Determination of Sulphur by Methylene Blue Method After Reducing to Hydrogen Sulphide with Molten Benzoin

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Summary: Elemental sulphur present in various pharmaceutical products is separated by reducing with molten benzoin to hydrogen sulphide. With the help of a nitrogen stream the volatile sulphide is passed through a solution of zinc acetate to form white turbidity of zinc sulphide. Aliquots of zinc sulphide turbidty are analysed by Methylene Blue method to determine sulphur content. The method has also been found useful for the determination of sulphur in a number of organic thiocompounds. The effect of a number of concentrated parameters have been investigated to optimise the conditions of the procedure.

Introduction

Free sulphur and oxyanions of sulphur can be separated from various matrices by reducing to hydrogen sulphide. The gaseous hydrogen sulphide is then removed by sweeping with a stream of inert carrier gas through a liquid reagent which reacts quantitatively with hydrogen sulphide to form non-volatile product.

Various reagents have been employed for this purpose. Field and Oldach [1] used a caustic soda solution for reduing sulphur to hydrogen sulphide. Jaboulay [2] obtained hydrogen sulphide by treating the mild steel samples with hydrochloric acid. Sulphides and reducible sulphur in alkalies can be converted to hydrogen sulphide by acidification or by stannite and nacent hydrogen reduction followed by passage into zinc acetate solution [3]. Johnson and Nishita [4] have briefly reviewed the techniques for reducing sulphates to sulphide. Zymaczynski [5] described a method for determining free sulphur by reaction with ketonic alcohols to liberate hydrogen sulphide. Oxidative and reductive methods for pyretic sulphur in solid fuels have been critically reviewed by Radmacher and Mohrhauer [6]. In another reduction method sample is treated with zinc and hydrochloric acid containing some stannous chloride [7]. A more powerful reducing agent, consisting of chromium powder and hydrochloric acid completely reduces the pyritic sulphur without attacking organic sulphur [7]. Recently, in author's laboratory, a method has been developed for sulphate determination by reducing the sample with a mixture of sodium hypophosphite and hydroiodic acid [8].

Feigl and Stark [9] have described a spot test for detection of elemental sulphur. In present work the same principle is used for quantitative separation and determination of sulphur in different samples. The procedure is based on treating the sulphur containing sample with molten benzoin. The hydrogen suphide produced by the following reaction was swept to zinc acetate solution where it formed white turbidity of zinc sulphide.

$C_6H_5COCHOHC_6H_5 + S^o \rightarrow C_6H_5COCOC_6H_5 + H_2S$

Aliquots of zinc sulphide turbidity were analysed for sulphur content by Methylene Blue method [10]. The procedure has been found adequately accurate, simple and selective for sulphur separation and determination in a number of sulphur-containing pharmaceutical preparations such as antiseptic ointments. The method has a significant potential of estimating sulphur in organic thiocompounds and sulpha drugs as the recovery of sulphur from these compounds as hydrogen sulphide was found not less than 95% of the theoretical values.

Experimental

Apparatus and Equipment

A hard glass vessel used for evalution of hydrogen sulphide is shown in Fig. 1. Benzoin was melted in this vessel and kept at a constant temperature. On adding sulphur sample the produced hydrogen sulphide was swept with nitrogen stream and absorbed by zinc acetate solution present in two absorbing bottles.

Absorption measurements were made with an SP-8400 UV/VIS double beam spectrophotometer using 10 mm glass cells.

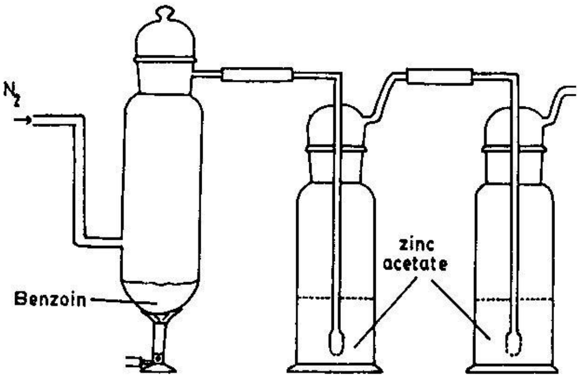

Fig. 1: Apparatus for H_2S generation and adsorption.

Reagents

Sulphur

Elemental sulphur, used for checking the percentage recovery of the procedure, was purified by recrystallizing twice from carbon disulphide and drying in hot air.

Sulphide Standard Solution

For sulphide standard solution 4.066g of hydrated sodium sulphide (containing 60% Na_2S determined iodimetrically) was dissolved in deionized water and diluted to one litre. This 1000 ug/ml solution was further diluted with appropriate volumes of water to get dilute solutions.

p-Aminodimethylaniline Solution

This solution, 0.005M, was prepared by dissolving 0.25 g of the reagent in 50% hydrochloric acid and diluting the solution with the same acid to 250 ml.

Iron(III) Solution

For 0.25M iron(III) solution 30 g of hydrated iron (III) ammonium sulphate (ferric alum) was dissolved in 1M hydrochloric acid and diluted with the same acid to 250 ml.

Zinc Acetate Solution

To preparae 0.25M solution 27.5 g of zinc acetate and 7.0 g of sodium acetate were dissolved in 500 ml of water.

General Procedure

Generation and Collection of H_2S

Assemble the glass apparatus as shown in Fig. 1. Add 20 ml of zinc acetate solution in each of the absorbing bottles and connect them in series with reducing vessel. Transfer 5 gm of solid benzoin in reducing vessel and heat the vessel at 180°C. An oil bath may be used for this purpose. To remove the air, pass nitrogen stream through the vessel at a constant flow-rate. Add a known weight of sulphur or sulphur containing sample (5-20 mg) to the molten benzoin in the vessel and replace the lid tightly. The produced hydrogen sulphide shall be taken to absorbing bottles by the continuous stream of nitrogen. White turbidity of zinc sulphide shall be formed in the absorbing bottles (mostly in the first). Give sufficient time (30 min.-1 hr) to complete the reaction. Check the completion of hydrogen sulphide evolution with a lead acetate paper. After completion of the reaction remove the absorbing bottles and mix their contents in a 100 ml volumetric flask. Dilute the turbidity to 100 ml with water.

Determination

Prepare a calibration graph for 1-10 ug/ml sulphide adopting Methylene Blue procedure [10]. Measure three samples of 1 ml of the thoroughly shaken zinc sulphide turbidity and treat them through the same procedure as used for the Calibration. Calculate the sulphur content in the original sample.

Results and Discussion

Percentage Recovery

To check the percentage recovery of reduction procedure different weights (5-20 mg) of recrystallized solid sulphur has been reduced with molten benzoin. The produced hydrogen sulphide was absorbed in zinc acetate solution and measured by Methylene Blue method [10]. The recoveries obtained with different amounts of sulphur are shown in Table-1.

Though in any case recovery was not less than 97% but better results were obtained with greater amounts of sulphur i.e. more than 10 mg. This is probably due to the fact that with minute amounts of sulphur the losses become more significant. The precautionary factors involved in the percentage recovery are addition of solid sulphur into molten benzoin, temperature of the reaction vessel, time given to reduction process and hydrogen sulphide absorption efficiency. The recoveries reported in Table-1 have been obtained after optimizing all the concerned factors.

Table-1 Recoveries Obtained for Different Amounts of Sulphur

Amount of sulphur added, mg	Number of determi- nations made	Amount of sulphur found, mg, (average)	% age recovery
5.0	5	4.852	97.05
7.0	5	6.805	97.22
10.0	3	9.825	98.25
13.0	3	12.740	98.00
15.00	3	14.730	98.20
17.0	3	16.753	98.55
20.0	3	19.745	98.70

Drug Samples

Different types of drug samples have been analyzed by the described procedure. These include sulpur containing ointments, tablets, injections and eye-drops. Injections and eye-drops, being liquids were used as such. Tablets were ground to fine powder and a known weight of sample was analyzed.

The results obtained for various drug samples are given in Table-2. The recoveries obtained for eye-drops and injections are in the range 97-100%. This is probably due to the fact that liquid samples being well homogeneous reacted more easily, completely and in a short time. The recoveries obtained in the case of sulphur containing tablets are relatively leser than the values reported by the manufacturer. This difference may be attributed to the hetrogenity of the sample. Besides the, solid sample of tablet powder slowly reacted with benzoin and took almost one hour to complete the reaction. Average percentage of sulphur content in ointment has been found slightly greater than that claimed by the manufacturer. This may be again due to the fact that sulphur has not been uniformly distributed in the sample.

Table-II: Determination of Sulphur Content in various types of samples

Sample	Sulphur present	No. of determinations made	Sulphur Content		
			Theoretical	Found (Average)	% age recovery
Superacid eye drops	$C_8H_{10}O_3N_2SNa$	3	27.11 mg/	26.35 mg/ml	97.2
Septran Tab.	$C_{10}H_{11}O_3N_3S$	5	63.2 mg/Tab,	59.2 mg/Tab.	93.8
Sulphadiazine	$C_{10}H_{10}O_2N_4S$	5	64.2 mg/Tab.	60.6 mg/Tab.	94.4
Thiopental Inj.	$C_{11}H_{17}N_2O_2SNa$	3	60.60 mg/ml.	60.4 mg/ml.	99.7
Sulpha Cream	Elemental	5	100 mg/g	102.2 mg/g	102.2
Thiourea	CSN_2H_4	3	42.1 %	41.3 %	98.1
Sulphanilamide	$C_6H_{r4}SO_2N_2H_4$	3	18.6%	17.6 %	95.0
Thioacetic acid	C_2H_4SO	3	42.1 %	40.6 %	96.5
Egg Yolk	-	3	-	-	-
Coal	-	3	-	-	-
Rubber	-	3	-	-	-

Organic Thiocompounds

Besides drugs a few organic sulphur containing compounds have also been analyzed by the described procedure. The compounds were recrystallized and dried in hot air before analyses. Each of the dried substance, 0.5m mole, was accurately weighed and carefully mixed with benzoin. The recoveries obtained for sulphur content in these compounds are shown in Table-2.

The maximum recovery i.e. 98% has been found for thiourea whereas the minimum recovery (95) was obtained in the case of sulphanilamide. The difference found in recoveries is not more than the value of standard deviation obtained for the complete procedure. However this difference may also be attributed to the fact that sulphur has been differently bonded in different compounds.

Oxyanions of Sulphur and Other Compounds

To check the response of oxyanions of sulphur, sulphate, sulphite, thiosulphate and persulphate salts were treated by the described procedure. None of these ions gave any significant quantity of hydrogen sulphite which could produce zinc sulphide turbidity or even turn the lead acetate paper black. This reveals that only elemental sulphur and sulphur present in certain thiocompounds can be reduced by the reaction with molten benzoin, whereas sulphur present in oxyanions remains unattacked. Similarly when a few other sulphur suspected sample like egg yolk, pieces of tyre rubber and coal samples were reacted with molten benzoin only traces of hydrogen sulphide were obtained which could be detected qualitatively but the amount was not enough to be determined quantitatively.

Effect of Time and Temperature

Solid benzoin melts at 160°C so obviously the reaction of sulphur with benzoin had to be carried out at a temperature more than this temperature. This has been observed that the temperature between 170-180°C facilitated the reaction and reduced the reaction time. Though reaction could be carried out in temperatujre range 160-170°C, but it took relatively long time. The use of temperatures higher than 200°C was not suitable because in that case vapours of benzoin started to come alongwith hydrogen sulphide. The time required for completion of the reaction was not only depended on temperature of the molten benzoin but also on the nature and quantity of the sulphur sample. Solid and complicated samples like rubber and coal etc. required more time to release hydrogen sulphide than that required by liquid samples like eye- drops or sulphur containing ointments.

Effect of Carrier Gas Flow-rate and Sorption of H_2S

Nitrogen gas was used to sweep the prdouced hydrogen sulphide into zinc acetate solution. Its flow-rate did not influence the main reaction but had a significant effect on transfer and sorption of hydrogen sulphide. Very small flow-rates enhanced the total time slightly while very fast flow-rates of carrier gas involved the risk of incomplete sorption of hydrogen sulphide.

To ensure the 100% sorption of hydrogen sulphide two absorbing bottles with zinc acetate solution were used. However practically with medium flow-rate of carrier gas precipitation of hydrogen sulphide took place in the first absorbing bottle. However with larger samples and fast nitrogen flow-rate very feeble quantity of zinc sulphide turbidity appeared in the second absorbing bottle.

Conclusions

The method described in present work is applicable for the separation and determination of sulphur in pharmaceutical preparations and certain thiocompounds. Recoveries obtained for most of the samples were in the rang 95-102%. Sulphur present in the form of sulphate, thiosulphate, sulphite and persulphate does not interfere.

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