

A Volumetric Method for the Determination of Sulphur from Organic Compounds

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(Received 20th May, 1994, revised 1st March, 1995)

Summary: A volumetric procedure has been described for the determination of sulphur from organic compounds. *N*-bromosuccinimide displaces iodine from potassium iodide which in turn reacts with sulphide and oxidizes it to sulphur. *N*-bromosuccinimide can be used as a primary standard and kept for several days if refrigerated and protected from light. The method is rapid, convenient and accurate.

Introduction

There are numerous sulphur organic compounds available in the market. Some of them are used in the synthesis of other compounds and some have their use in medicine. Certain sulpho-organic compounds are used as insecticides and fungicides. The importance of these compounds and their products led several investigators to develop new methods for the determination of sulphur.

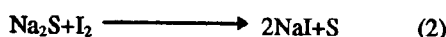
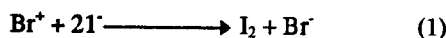
Attempts have been made to determine sulpho-organic compounds using mercuric chlorate as titrant, after the sample was burnt and treated with hydrogen peroxide. The method is quite tedious and requires exact control of pH [1]. The determination of sulphur by Josef's technique involves the oxidation of sulphur dioxide to sulphur trioxide which in turn is titrated against sodium hydroxide. If a little time is lost, the quantity of sulphurous acid might change thus making the method inaccurate and prone to errors [2]. Wilsen *et al.* determined sulphur in rocks such as pyrite by wet oxidation. This method is inconvenient and required use of combination of aqua regia, hydrofluoric acid and perchloric acid [3], sulphur in petroleum fractions is determined by converting them to hydrogen sulphide by non catalytic hydrogenolysis, which is determined by Houston Atlas H₂S analyzer [4]. Schluter pyrolysed a sample of 0.2 g of organic compound in hydrogen stream and reduced the sulphur over a nickel catalyst at 1200°C. A colorimetric determination gave a sensitivity of 5 ppm [5]. A turbidimetric procedure is described by Lachia for the determination of sulphur in dried plant materials [6]. In another procedure sulphur from organic

compounds is determined by combining oxygen flask combustion method of Schoniger with spectrophotometric determination of resulting sulphate using barium chloralnitrate [7]. Pohlandt and Cameron also used combustion oxygen flask for organic materials. The combustion gases were collected in suitable absorption solution which is analyzed by ion exchange chromatography [8]. Raney nickel reduction method is used by Dixit *et al.* to reduce sulphur to H₂S, which is trapped in (ACO)₂Zn, dissolved in HCl and treated with iodine, the excess of which is titrated against standard thiosulphate [9]. In another method oxygen flask combustion technique is followed by atomic absorption spectroscopy to determine sulphur in a variety of organo-sulphur compounds [10]. A strong base anion exchange resin with a porous polymer gel, modified with hydroxy group and packed in a small column is used for separation of anions in the sample solution, which are then detected by conductometry. Sulphate is determined within 15 minutes. By the use of the flask combustion technique together with this method organic sulphur is also determined [11]. *N*-bromosuccinimide is used for the determination of thiourea and thioacetamide. The excess of the reagent is back titrated iodometrically [12]. The same reagent has also been used for the selective determination of various substances [13-20].

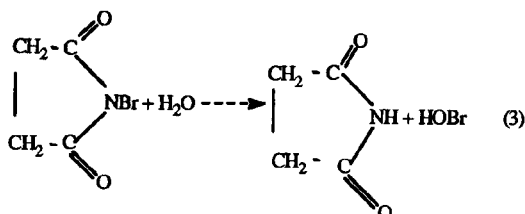
In the present investigation sulphur from organic compounds has been determined quantitatively using *N*-bromosuccinimide as a direct titrant. The method is quite convenient, rapid, precise and reasonably accurate.

Results and Discussion

In this investigation, the determination of sulphur is carried out by an iodine displacement titration. *N*-bromosuccinimide oxidizes iodide to iodine which in turn reacts with sulphide to convert it into elemental sulphur according to the following reactions:



In oxidimetric titrations one can assume that hypobromous acid formed during hydrolysis of *N*-bromosuccinimide is the actual oxidizing agent as shown in equation (3).



As it is clear from equation (1) that positive bromine from *N*-bromosuccinimide goes to -1 state with the gain of two electrons. Equation (2) shows that sulphur from -2 goes to zero oxidation state with the loss of two electrons. These electronic changes are taken into consideration while calculating the normalities or equivalent weights of the substances.

The results of the determinations are shown in Table-1. It can be seen from the results that sulphur can be determined precisely with this reagent. The maximum relative standard deviation is 2.2%. *N*-bromosuccinimide is stable for at least 3 weeks or more depending upon the concentration, when refrigerated and protected from light.

Experimental

Reagents

N-bromosuccinimide is prepared by dissolving 89.0 mg of the recrystallized compound in distilled water and diluting to 100 ml.

Table-1: Determination of sulphur

Compound	Wt. of the sample taken (mg)	Theoretical Sulphur present (mg)	Sulphur found (mg)	Rel.Std. Dev.*
Sulphathiazole	74.20	18.62	18.36	2.20
Dithio-oxamide	50.26	26.80	26.78	0.98
Thio-urea	82.50	34.74	34.73	1.10
Sulpho-salicylic acid	100.00	12.60	12.59	0.25
Sulphamic acid	60.00	17.14	17.10	0.82
Sulphanilic acid	78.50	14.52	14.45	1.92
Chloramine-T	100.00	11.36	11.33	1.30
D-L cystine	55.00	14.66	14.66	0.50
Ethyl potassium xanthate	45.00	18.00	17.98	0.90
Amyl potassium xanthate	83.50	26.45	26.35	1.70

*Results of 5 determinations

Potassium iodide 10% w/v.

Starch solution 2% w/v.

Fusion mixture 5 parts of potassium carbonate, 5 parts of sodium carbonate and 1 part of glucose.

Acetic acid 10% solution

Sulpho-organic compounds and all other reagents used were of analytical grade.

Procedure

An accurately weighed organic compound (20-50 mg) is fused with sodium metal in a fusion tube along with 1 g of fusion mixture. It is heated on the flame until the reaction is complete and tube is red hot. It is then plunged into a beaker containing distilled water. It is crushed, warmed and filtered through Whatman 41 filter paper. The broken glass pieces are washed with distilled water and washings are added to the previous solution after filtration. The final volume is made upto 100 ml.

An accurately measured volume (10 ml) of the above prepared solution is taken in a 50 ml Erlenmeyer flask. 1.0 ml of 10% potassium iodide solution is added and the contents are acidified with a few drops of 1 N acetic acid. After the addition of a few drops of starch solution, the contents of the flask are immediately titrated with standard *N*-bromosuccinimide, added dropwise

with constant stirring from a microburette graduated at 0.02 ml intervals. The end point is reached when the blue colour persists for 30 seconds.

Calculations

Amounts of sulphide in mg = NVE

Where

N= Normality of *N*-bromosuccinimide

V= Volume of *N*-bromosuccinimide used

E= Equivalent weight of sulphide which is

From the amount of sulphide found, the amount of sulphur was calculated as follows:

$$\text{Amount of sulphur: } \frac{32 \times \text{mg of sulphide}}{78}$$

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