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Analysis Report

Water content in petroleum oil

Measurement of water content in petroleum oil

1. Measurements overview

The water content of petroleum oil is measured by Karl Fischer coulometric titration with MOICO-A19S. The measurement method was performed according to procedure A of ASTM D6304, the method of adding the sample directly to the cell.

2. Equipment and reagents used

2.1. Equipment and laboratory instruments

- | | |
|------------------------|-------------------------------------------------------------------------------|
| (1) MOICO-A19S | Coulometric Karl Fischer titrator
incl. ; Electrolytic cell with diaphragm |
| (2) Electronic balance | 0.1mg of reciprocal sensibility, calibrated |
| (3) Syringe | Luer lock type |
| (4) Needle | 1.0 mm of inner diameter for low viscosity sample |

2.2. Reagent for coulometric titration

- | | |
|----------------------|----------------------------------|
| (1) Anode solution | Hydranal Coulomat AG (Honeywell) |
| (2) Cathode solution | Hydranal Coulomat CG (Honeywell) |
| (3) Toluene | Reagent grade |

2.3. Experiment environment

Date: 20/Sep./2022, Temperature: 26 – 28 °C, Humidity: RH 85 – 90 %

3. Sample

Petroleum oil, 3 samples,

- (1)B02012, (2)B02108, (3)B02204

4. Measurement procedures

- (1) 60 mL of anode solution and 40 mL of toluene are added into electrolytic cell with using volumetric cylinder. The blank operation is started in order to dehydrate electrolytic cell inside. The blanking is continued until the background value (hereafter called "BG".) becomes low and stable.
- (2) Syringe is washed with sample and then filled with sample. The syringe is weighed and its read (S_1 [g]) is recorded.
- (3) The sample is injected after press the **SAMPLE** key. Injection amount is 3 mL.
- (4) Measurement is started by pressing **Titration**. Measurement is terminated when "interval Time" 30sec is detected. The measurement condition is shown in figure 1.

(5) The syringe is weighed again and its read (S_2 [g]) is recorded. The difference of ($S_1 - S_2$ [g]) is set as sample size.

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===== Master File =====
M.No.                1
Analysis Name        2C RSA6+TOL4/CX
C.No.                1

===== Condition File =====
C.FILE No.          1

[Parameter1]
0:sample weight(net)
(M-b)/w
Interval Time       20 sec
Current             MEDIUM
S.Timer             0 min
Blank Value         0.0 ug
Unit Mode           AUTO
Auto Interval       0.00000 g
Minimum Count       5 ug
Back Ground         ON
Sample Size Input   Every Time
Cell Type           standard

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Figure 1 The measurement conditions.

5. Measurement result

The measurement results are shown in table 1, the example of measurement result printout is shown in figure 2-4.

Table 1 Measurement results of petroleum oil

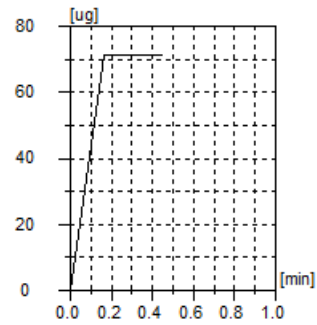
Sample	Meas. No.	Meas. Time	Sample Size (g)	B.G. (ug/min)	H ₂ O (ug)	H ₂ O Conc (ppm)	Statistical results
B02012	1	0:00:29	0.8464	6	27.7	32.7	(*1)
	2	0:00:27	2.3172	7	71.2	30.7	Avg. 29.3 ppm
	3	0:00:27	2.4086	7	71.8	29.8	SD 0.8 ppm
	4	0:01:00	2.4176	8	69.8	28.9	RSD 2.7 %
	5	0:00:34	2.4174	8	70.5	29.2	
	6	0:00:26	2.3826	7	67.5	28.3	
	7	0:00:35	2.4842	8	70.6	28.4	
	8	0:00:36	2.4932	7	73.2	29.4	
	9	0:00:26	2.6102	8	77.5	29.7	
B02108	1	0:00:27	0.8986	6	22.7	25.3	(*1)
	2	0:00:35	2.5743	6	57.3	22.3	Avg. 21.1 ppm
	3	0:00:52	2.6154	6	51.0	19.5	SD 1.4 ppm
	4	0:00:35	2.5960	8	55.7	21.5	RSD 6.8 %
B02204	1	0:00:26	1.0290	6	40.0	38.9	(*1)
	2	0:00:53	2.5086	6	95.8	38.2	Avg. 39.4 ppm
	3	0:01:00	2.4530	7	96.8	39.5	SD 1.1 ppm
	4	0:01:06	2.5300	6	102.3	40.4	RSD 2.8 %

(*1) The results of the first measurement to determine the sample size were excluded from subsequent statistical calculations of repeated measurements.

```

===== AQ Result =====
Analysis Name      2C RSA6+TOL4/CX
Date              2022/09/20 10:28:38
TS No.           1
Sample No.       6
ID Code          B02012
Total H2O        71.2 ug
Back Ground      7 ug/min
Tit Time         0:00:27
Blank Value      0.0 ug
Sample Size      2.31720 g
H2O              71.2 ug
*H2O Conc        30.7 ppm

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T-Data 01 -----
0:00:27  71.2   30.7 ppm

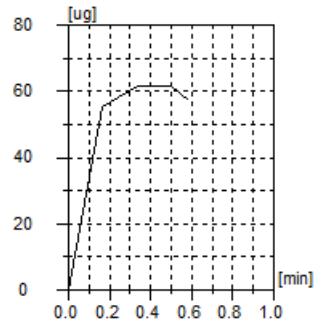
```

Figure 2 measurement result of sample B02012.

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===== AQ Result =====
Analysis Name      2C RSA6+TOL4/CX
Date              2022/09/20 13:59:06
TS No.           1
Sample No.       2
ID Code          B02108
Total H2O        57.3 ug
Back Ground      6 ug/min
Tit Time         0:00:35
Blank Value      0.0 ug
Sample Size      2.57430 g
H2O              57.3 ug
*H2O Conc        22.3 ppm

```



```

T-Data 01 -----
0:00:35  57.3   22.3 ppm

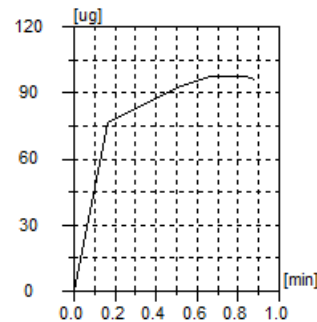
```

Figure 3 measurement result of sample B02108.

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===== AQ Result =====
Analysis Name      2C RSA6+TOL4/CX
Date              2022/09/20 14:13:50
TS No.           1
Sample No.       6
ID Code          B02204
Total H2O        95.8 ug
Back Ground      6 ug/min
Tit Time         0:00:53
Blank Value      0.0 ug
Sample Size      2.50860 g
H2O              95.8 ug
*H2O Conc        38.2 ppm

```



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T-Data 01 -----
0:00:53  95.8   38.2 ppm

```

Figure 4 measurement result of sample B02204.

6. Summary

(1) Sample size

In the first measurement, the amount of water in the sample was unknown, so the amount of added was small. The first measurement results were compared with Table 1 of ASTM D6304 to determine sample size for repeat measurements. The results of the first measurement to determine the sample size were excluded from subsequent statistical calculations of repeated measurements.

(2) Replacement of anode solution

According to the ASTM, replacement of the anode solution will occur when one of the following conditions is reached:

- (i) Unstable background electrolysis current
- (ii) Phase separation in anode solution
- (iii) Total added amount of oil exceeds one quarter of the volume of anode solution (25 mL)

Therefore, sample (B02012) was repeatedly measured until the total added amount of oil reached to 25 mL. Within the number of times measured, the water content measurement results were consistently obtained with an RSD of 3%.

For Samples (B02018) and (B02204), after blanking with a new anode solution, one preliminary measurement to determine the sample amount and three repeated measurements were performed for each sample.

(3) Solubility of sample and measurement result

In the direct injection method, solubility of these oil samples is not sufficient. Anode solution is suspended after a few times of measurement. But water in oil seems to be extracted to anode solution completely because the constant water content is obtained with intentional variation of sample size in each measurement. If water in oil is not extracted to anode solution completely, obtained water content is affected by sample size. Therefore, we concluded that the water content of this oil sample was successfully determined.