To measure 100 µg or less water detection, make sure stability of blanking. Low and stable background value is important factor for trace level of water measurement.
- (3) Put appropriate anode solution in use according to the solubility of the sample. For example, Hydranal Coulomat AG-H and Oil are suitable for oils with direct injection method.

Note : these reagents does not correspond to Fritless cell.