HIRANUMA APPLICATION DATA	Karl Fischer Titrator	Data No.	KF19	Feb. 10, 2021
Water contents	**Sugars – KF Volumetry, granulated sugar Factor standardization with water standard**			

1. Abstract

Water contents of granulated sugar could be determined by Karl Fischer volumetric titrator. In volumetric titration, titrant have a factor which means the amount to react with water per 1 mL of titrant. The factor is pre-determined before sample measurement and water content of sample is calculated from the consumed titrant volume by sample measurement.

This application introduces an example for the water determination in granulated sugar. Due to the low water content of this sample, a relatively large amount of sample must be added, but the solubility in methanol as titration solvent is not sufficient. Sugars have tendency to dissolve in formamide. Therefore a mixed solvent of formamide and methanol was chosen as the titration solvent. To make it easier to dissolve the sample, the titration cell was heated to 45 °C using an outer chamber for flowing warm water.

Since the water content of the granulated sugar is often a few hundred ppm, the titrant with low factor value, as 1 mg/mL was used. When pure water is used as the standard material of factor standardization for low factor titrant, the amount of pure water added should be as small as 10 to 20 mg, which makes accurate addition and weighing difficult. Therefore, water standard material which is the solution containing 1 % of water sealed in glass ampoule is used for the factor standardization.

2. Apparatus and Reagents

(1) Apparatus

Titrator	:	Karl Fischer Volumetric titrator	AQV-series
Titration cell	:	Titration cell with cooling chamber	P/N D327510-1
		* This cell could not fit to the stirrer of AQV-300.	
Powder funnel	:	less than 12 mm outer diameter of leg	
Syringe	:	Glass, 10 mL	

(2) Reagents

Titrant	:	HYDRANAL Composite 1 (Honeywell)
Methanol	:	HYDRANAL Methanol (Honeywell)
Formamide	:	HYDRANAL Formamide dry (Honeywell)
Titration solvent	:	Mixed solvent of methanol and formamide at a volume ratio of 1: 2
Standard material	:	Water standard 10 (certificate of analysis : 10.00 mg/g)

* Equivalent product can be substituted these reagents.

(3) Other

Heating device	:	Temperature-controlled bath with circulation function
		* Commercial item

3. Procedure

3.1 Factor standardization

(1) Fill 50 mL of titration solvent into the titration cell as shown in Fig.3.1.

(2) Circulate 45 °C water in the outer chamber of the titration cell with using a temperature-controlled bath, to heat the titration solvent.

(3) Start blanking to attain stable background.

(4) Open an ampoule of water standard 10 and collect the contents in a syringe. To prevent injury when opening the ampoule, handle it according to the instructions of standard material.
To make easier to collect, it is helpful to use packing box of standard material to stand the ampoule as shown by an example in Fig.3.2.

(4) Put the syringe on the balance. Record its read (S_1 [g]).

(5) Inject sample from rubber septum of titration cell as shown in Fig.3.3.

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

(7) Weigh the syringe again and record its read (S_2 [g]). The difference of (S_1-S_2 [g]) is set as sample size.

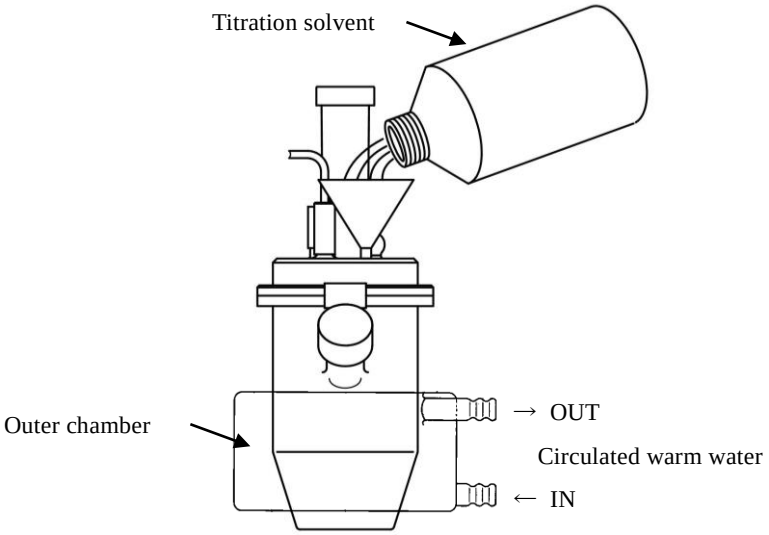
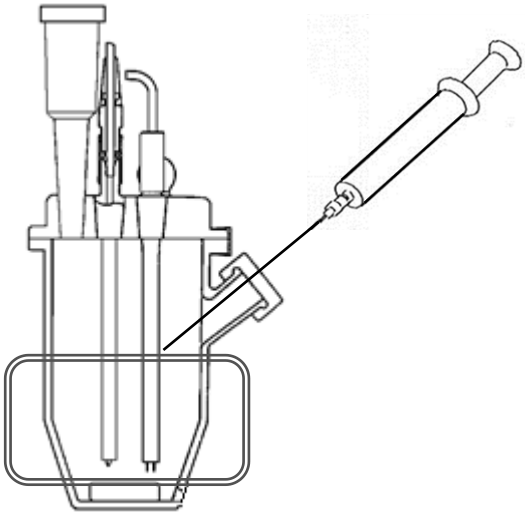


Fig.3.1 Preparation of the reagents

Fig.3.2 Example of water standard ampoule and its packing box.



Note

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

(2) When injecting, set the tip of needle as below figure. The diagonally cut surface of the needle tip faces downward.

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

Fig.3.3. Injection of sample.

3.2. Sample measurement

(1) Fill 50 mL of titration solvent into the titration cell as shown in Fig.3.1.

(2) Circulate 45 °C water in the outer chamber of the titration cell with using a temperature-controlled bath, to heat the titration solvent.

(3) Start blanking to attain stable background.

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

(5) Open the glass stopper of titration cell lid to introduce the sample with powder funnel as shown in Fig.3.4.

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

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

＊ If the sample adheres to the spatula or funnel, include these in the tare of balance.

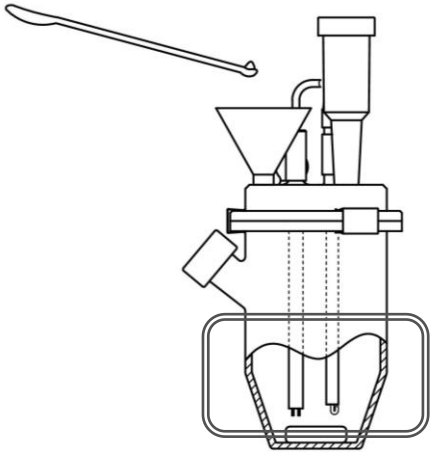


Fig.3.4 Introduction of sample with powder funnel

4. Parameters and results

Table 4.1 Parameters of factor standardization

Item		
Cal Mode	8:KF Factor(By Standard)	
Interval Time	30	sec
Max Volume	20	mL
Min Feed Vol.	0.01	mL
S.Timer	0	min
KF Buret No.	1	
STD H2O Conc.	1.000	%
KF Speed(OUT)	24	mL/min
KF Speed(IN)	24	mL/min
Back Ground	ON	
Sample Size Input	Every Time	
Blank Value	0	mL
E.P Detection	mV	
Solvent	FM	
C.P Level	150	mV
E.P Level	4	
Auto Interval	0	g
Auto Input	OFF	

Table 4.2 Parameters of sample measurement

Item		
Cal Mode	0:Sample weight (net)	
Interval Time	30	sec
Max Volume	20	mL
Min Feed Vol.	0.01	mL
S.Timer	10	min
KF Factor	1.0853	mg/mL
KF Buret No.	1	
KF Speed(OUT)	24	mL/min
KF Speed(IN)	24	mL/min
Back Ground	ON	
Sample Size Input	Every Time	
Blank Value	0	mL
Unit Mode	AUTO	
E.P Detection	mV	
Solvent	FM	
C.P Level	150	mV
E.P Level	4	
Auto Interval	0	g

Table 4.3 Results of factor standardization

Sample	Meas. No.	Sample size (g)	BG (mL)	Titrant volume (mL)	Factor (mg/mL)	Statistic result		
Water standard 10 mg/g	1	0.8749	0.020	8.13	1.0788	Avg.	1.0853	mg/mL
	2	1.0943	0.036	10.11	1.0863	SD	0.0051	mg/mL
	3	1.0697	0.052	9.87	1.0895	RSD	0.47	%
	4	1.0814	0.054	9.97	1.0906			
	5	1.0263	0.050	9.54	1.0815			

Table 4.4 Results of water content measurement in granulated sugar

Sample	Meas. No.	Sample size (g)	BG (mL)	Titrant volume (mL)	Water (mg)	Water content (ppm)	Statistic result		
Granulated sugar	1	3.1130	0.096	0.81	0.775	249.0	Avg.	239.2	ppm
	2	3.1342	0.130	0.81	0.738	235.5	SD	9.2	ppm
	3	3.1568	0.119	0.82	0.761	241.1	RSD	3.86	%
	4	6.2303	0.121	1.48	1.475	236.7			
	5	6.2351	0.132	1.56	1.550	248.6			
	6	6.2127	0.136	1.42	1.394	224.4			

5. Note

(1) The blanking might become unstable when time has passed since the solvents of methanol and formamide were mixed. The cause could be due to the ammonia generated by mixing these solvents. Adding 3 g of benzoic acid to 50 mL of the titration solvent improves the unstable state of blanking.

(2) In the measurement of granulated sugar, the dissolution time of the sample was set to 10 minutes in the parameter “S-Timer”. If the sample becomes difficult to dissolve due to repeated measurements, replace it with a new solvent. In this report, the titration solvent was replaced with a new one every 3 sample measurements.

(3) In the measurement of this report, the measurement condition “Background” is set to ON for background correction. The background is the consumed volume of KF titrant to keep the titrant solvent anhydrous during blanking. With this function, the amount of titrant consumed by the background is subtracted from the measurement result.

The reasons for using the background correction in this report are as follows:

In the measurement of this report, the experimental conditions are such that the blanking is relatively less stable than in the normal measurement, and about 0.01 mL/min of KF titrant is consumed in blanking. This is due to the following experimental conditions.

(i) Low factor of KF titrant
(ii) Formamide-containing titration solvent
(iii) Heating of titration solvent

Since one measurement takes about 10 minutes to measure the sample, the volume of KF titrant consumed to maintain the anhydrous state during the measurement is about 0.1 mL. The amount of KF titrant consumed by sample measurement is approximately 1 mL, and the background has a large effect on the measurement results, so the correction is required.

Keywords：Karl Fischer, Volumetric titration, Granulated sugar, Formamide, Heating