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Quantitative Sulphur Estimation: Fast Method Using Microwave Irradiation

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Sulphur estimation is very much important to the synthetic chemists and quality controllers of various industrial products. Although, there have been various methods for the quantitative estimation of sulphur in organic compounds, some of them involve complete degradation and gravimetric measurement of sulphur as barium sulphate. The time required for the actual degradation by normal heating is very high, which has been considerably reduced using microwave irradiation. In present work, the safe use of modified microwave oven, satisfactory and faster quantitative sulphur measurement has been discussed. This method has established its time saving potential over normal sulphur estimation. Wide variety of high purity chemicals have been tested for its sulphur content.

Key Words: Microwave, Quantitative analysis, Sulphur.

INTRODUCTION

Sulphur is an important constituent in various class of compounds such as antibacterial drugs, organic dyes, plastics, amino acids (methionine, cystine and cysteine), Vitamins (thiamin and biotin), Heparins, chondroitin sulfates (bones), keratin sulfates (connective tissues), vulcanised rubber, plastics, coal, fertilizers and petroleum products[1], etc.

Estimation of sulphur is an important parameter towards the confirmation and quantitative determination in various compounds[2]. Several methods have been known for the quantitative estimation of sulfur for varieties of compound such as iodometric titration, total and selective combustion method, fusion method, carius method, messengers method etc. Out of these, the messenger method is one of the widely used gravimetric techniques[3]. It is particularly a method of choice to the synthetic organic chemists. The classical gravimetric analysis remains the most accurate technique for determination of many species because its application to an analytical problem is independent of the availability in standard materials. It is often used in "Umpire situation".

The disadvantage of this method is that it is a time consuming process. To overcome this difficulty the use of microwave energy has proved to be most useful. It is easy and time saving for the estimation of sulphur which could be a routine part of the curriculum or a necessity of postgraduate and research laboratories.

Here is a report of microwave enhanced oxidative degradation of various classes of sulphur containing compounds. The degradation of sulphur compounds by conventional methods takes 5–6 h while the same was conveniently carried out on the modified microwave oven within a time span of 25–35 *min* by pulse irradiation at full power and normal pressure (Table-1). Overall, the results were found to be highly satisfactory and encouraging in time saving.

The microwave region of an electromagnetic spectrum lies in the range 1 mm to 1 m wavelength or 300 MHz to 300 GHz frequency. In order to avoid interference with radar and telecommunication activities which operate within this range, most domestic and commercial microwave instruments operate at the allocated frequency of 2.45 GHz. The heating effect utilized in microwave assisted organic transformation is due mainly to dielectric polarization. Though, the polarizability of a molecule is the sum of a number of contributions, only polar and interfacial polarization are important to the heating effect associated with microwave irradiations. When a molecule is irradiated with microwaves, it causes dipolar molecules to rotate and ions to migrate which is particularly significant in the context of microwave dielectric heating. Consequently, the energy absorbed is dissipated as heat.

Microwave dielectric heating is a well established procedure not only for the domestic preparation of meals, but also it is widely used industrially for processing of food and industrial materials. Microwave application has been designed for the volumertric heating of rubber, wood, paper and agricultural products and for the inclusion of waste materials into glasses[5]. It has been found to be a convenient source of energy for accelerating chemical reactions[6, 7]. This includes applications in waste treatment[8], polymer technology[9], drug targeting[10], ceramics[11] and rapid synthesis of organic compounds such as cyclization reaction[12], oxidation processes[13], catalytic transfer hydrogenation[14], decarboxylation reaction[15] etc. The experimental compliments were published in favour of curriculum[16].

Microwave irradiation has more advantages over conventional methods, such as the reaction time reduction, by many folds. The researcher gets more time to perform other post-degradation laboratory works such as precipitation, digestion of precipitate, drying, ash treatment and weighing etc. Secondly, the mild experimental condition obviates the need of sand bath and heating assembly. And also simplicity in processes and handling. Further, the microwave degradation generally occurs fast, environmentally benign and clear reaction mixture is obtained for further estimation. Finally, the microwave energy using modified microwave oven gives the systematic approach for reactions to be performed at normal pressure.

Besides these advantages there are some disadvantages too that need to be mentioned. Microwave irradiation is not appropriate for reactions involving low boiling point solvents as it may need special efforts to control the evaporation of solvents. Second, stirring the content during microwave irradiation needs special modification. Third, temperature monitoring during microwave reaction is rather difficult[17].

The microwave oven used in our experiment was modified for the use of reflux condenser and to perform the reaction at normal pressure (Fig. 1). The microwave oven is designed in such a way that the reflection of microwave occurs from all sides, therefore the heating is uniform and fast. We recommend that the microwave reactions be performed with a microwave oven and it must be introduced in postgraduate and higher studies.

EXPERIMENTAL

Potassium permanganate, potassium hydroxide, barium chloride and various sulphur containing compounds used such as thiourea, methyl thiourea, thioacetamide, 8-hydroxyquinoline-5-sulfonic acid, 1-amino-2-naphthol-4-sulfonic acid, 1,8-dihydroxy naphthalene-3,6-disulfonic acid disodium salt (chromotropic acid), sodium diethyl dithiocarbamates, dithiazone, sulphamic acid, sulfanilamide, sulfanilic acid, orthanilic acid, L-cystein hydrochloride, congo red, and brilliant green were purchased from Fluka Chimika and some were of AR grade. and were used without further purification. The compounds taken for estimation and precipitate of barium sulphate were weighed during gravimetric estimation on electronic balance, type AX 200 Shimadzu Corporation, Japan.The microwave oven used for oxidative degradation of sulphur compounds was Kenstar model no. OM-9918C, 900 watts, which was modified for the use of reflux condenser so as to perform the reactions at normal pressure.

Procedure

Caution Concentrated sulphuric acid and hydrochloric acid cause burns; Exercise care in working with these chemicals and avoid contact with skin and clothing, wear gloves and use long pair of tongs while handling hot silica crucible.

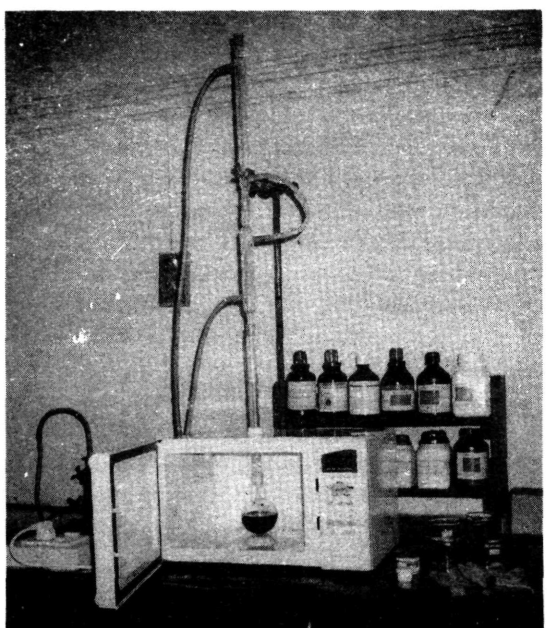

Fig. 1. Modified microwave oven

Degradation of sulphur compounds

In a 250 mL round bottom flask 0.2 g of sulphur compound, 2.0 g of solid potassium permanganate and 0.6 g of solid potassium hydroxide dissolved in 40 mL distilled water and 2–3 pieces of porcelain were taken. The mixture was refluxed in a modified microwave oven using reflux condenser for 25–35 min at normal pressure. It was allowed to cool, 20–25 mL of concentrated hydrochloric acid was added and further heated in the microwave oven for 1 min when it became colourless; it was allowed to cool and treated with hot 2% excess barium chloride solution. The white precipitate of barium sulphate was obtained, which was filtered and washed with distilled water to remove excess of chloride ions. It was dried in an oven at 130–150°C. Now it was treated with a drop of concentrated sulphuric acid, heated strongly in a silica crucible and finally weighed to calculate the percentage of sulphur.

Analysis Data

The theoretical and experimental values of sulfur percentage and time required for complete degradation of various sulphur containing organic compounds using microwave er.ergy have been given below.

TABLE-1

Ser. No.	Name of sulphur compound	m.f.	% S		Raction time (min)
			Theoretical	Experimental	
1.	Thiourea	CH_4N_2S	42.1052	41.9412	30
2.	1-Methyl thiourea	$C_2H_6N_2S$	35.5555	35.2615	25
3.	Thioacetamide	C_2H_5NS	42.6666	42.3521	30
4.	Sulfanilamide	$C_6H_8N_2O_2S$	18.6046	18.2846	35
5.	Sulfamic acid	H_3NO_4S	28.3185	28.0185	25
6.	Sulfanilic acid	$C_6H_7NO_3S$	18.4971	17.9012	35
7.	Orthanilic acid	$C_6H_7NSO_3$	18.4971	18.3661	25
8.	Sodium diethyl dithiocarbamate	$C_5H_{16}NOS_2Na$	33.1606	32.9256	25
9.	Dithiazone	$C_{13}H_{12}N_4S$	12.5000	12.4012	25
10.	8-Hydroxy quinoline 5-sulfonic acid	$C_9H_9NO_5S$	13.1687	12.9991	35
11.	1-Amino-2-naphthol 4-sulfonic acid	$C_{10}H_{10}NO_4S$	13.3333	13.0356	35
12.	Chromotropic acid	$Na_2C_{10}H_{10}O_{10}S_2$	16.0000	16.0137	30
13.	L-Cystein hydrochloride	$C_3H_{10}NO_3SCl$	18.2857	18.1801	30
14.	Congo red	$Na_2C_{32}H_{22}N_6O_6S_2$	9.1954	8.9872	35
15.	Brilliant green	$C_{27}H_{35}N_2SO_4$	6.6252	6.6700	25
16.	Industrial waste Lignin	–	–	3.7000	35

Conclusions

- The results summarised in the Table show that the oxidative degradation of sulphur compounds takes place within a shorter time and more safely in a microwave irradation than by conventional heating.
- Use of modified microwave oven avoids hazards associated with solvents used, especially in sealed reaction vessels. It is simple and safe to handle.
- Successful use of various types of sulphur containing organic compounds shows that microwave irradiation can be used for a wide range of sulphur containing organic compounds. It demonstrates its potential of rate enhancement and cleaner technology.

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