

A NEW VOLUMETRIC METHOD FOR THE ESTIMATION OF THIOCARBAMIDE

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A new method for the volumetric determination of thiocarbamide with iodine and bicarbonate buffer is described.

Several methods have been proposed from time to time for the determination of thiocarbamide, mostly based on its desulphurisation or complex formation with metal ions or its oxidation with various oxidising agents. None of them has been found to be entirely satisfactory. Most of the methods require extremely dilute solutions of thiocarbamide to be titrated and are very sensitive to slight variation of experimental conditions or are time-consuming. The external end-point used in Volhard's method is not sufficiently sharp to provide accurate results. Oxidation with permanganate does not afford a satisfactory means of determining thiocarbamide (Cuthill and Atkins, *J. Soc. Chem. Ind.*, 1937, 65, 51). Cuthill *et al.* also observed that in oxidation with chloramine-T in neutral solution, the oxygen consumption was less than the theoretical quantity. Moreover, oxidation with chloramine-T proved to be too sensitive to slight variations in experimental conditions to be useful. Oxidation with alkaline hypiodite is also not very satisfactory, and oxidation with ceric sulphate or potassium dichromate in acid solution requires boiling under reflux and has other unsatisfactory features (Cutbill and Atkins, *loc. cit.*). That Mahr's method (*Z. anal. Chem.*, 1939, 117, 91), employing bromide-bromate mixture does not yield accurate or reproducible results has been shown by Appa Rao and Neelakantam (*Indian J. Pharm.*, 1952, 14, 50). The iodimetric method of Werner (*J. Chem. Soc.*, 1912, 101, 2166) though simplest in technique and therefore most extensively used for thiocarbamide estimations, suffers from the disadvantage that the end points are not always sharp and the results are accurate only when the amount of thiocarbamide present does not exceed 0.2 g./litre. Later modifications of the iodimetric method by Cuthill and Atkins (*loc. cit.*) also did not prove very useful. In view of these facts, the determination of thiocarbamide was reinvestigated.

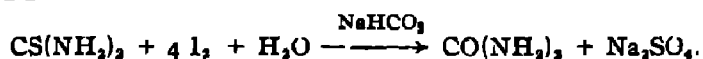
The oxidation of thiocarbamide by iodine was tried under diverse experimental conditions in various media. It has now been found that thiocarbamide can be estimated more accurately in dilute or strong solutions by using iodine in presence of a bicarbonate buffer. The end-point of the reaction was observed by all the following three techniques, which further adopted the present reaction to a variety of conditions in which thiocarbamide might have to be estimated :

(a) Visually—disappearance of iodine colour itself or the blue colour with starch solution.

(b) Potentiometrically—when a sudden fall in the E. M. F. of the system occurs near the equivalence point.

(c) By employing excess of oxidant and back-titrating the excess of iodine with standard arsenious oxide solution.

The corresponding amounts of thiocarbamide and iodine showed that the thiocarbamide was completely oxidised to urea and sulphate. The reaction involved may be represented as :



The effect of the quantity of bicarbonate as well as the concentration of thiocarbamide over a wide range has been investigated. Experiments were also conducted taking an excess of iodine solution, adding to it a known volume of thiocarbamide solution and titrating back the excess oxidant with arsenious oxide solution. The use of arsenious oxide in these estimations is of great advantage as it is obtainable in a very pure form and its solutions are stable even on long standing (*Analyst*, 1950, 75, 577) ; besides it serves as a direct primary standard for a rapid and accurate determination of iodine. This eliminates the need of prior standardisation of iodine solution. As will be seen from the results (Tables I to VI) thiocarbamide can be accurately estimated by all these techniques.

EXPERIMENTAL

Titrations using Starch End-points (Visual observation of end-point).—In each case, iodine solution (20 c.c.) of known strength was taken in a 250 c.c. conical flask and a 10% solution of 'Analar' NaHCO₃ (20 c.c.) added. Thiocarbamide solution was then added dropwise from the burette and the end-point observed visually as usual by adding starch solution near the end-point. Results are presented in Table I.

TABLE I
(End-point observed visually)

CS(NH ₂) ₂ soln. taken.	Iodine soln. (20 c.c. taken).	Eq. vol. of thiocarb- amide soln.	CS(NH ₂) ₂ found	
0.1170 g./litre	0.01392 N	22.85 c.c.	0.1159 g./litre	99.08%
0.4680	0.05500	22.40	0.4673	99.84
0.7600	0.08913	22.40	0.7572	99.63
1.1624	0.09391	15.40	1.1605	99.83
1.2120	"	14.80	1.2075	99.63
1.9980	"	8.95	1.9970	99.94
"	0.1040	9.90	1.9992	100.08

Potentiometric Titration.—A Ni-Fe cell capable of producing a constant potential of 4 or 6 volts, was employed as a convenient and reliable source of current for the potentiometer for preliminary adjustments, and a moving coil mirror-galvanometer with lamp and scale, for finer adjustments, were included in the circuit through a double pole double-throw switch. The 'unknown cell' was made of three parts : (i) a platinum wire which served as an indicator electrode, (ii) a saturated calomel electrode, serving as the reference electrode, and (iii) the salt bridge, obtained by filling a jelly of 3% agar in a saturated potassium chloride solution. Cambridge (Pye) Instrument in which

the E.M.F. was read directly on the dial was employed as the potentiometric system. The instrument was always standardised prior to actual experiments, with the help of a Weston cadmium cell. The end-point or the equivalence point was detected quite easily by a sudden and large change in potential which occurred very close to the equivalence point or by calculating $\Delta E/\Delta V$, i.e., the change in E.M.F. per unit volume, as proposed by Hostetter and Roberts (*J. Amer. Chem. Soc.*, 1919, 41, 1337), $\Delta E/\Delta V$ being maximum near the equivalence point.

The potentiometric titrations of thiocarbamide against standard iodine solutions were performed in the following manner. To an aliquot of iodine solution, taken in a 150 c.c. Pyrex beaker, a known volume of the buffer (viz., a 10% solution of sodium bicarbonate) was added. The titration vessel was kept in cold water to avoid any loss of iodine. The platinum electrode was dipped into the solution. The 'unknown cell' was placed in position A or B and the initial E.M.F. was measured by adjusting the slide-wire contact to zero deflection in the galvanometer. The thiocarbamide solution was run in slowly dropwise and after each addition the solution was stirred well and the potential value noted. Near the equivalence point, the titration was performed with dropwise addition of the thiocarbamide solution with vigorous stirring. In the beginning a gradual decrease in the potential was observed which showed a sudden fall at the equivalence point. After this the E.M.F. changed very slowly when an excess of the thiocarbamide solution was added. Observations of a typical experiment (marked with an asterisk in Table III) are represented in Table II. Influence of (i) sodium bicarbonate buffer added, (ii) thiocarbamide concentration and (iii) iodine concentration was investigated. The results of various experiments have been summarised in Tables III, IV and V.

TABLE II

[0.09391 N-iodine soln. (20 c.c.) + 10% NaHCO₃ (20 c.c.)]

Thiocarba- mide added.	E/MVS.	$\Delta E/\Delta V$.	Thiocarba- mide added.	E/MVS.	$\Delta E/\Delta V$.	Thiocarba- mide added.	E/MVS.	$\Delta E/\Delta V$.
0.00 c.c.	368.5		5.00 c.c.	351.3	4.70	8.80 c.c.	301.0	60.00
		3.00			6.00			153.00
0.50	367.0		6.00	345.3	7.10	8.90	285.7	1183.00
		3.00			11.60			35.80
1.00*	365.5		7.00	338.2	24.00	9.00*	167.4	20.00
		3.30			38.00			10.50
2.00	362.2		8.00	326.6		9.50	149.5	
		2.90						
3.00	359.3		8.50	314.6		10.00	139.5	
		3.30						
4.00	356.0		8.70	307.0		11.00	129.0	

* Vol. of thiocarbamide soln. equivalent to the iodine soln. taken.
Observed = 9.00 c.c. Calc. = 8.9449 c.c.

TABLE III

Effect of sodium bicarbonate added.

Thiocarbamide soln. added = 1.998 g./litre. 0.09391 N-Iodine soln. taken = 20 c.c.

10% NaHCO ₃ added (c.c.)	0.0	5.0	10.0	*20.0	30.0	40.0	50.0	60.0	70.0
CS(NH ₂) ₂ found (g/litre)	...	1.8424	1.9856	1.9856	1.9856	1.9856	1.9856	1.9856	1.9856
%	...	92.2	99.4	99.4	99.4	99.4	99.4	99.4	99.4

* Full details of this experiments are presented in Table II

It has been observed that whereas too small an amount of the bicarbonate causes incomplete oxidation of thiocarbamide, too large an excess of it has little adverse effect on the accuracy of the results. Presence of small amounts of sodium carbonate interferes.

TABLE IV

Effect of thiocarbamide concentration.

Taken (g./litre).	Amount of thiocarbamide		Taken (g./litre)	Amount of thiocarbamide	
	Found.			Found.	
0.1170	0.1159 g./litre	99.09%	1.1614	1.1605 g./litre	99.83%
"	"	"	1.2120	1.2075	99.64
0.4680	0.4673	99.85	1.9980	1.9970	99.94
0.7600	0.7572	99.64	"	1.9992	100.08

TABLE V

Effect of iodine concentration.

	Thiocarbamide soln. taken	Iodine soln. used.	Thiocarbamide found.	
A.	0.4680 g./litre	0.0550 N	0.4672 g./litre	99.85%
"	"	0.08882	0.4668	99.77
B.	1.9980	0.0550	1.9976	99.86
"	"	0.09391	1.9860	99.40

Back-titrations of Excess Oxidant against Arsenious Oxide.—In certain experiments, a known (excess) volume of iodine solution was taken, to which was added a 10% sodium bicarbonate and a known volume of thiocarbamide solution. The excess iodine was titrated potentiometrically against a standard solution of arsenious oxide. The difference between the initial (blank) and final titre values of As_2O_3 corresponds to the iodine consumed, and therefore a direct determination of thiocarbamide can be achieved.



or



The results of these experiments are represented in Table VI.

TABLE VI

S. No.	Thiocarbamide present.	Thiocarbamide found.	
1.	0.4680 g./litre	0.4692 g./litre	100.20%
2.	"	"	"
3.	"	"	"
4.	1.2120	1.2145	"
5.	"	1.2136	99.95
6.	"	"	"

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