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Determination of Moisture Content in Thioalcohols by Karl Fischer Coulometry

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The sulfhydryl group in thioalcohols can very easily react with iodine in Karl-Fischer reagent, so it will change the stoichiometrical ratio of Karl-Fischer reaction, then the results of the determination will be inaccurate. Hence, an indirect method was adopted to mask the active sulfhydryl group and then determined the water content in masked thioalcohols. One kind of masking agent and the reactive condition were selected to mask the thioalcohols experimentally and sought the optimal condition from the obtained data. The recovery is among 100-105 % and the relative standard deviation is less than ± 4 %.

Key Words: Karl-Fischer coulometry, Thioalcohols, Moisture content determination.

INTRODUCTION

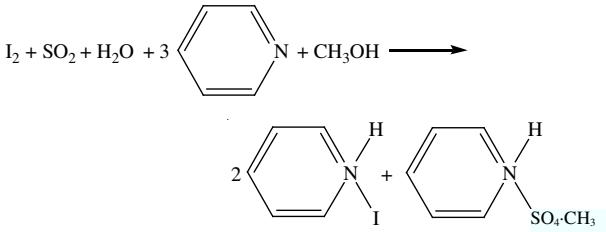
The thioalcohols are widely employed in the chemical industry, the alkyl thiols act as the high polymer molecular weight regulator in the emulsion polymerization[1-7]. In addition the thioalcohols are also used in many kinds of medicine synthesis. Therefore, the moisture content in thioalcohols is required strictly. Karl-Fischer coulometry is an absolute quantitative method. Nowadays, this method is widely used in determining the moisture content in all sort of substances because it has several advantages, such as the low detection limit, the high accuracy, the well repetition and the wide linear range. Thioalcohols with the sulfhydryl group can easily react with iodine in Karl-Fischer reagent and the stoichiometrical ratio of Karl-Fischer reaction will be changed, then the results of the determination will be inaccurate. So the moisture content in thioalcohols could not be determine by Karl-Fischer coulometry directly. The moisture content in thioalcohols was determined by an indirect method,which used a masking agent to mask the thiol for removing or reducing the reaction between thiols and iodine and the product masked shouldn't interfere with the determination. For this problem, choosed the optimum experimental conditions and tested the moisture content in thioalcohol by the indirect method with Karl-Fischer coulometry.

According to the quantitative principle for Karl-Fischer reaction, the reaction formula is followed:

$$I_2 + SO_2 + 2H_2O \rightleftharpoons 2HI + H_2SO_4$$

However, it is a reversible reaction, when the concentration of the sulfuric acid in the system surpasses 0.05 %. Therefore, suitable alkaline substance (for example pyridine) should be added to react with the produced acid in this system and then a buffer system will be formed. The classical Karl-Fischer reagent is prepared in term of the proportion among the iodine, the pyridine, the sulphur dioxide and the methyl alcohol react with the added water follow a stoichiometric quality.

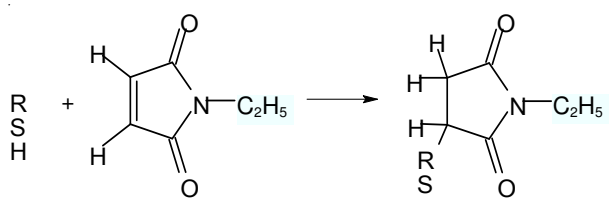
The total reaction equation[8] may be denoted as



Karl-Fischer reagent can determine the moisture content in nearly every organic matters, but there are some minority interferential substances, for example the thioalcohol with the active sulfhydryl group will react with the iodine in Karl-Fischer reagent, then the stoichiometric ratio between water and iodine will be changed and the determination results with Karl-Fischer coulometry can't be accurate on testing the moisture content in thioalcohol. The side reaction as follows:

$$2RSH + I_2 \longrightarrow RSSR + 2HI$$

According to this problem, a masking agent can be employed to mask the thioalcohol and the side reaction will be removed or reduced as possible. The reaction equation[9] between thioalcohol and N-ethylmaleimide is as follows:



EXPERIMENTAL

KLS-411A micro water Karl Fischer coulometer (Shanghai Rex Instrument Factory); 100 µL trace quantity sample injector (Shanghai Medical Laser Instrument Plant); vacuum cabinet dryer (Tianjin Sanshui Scientific Instrument Co., Ltd.); electronic balance (Shanghai Exact Sciences Instrument Co., Ltd.).

Iodine (A.R.) and imidazole (A.R.); N-ethylmaleimide (B.R.) dried several days in the dryer with anhydrous cupric sulfate; methanol (A.R.), chloroform (A.R.) and carbon tetrachloride (A.R.): dehydrated with the 5A molecular sieve; sulphur dioxide: should be dehydrated with concentrated sulfuric acid and dried with anhydrous calcium chloride; 1-pentanthiol (> 97 %).

Masked 1-pentanthiol: Taken 80 g of N-ethylmaleimide into the clean and 250 mL reagent bottle dried and removed 50 mL of 1-pentanthiol in this bottle quickly. This bottle was put in 95 ºC water bath and taken out after 9 h and kept more than 24 h.

Preparing process of Karl-Fischer reagent: There are cathode compartment and anode compartment in the Karl-Fischer coulometry cell and the Karl-Fischer reagent should be divided into two solutions -A and B-prepared separately. The specific method is as follows: (1) Removed 50 mL of methanol into the 500 mL reagent bottle accurately, takes the 4.4125 g iodine with the electronic balance and put the iodine into the bottle with methanol rapidly, capping it and making the iodine dissolve completely by shaking (solution **A**). (2) Takes 7.5631 g imidazole into the 500 mL of reagent bottle accurately, the stopper must be capped after this operation to prevent the water entering. At the same time, removed 100 mL methanol into the reagent bottle with imidazole accurately and 30 mL chloroform was joined, capping it (solution **B**) and then 4 g sulphur dioxide should be mixed approximately. (3) Added 4 mL solution **A** and **B**, respectively into a small reagent bottle and 2 mL carbon tetrachloride was joined too, this is the catholyte. Karl-Fischer anolyte is a mixture of the remained solution **A** and **B**. The catholyte and the anolyte could be used in cell after 24 h in dark place.

RESULTS AND DISCUSSION

In order to ensure whether this indirect method was accurate or not, then determined the moisture content in 1-pentanthiol with the home-made Karl-Fischer reagent. The results of determination were shown in Table-1:

According to the Table-1, the results of determination showed well parallelism. The relative deviation was lower than 3 %. The linear range between the results and the volume of injected sample was very good, so the precision of results of determination was better.

In order to saw the parallelism of the results clearly, according to the table above (Fig. 1).

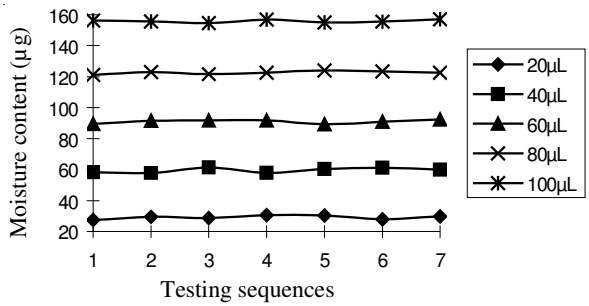


Fig. 1. Results of parallel determination for 1-pentanthiol with different injecting volumes

The better parallelism of the results in Fig. 1 shows that the precision of the determining results is well in a definite range of injected volume. A relation curve between the moisture content and the volume of injected sample was drew for seeing the accuracy of the determining results easily, as Fig. 2.

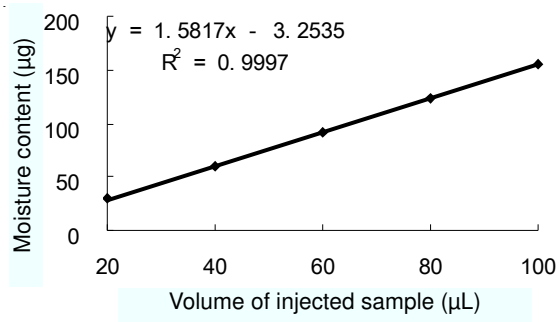


Fig. 2. A curve between the moisture content and the volume of injected samples

Takes 0.3551 g water into 25 mL volume bottle and definited the volume with the masked 1-pentanthiol, then tested it 7 times per sample. The formula of recovery is:

$$R = \frac{100 \times b - (100 - m) \times a}{100 \times m} \times 100\ \%$$

R: recovery, a = moisture content in masked 1-pentanthiol, b = moisture content in masked 1-pentanthiol after adding water, m = quality of water added

TABLE-1
RESULTS OF DETERMINING THE MOISTURE CONTENT IN 1-PENTANTHIOL

Volume of injected sample (µL)	Results of determination (µg)							Average (µg)	Relative deviation (%)
	1	2	3	4	5	6	7		
20	27.524	29.548	28.659	30.567	30.451	27.962	29.813	29.22	3.43
40	58.363	57.851	61.265	57.962	60.315	61.085	59.954	59.54	2.14
60	89.387	91.523	91.773	91.947	89.286	90.923	92.374	91.03	1.10
80	121.030	122.970	121.740	122.670	124.020	123.260	122.530	122.60	0.58
100	156.312	155.790	154.620	156.810	154.990	155.440	157.070	155.86	0.48

TABLE-2
RESULTS OF DETERMINATION OF 1-PENTANTHIOL AFTER ADDING WATER

Volume of injected sample (μL)	Average results (μg)	Average results after adding water (g/L)	Average moisture content (g/L)	Recovery (%)
20	380.63	19.0316	1.5018	101.12
40	761.02	19.0256	1.5032	101.08
80	1525.23	19.0654	1.4977	101.32
Average	–	19.0409	1.5009	101.17

According to the Table-2, the recovery is between 95 and 105 %. A relation curve between the volume of injected samples and the moisture content is drawn as follows:

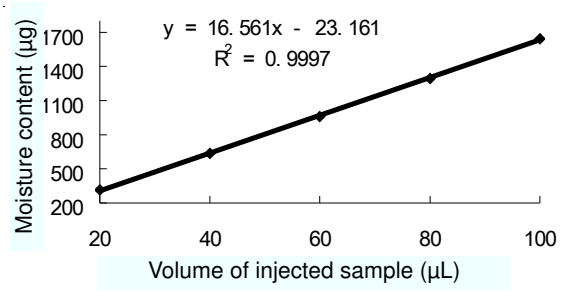


Fig. 3. Results of parallel determination of 1-pentanthiol with home-made Karl-Fischer reagent

Similarly, it is observed that there is a proportion relation between the moisture content and the volume of injected samples after adding water and this better linear relation shows that there is a better repetition and accuracy.

Conclusion

It manifested the better parallelism and accuracy on determining the thioalcohols with home-made Karl-Fischer reagent and the recovery is in the allowed error range. It is feasible that the indirect method determine the moisture content in thioalcohols.

REFERENCES

1. Y. Wang, *Chin. Synth. Rubber Ind*., **13**, 282 (1990).
2. W. Guangcheng, M. Yan and L. Ma, *Asian J. Chem.*, **21**, 5345 (2009).
3. W. Guangcheng, L. Ma, M. Yan and X. Rong, *Asian J. Chem*., **21**, 5299 (2009).
4. M. Rong and S. Rutian, *J. Chem. Reagent*, **23**, 39 (2001).
5. M. Farazmand, A.A. Miran Beigi, K. Torkestani and E.Z. Karimi, *Anal. Lett*., **36**, 933 (2003).
6. Z. Yongxi, The Statistics Method in Analytical Chemistry [M], Science Press, China, pp. 182-211 (1986).
7. U. Nordmark and A. Cedergren, *Anal. Chem*., **367**, 519 (2000).
8. W.T. Wang, Trace Water Analysis, Science Press, China, p. 14 (1982).
9. M. Farazmand, A.A. Miran Beigi, K. Torkestani, *Anal. Lett*., **5**, 933 (2003).