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Determination of Aldehyde by Karl-Fischer Reagent

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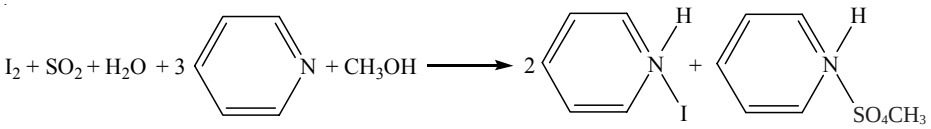
A new Karl-Fischer reagent was prepared by improving conventional Karl-Fischer reagent with an organic solvent and imidazole. The results of determining water content in aldehydes showed that the method possessed many advanced characteristics such as accuracy, rapid, excellent stability and clear end point. The method recovery is 95-105 %, relative standard deviation is less than 5 %.

Key Words: Karl-Fischer reagent, Aldehydes, Moisture determination, Coulometry.

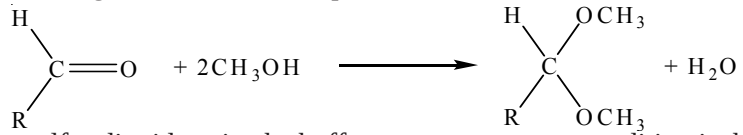
INTRODUCTION

Determination of moisture is an analytical subject which involves many fields and it is an important technical guide line for many products. Karl-Fischer coulometry possesses many advanced characteristics, such as no benchmark, simple operation, lower deviation and high precise. So Karl-Fischer coulometry is used widely[1-4].

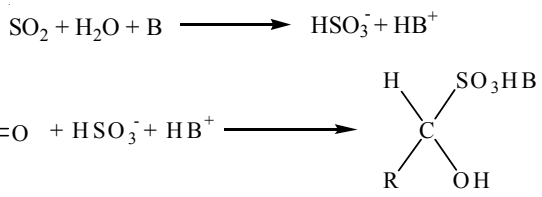
The principle for Karl-Fischer reaction bases on the reaction of I_2 and SO_2 which is required for determination of quantity water. The added base (pyridine) and the acid made up a buffer system. The reaction formula[5]:



The active aldehyde may react with the alcohol and produce acetal and water, then cause the high results or no end point. The acetal reaction:



As the sulfur dioxide exist the buffer system, common condition is the pH < 7. In this condition the water will be consumed, then the results of determination is lower[6,7]:



EXPERIMENTAL

Preparation of Karl-Fischer reagent: To illuminate the method of preparation for Karl-Fischer reagent, the KS01 (Table-1) is an example. Removing 50 mL THFA (tetrahydrofurfuryl alcohol) to the 500 mL reagent bottle and 2.3961 g iodine added rapidly to the reagent bottle, then sway the bottle to make I_2 dissolved, it is marked as A; removing 100 mL THFA and 30 mL chloroform to 500 mL reagent bottle and 4.9528 g imidazole added, then 3 g sulfur dioxide, it is marked as B. The mixture of 4 mL A and 4 mL B, then 2 mL carbon tetrachloride added, it is Karl-Fischer catholyte; the rest A and B is mixed to made up the anolyte.

RESULTS AND DISCUSSION

According to the overall design, four factors are considered. Three levels are selected in every factor, then an orthogonal experiment is designed under no reciprocal effect. Orthogonal table of $L_9(3^4)$ is adopted to design the experiment. Through the results of experiment to find out the most important factor which influence the procedure of experiment[8]. Criteria for evaluation is the recovery. The specific experiment conditions and the results are showed in Table-1.

TABLE-1
EXPERIMENT CONDITIONS AND RESULTS

S. No. (Karl-Fischer reagent)	A (solvent)	B(I_2) (mol/L)	C (the mole ratio of SO_2 to I_2)	D (the mole ratio of organic base to SO_2	Recovery (%)	Evaluation
KS01	THFA	0.1	2	2	136.62	36.62
KS02	THFA	0.3	3	3	119.48	19.48
KS03	THFA	0.5	4	4	128.67	28.67
KS04	2-Chloroethanol	0.1	3	4	147.57	47.57
KS05	2-Chloroethanol	0.3	4	2	143.86	43.86
KS06	2-Chloroethanol	0.5	2	3	145.16	45.16
KS07	Methyl digol	0.1	4	3	91.25	8.75
KS08	Methyl digol	0.3	2	4	85.59	14.41
KS09	Methyl digol	0.5	3	2	90.76	9.24
Average result	–	–	–	–	–	28.20

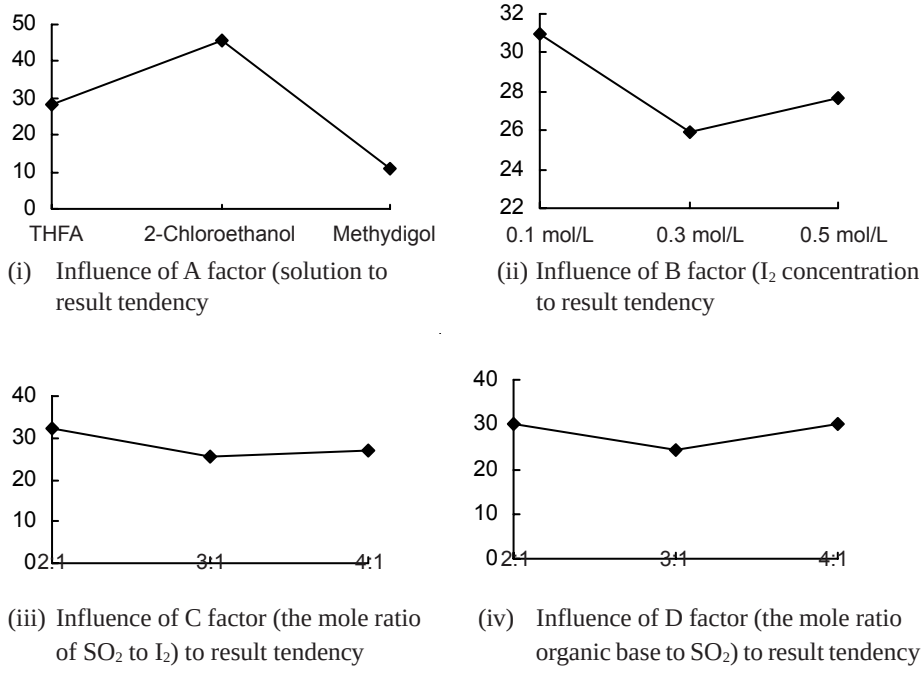
*100 µL sample added. The preparation for the sample of quantity water added: 0.1048 g water added in 100 mL volumetric bottle and then add benzaldehyde to the scale.

Each level appraisal target was carried on the analysis to above table under each factor, calculates each factor separately under some level and the average value (K) and figures out various factors under every horizontal effect and finally calculate various factors deviation (S). The concrete analysis result given in Table-2.

In order to check the test result to select the approximately relations along with various factors level which but changes, according this level average value to draw every level chart like Fig. 1.

TABLE-2
EXPERIMENTAL RESULTS OF ORTHOGONAL DESIGN

	Factor A	Factor B	Factor C	Factor D
Level average result	K_{A1}=28.26	K_{B1}=30.98	K_{C1}=32.06	K_{D1}=29.91
	K_{A2}=45.53	K_{B2}=25.92	K_{C2}=25.43	K_{D2}=24.46
	K_{A3}=10.80	K_{B3}=27.69	K_{C3}=27.09	K_{D3}=30.22
Level effect	a_1=0.06	b_1=2.78	c_1=3.86	d_1=1.71
	a_2=17.33	b_2=-2.28	c_2=-2.77	d_2=-3.74
	a_3=-17.40	b_3=-0.51	c_3=-1.11	d_3=2.02
Factor deviation	S_A=603.09	S_B=13.20	S_C=23.78	S_D=21.00



(i) Influence of A factor (solution to result tendency

(ii) Influence of B factor (I_2 concentration to result tendency

(iii) Influence of C factor (the mole ratio of SO_2 to I_2) to result tendency

(iv) Influence of D factor (the mole ratio organic base to SO_2) to result tendency

Fig. 1. Influence of various factors on result tendency

The tendency figure shows that diethylene glycol monoethyl ether is best solvent to determine the moisture concentration in the aldehyde sample, the best iodine concentration is 0.3 mol/L. The best sulfur dioxide quantity should be the ratio of three times to iodine in mole. The base quantity should take a sulfur dioxide mole of number 3 times. The ratio should be adopted in the later experiment to carry on the test.

Table-2 indicates SA >> SC > SD > SB in the designation experimental scope, it shows that factor A is the most main influence factor, but the influence of factor C and factor D are smaller, factor B is the smallest.

According to the optimum condition selected with the orthogonal design the benzaldehyde and the butyric aldehyde separately carried on the test. The test result shows that the results don't enter the scope of the permission (95-105 %). It is not difficult from the result to discover that the leading side reaction is a reaction of the water consumed. Because the speed of this side reaction is quite low under the high pH value[9], the pH value higher, more advantageous to terminate this reaction. But, it is not difficult to discover from Fig. 1(iv) that the base concentration higher and the experiment result is not certain better. With the alkalinity increasing the reagent become is more unstable and affects the final result.

Since the base can not carry on the adjustment, then duplicate solvent system should be adopted. In the Karl-Fischer system, two kinds of reaction ways cause possibly the different stoichiometry between iodine and water[9]. The most appropriate solvent obtained from the experiment and they are the mix of diethylene glycol monoethyl ether and propylene carbonate. The test results to benzaldehyde and the butyraldehyde are given in Table-3.

TABLE-3
DETERMINATION RESULT OF MOISTURE CONTENT
WITH MIX REAGENT OF SOLVENT

Sample determined	Quantity injected (μL)	1*	2	3	4	5	6	7	Average value (μg)	RSD (%)
Benzaldehyde	20	49.53	47.32	43.28	46.35	49.64	50.38	44.94	47.35	4.52
	40	97.23	94.62	90.54	89.32	88.03	93.58	95.25	92.65	3.10
	60	142.93	143.88	138.53	135.96	139.51	137.61	140.37	139.83	1.57
	80	190.37	184.52	187.39	184.27	186.33	182.59	191.20	186.67	1.37
	100	241.59	239.71	235.51	229.88	237.46	240.13	239.01	237.61	1.20
Butyraldehyde	20	99.35	90.36	98.16	92.76	91.65	93.52	97.86	94.81	3.30
	40	195.82	192.55	188.37	184.53	185.29	183.52	184.36	187.78	2.04
	60	286.66	281.79	282.54	289.36	288.83	287.51	281.06	285.39	1.08
	80	365.56	362.45	363.87	368.59	368.75	369.55	367.24	364.35	0.80
	100	461.58	460.21	465.45	467.38	460.51	468.55	469.25	464.70	0.73

*Digital 1-7: Determinations ordinal number; under ordinal number values: determination primary data, unit μg.

In order to more direct-viewing sees the above determination result parallelism, according to above table mapping (Figs. 2 and 3).

The Table-5 and Figs. 2 and 3 showed obviously that the results parallelism of determining benzaldehyde sample is good. It indicated that determination result accuracy is good in certain quantity scope.

In order to easily see the accurate degree of determination result, the relation curve was done between determination value and the quantity injected (Figs. 4 and 5).

Figs. 4 and 5 show that the linear relations is good between determination results and the quantity injected, so they are in proportion.

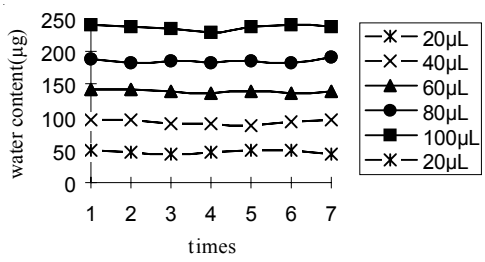


Fig. 2. Level determination results to different benzaldehyde samples injected

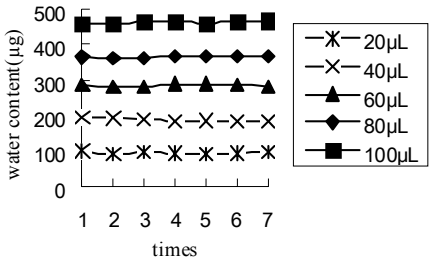


Fig. 3. Level determination results to different butyraldehyde samples injected

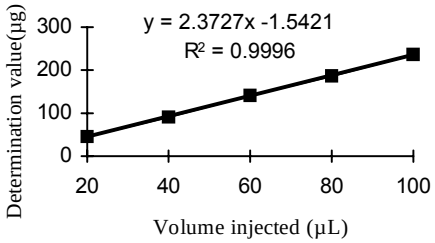


Fig. 4. Relation curve of water determination value in benzaldehyde samples to volume injected

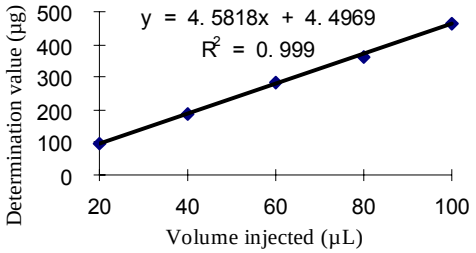


Fig. 5. Relation curve of water determination value in butyraldehyde samples to volume injected

Table-4 shows that the recovery is in the allowance error scope, so the accuracy of determining aldehyde sample is good with self-made karl-fischer reagent.

TABLE-4
RECOVERY OF THE BENZALDEHYDE AND THE BUTYRALDEHYDE SAMPLE ADDED

Sample determined	Quantity	Average value determined (μg)	A (g/L)	B (g/L)	Recovery (%)
Benzaldehyde	20	67.56	3.3780	2.3674	99.22
	40	134.36	3.3590	2.3163	102.36
	60	203.20	3.3867	2.3305	103.68
	80	273.35	3.4169	2.3333	106.36
	100	347.27	3.4727	2.3761	107.64
	Average value	–	3.4026	2.3447	103.85
Butyraldehyde	20	116.37	5.8185	4.7404	95.29
	40	232.33	5.8082	4.6944	98.43
	60	356.27	5.9079	4.7565	104.37
	80	467.16	5.8395	4.5544	113.48
	100	595.26	5.9526	4.6470	115.29
	Average value	–	5.8713	4.6786	105.37

*0.1021 g/mL water added in the benzaldehyde original sample; 0.1137 g/mL water added in the butyraldehyde original sample.
*A: The determination value for sample of quantity water added; B: the determination for original sample.

Similarly, Figs. 6 and 7 show that determining results is proportion to the quantity injected. The good linear relations of the result and the quantity indicate that the recovery is very good in determining moisture of the aldehyde.

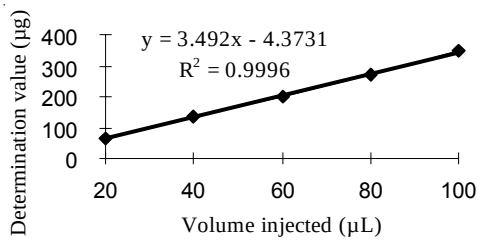


Fig. 6. Relation curve for water determination value in benzaldehyde samples which water added to volume injected

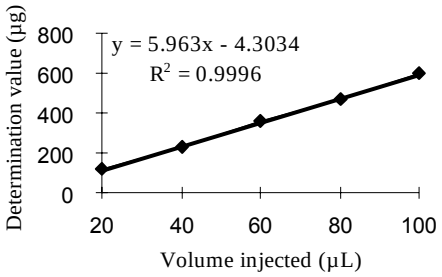


Fig. 7. Relation curve for water determination value in butyraldehyde samples which water added to volume injected

In summary, both of parallelism and the accuracy are good in determining moisture of the aldehyde with self-made reagent and the error of recover is in the allowance scope. So the new Karl-Fischer reagent is feasible in determining the moisture of the aldehydes.

Conclusion

The preliminary experiment confirms that the single solvent is not very good in determining moisture of the aldehyde, so mix solvents are adopted. Find out the optimum solvent and the ratio and prepare a new Karl-Fischer reagent which is suitable to determine moisture of the aldehyde. The experiment results indicate that the expectation direction of experiment is right.

The optimum solvent ratio of diethylene glycol monoethy ether to propylene carbonate is 3 to 1 in volume, sulfur dioxide to iodine and base to sulfur dioxide is the same 3 to 1 in mole. Iodine concentration is 0.3 mol/L. According to the ratio, the recovery is 95-105 %.

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