UREA AS THE BASIC COMPONENT IN PYRIDINE-FREE KARL FISCHER REAGENT

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Summary—A solution of urea, sulphur dioxide and sodium salicylate in methanol is proposed as the solvent in the Karl Fischer titration, with a separate iodine solution as titrant. Comparison of the performance of this solvent with that of some commercial reagents shows that it has distinct advantages for use with amine samples.

Since the elucidation of the reaction mechanism of the Karl Fischer titration by Verhoef and Barendrecht,^{1,2} a number of compounds have been proposed to replace the pyridine in the classical reagent, viz. sodium acetate,³ diethanolamine⁴ and imidazole.⁵ These components serve, as the pyridine did, to buffer the titration medium at a pH-value that ensures a convenient overall titration rate and a stable end-point. Other criteria that determine the usefulness of the reagents are the long-term stability of the solution and the number of classes of compound for which the water determination can be done without problems.

The goal of the investigation described here was the preparation of a new reagent that—just like the original pyridine-containing reagent—would have its buffering action in a more acidic range than that of the reagents mentioned above.

EXPERIMENTAL

Reagents

The following substances were used as received: urea (puriss. p.a.), triethanolamine (puriss. p.a.) and imidazole (purum) from Fluka, sodium salicylate (zur Analyse) from Merck, triethylamine (puriss.) from Koch-Light, salicyclic

acid from ACF, sulphur dioxide from Matheson, and the sodium salt of benzenesulphonic acid from Janssen. The methanol used to prepare the Karl Fischer solvents was reagent grade from Baker, and dried with 3A molecular sieve (Union Carbide) for 24 hr before use. The lithium chloride (Merck, Suprapur) was dried for 24 hr at 150°.

The commercial Karl Fischer solvents used were Karl Fischer Lösung A (Merck, Pyridin Schwefeldioxid Lösung), Karl Fischer Lösungsmittel Pyridinfrei (Merck) and Hydranal solvent (Riedel-de Haën).

Apparatus

The titrations were done with Radiometer Karl Fischer titration equipment consisting of the Karl Fischer titration assembly TT-A1-KF, titrator TTT11b and mV/pH-meter PHM28. The pH of the titration medium was measured with a Knick pH-meter, type PH60, and an Ingold combined glass/reference electrode, type 405, of which the reference electrode compartment was filled with a saturated solution of lithium chloride in methanol. The electrode was calibrated with methanolic solutions of salicylic acid and sodium salicylate as described by Bos and Lengton.⁶

Procedure

The titration procedure is based on the separate titrant/solvent-reagent system and was performed as follows. The titration vessel was filled with 20 ml of the reagent under study (SO₂/base/methanol) and pretitrated with the iodine/methanol titrant to a preset end-point (300 mV) with

Table 1. The amount of water that can be titrated in 20 ml of reagent, and the resulting pH-change

Reagent	pH-change	Water capacity, mg
Karl Fischer (Verhoef)	5.0-2.1	55
Hydranal (Riedel-de Haën)	5.6-2.6	130
Karl Fischer Lösung A (Merck)	4.2-1.2	250
1M Imidazole/ 0.5M SO ₂ /MeOH	6.7-4.7	100
1.5M Urea/1.5M SO ₂ / 0.5M Na salicylate/MeOH	1.6-0.9	140
0.5M Urea/0.5M Na benzenesulphonic acid/ 1M SO ₂ /MeOH	2.1-0.9	90
0.5M Triethylamine/ 0.5M triethanolamine/ 1M SO ₂ /MeOH	9.0-7.0	110

Table 2. Long-term stability of Karl Fischer solvent with composition 1.5*M* urea/0.5*M* Na salicylate/1.5*M* SO₂/MeOH

Storage time, weeks	Water content of 20 ml of solvent, mg
—	4.63
1	4.64
2	4.63
3	4.65
4	4.70
5	4.82
6	4.91
7	5.03
8	5.25
9	5.39

Table 3. Titration speed and pH-change for the titration of 100 mg of water in 20 ml of urea/Na salicylate/SO₂/methanol reagent

[Urea], M	[Salicylate], M	[SO ₂], M	pH-change	Titration time, min
1.0	0.5	1.0	1.8–0.9	10.0
1.2	0.5	1.0	1.7–1.0	8.5
1.4	0.5	1.0	1.7–1.0	7.0
1.6	0.5	1.0	1.8–1.0	6.0
1.8	0.5	1.0	1.9–1.0	5.5
2.0	0.5	1.0	1.9–1.0	5.0
1.4	0.5	1.5	1.6–1.3	7.5
1.6	0.5	1.75	1.6–1.3	5.0
1.8	0.5	2.0	1.7–1.3	4.0
2.0	0.5	2.25	1.7–1.3	3.8

Table 4. Comparison of 1.5*M* urea/0.5*M* Na salicylate/1.5*M* SO₂/MeOH with commercial Karl Fischer solvents

Sample	H ₂ O found, % remarks		
	Hydranal	KF Lösungsmittel pyridinfrei (Merck)	Urea/Na salicylate/SO ₂ /MeOH
Na tartrate.2H ₂ O 2aq.	15.65 precipitate when >250 mg sample added	15.64	15.64
acetone	no results, owing to ketal formation	no results, owing to ketal formation	no results, owing to ketal formation
methyl acetate	0.0597	0.060	0.0585
ethanol	0.0718	0.0720	0.0719
acetic acid	0.0593 dragging end-point with increasing number of samples	0.0643 dragging end-point with increasing number of samples	0.0665 dragging end-point with increasing number of samples
chloroform	0.00989 large variations in results	0.0100 no problems	0.0107 no problems
diethyl ether	0.0424 accurate results after 3 samples	0.0441 first determination inaccurate	0.0474 first determination inaccurate
dimethylformamide	0.0343 solvents turns dark	0.0359 solvent turns dark	0.0346 slight darkening
petroleum ether	no results, owing to precipitation	no results, owing to precipitation	0.00903 precipitation only after 4 g of sample added
n-butylamine	no results strongly dragging end-point	2.30 dragging end-point	2.29 stable end-point
n-dibutylamine	0.619 inaccurate, dragging end-point	0.462 first determination inaccurate, somewhat dragging end-point	0.451 no problems
tributylamine	0.166 inaccurate, dragging end-point	0.115 dragging end-point	0.105 no problems
quinoline	0.160	0.151	0.148
benzylamine	1.30 inaccurate, dragging end-point	1.20 no problems	1.21 no problems

the bipotentiometric detection system, operated with a fixed current in the range 2–3 μ A. The value of 300 mV should persist for at least 20 sec. After this pretitration the water-containing sample was introduced into the titration vessel and the titrator was started again.

The short-term stability of the reagent was checked by measuring the iodine titrant consumption after the stop criterion of the titration was met, by continuing the titration in the "no stop mode". The iodine/methanol reagent was standardized against weighed samples of pure water. The long-term stability of the reagent was checked by periodically measuring the amount of iodine titrant consumed in the pretitrations.

RESULTS

Table 1 shows the amount of water that can be titrated in 20 ml of solvents of various compositions, together with the change in pH that accompanies the process.

A solvent with the composition 1M urea/1M SO₂/methanol gave inaccurate results because the reaction proceeded very slowly, and was not studied any further.

As can be seen, the urea/sodium salicylate/SO₂/methanol mixture is the most acidic of the reagents tested and the only one that shows overlap in pH-range on the acidic side with the classical pyridine/SO₂/methanol reagent as manufactured by Merck. The amount of water that can be titrated in 20 ml of this reagent compares favourably with that for the commercial products not containing pyridine.

The urea/sodium salicylate/SO₂/methanol mixture was investigated somewhat further with regard to its stability on storage (Table 2) and with regard to the influence of the concentrations of its constituents on the speed of the titration (Table 3).

Table 2 shows that the stability on storage is rather good. No significant increase in the water content of the reagent was observed during the first 4 weeks of storage at room temperature, and only a minor increase after that period.

From Table 3 it can be seen that an increase in the concentrations of urea and sulphur dioxide considerably speeds up the titration of 100 mg of water. At concentrations of urea and sulphur dioxide above 1.5M the gain in titration speed levels off. This composition seemed a good compromise between reagent cost and titration speed and was compared with two commercial products in the consecutive titration of a number of actual samples of different chemical classes (Table 4). All titrations were performed with 20 ml of reagent as solvent. The sample size varied between 1 and 4 g, depending on the water content. For the entries marked "no problems" in Table 4, the reproducibility was better than $\pm 1\%$.

In general the results obtained with the urea-containing reagent are comparable with those obtained with the commercial reagents. However, for the amine samples there is a significant difference; these can only be titrated successfully in the urea-containing reagent. It is likely that this is due to the more acidic nature of this reagent. The effect of varying the sodium salicylate concentration was not examined, since the 0.5M concentration initially used seemed suitable enough.

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REFERENCES

1. J. C. Verhoef and E. Barendrecht, *J. Electroanal. Chem.*, 1976, **71**, 305.
2. *Idem*, *ibid.*, 1977, **75**, 705.
3. J. C. Verhoef, *Mechanism and Reaction Rate of the Karl Fischer Titration Reaction*, Dissertation, University of Amsterdam, 1977.
4. E. Scholtz, *Z. Anal. Chem.*, 1981, **309**, 30.
5. *Idem*, *ibid.*, 1982, **312**, 462.
6. M. Bos and W. Lengton, *Anal. Chim. Acta*, 1973, **76**, 149.