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Estimation of sulfur by gas-phase molecular absorption spectroscopy (GPMAS) and use in pharmaceutical analysis

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In the present study, gas-phase molecular absorption spectroscopy (GPMAS) is used to estimate sulfur in organic compounds and drugs. Organosulfur compounds or drugs were fused with sodium (metal) to convert available sulfur to sodium sulfide, followed by dissolution in water. Afterwards, the filtered solution was treated with sulfuric acid (concentrated) to release H_2S. Hydrogen sulfide swept with nitrogen into a long absorption cell through which light of wavelength 198 nm produced by suitable lamp passed to record absorbance. The proposed method was also used to find out the effect of concentration and time on the stability of sulfide solutions. The method has low standard deviation and can produce accurate results down to $2\,\mu g/mL^{-1}$ sulfide concentration.

Keywords: sulfa drugs; GPMAS; absorption spectroscopy; molecular spectroscopy; sulfur

1. Introduction

Gas-phase molecular absorption spectroscopy (GPMAS) is a sensitive and adequately accurate analytical technique, used to find out gaseous compounds such as sulfur dioxide (*1–3*) and ammonia (*4*, *5*). In addition, the technique has been employed to discover nitrogen and sulfur in solid compounds by converting available nitrogen and sulfur into ammonia and sulfur dioxide or hydrogen sulfide, respectively.

Cresser (*4*) has estimated ammonia by reducing nitrate to ammonia, using titanium (III) sulfate as reducing agent and in another work, by adding sodium hydroxide to the solution of ammonium sulfate (*5*). GPMAS has also been employed successfully in flow injection analysis of ammonium and nitrate (*6*) and nitrite (*7*).

The present work deals with the estimation of sulfur in sulfur-containing organic compounds by converting the available sulfur to hydrogen sulfide, and additionally looks at its application in sulfur estimations of sulfa drugs. Sulfite was determined using GPMAS by converting it to sulfur dioxide and measuring the absorbance at 201 nm (*3*). In the past, GPMAS has been used in the environmental analysis of sulfur dioxide in stack gases (*2*). Dimethyl arsinic acid (*8*), monobutyl tin chloride (*9*) and dimethyl tin chloride (*10*) have been determined using GPMAS. GPMAS has some applications in pharmaceutical analysis, such as determination of antimony in

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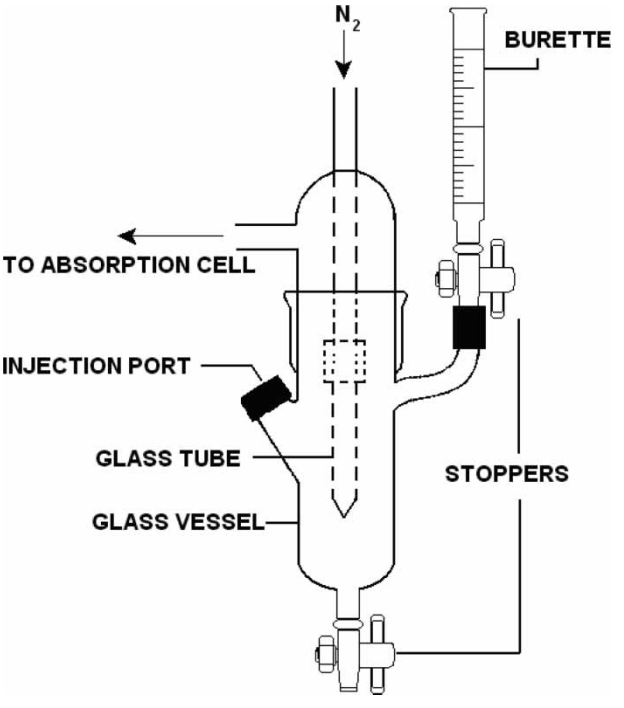

Figure 1. Reaction vessel.

oral homeopathic products (*11*) and in anti-leishmanial drugs (*12*); however, no known literature is available regarding the use of GPMAS in the sulfur estimation of drugs.

In this work, sodium, being reactive, converts organic sulfur (present either in the organic compound or in the drug) to sodium sulfide, as shown in Equation (1):

$$\mathrm{S\ (s) + Na\ (s) \rightarrow NaS\ (s).} \tag{1}$$

Sulfuric acid converts sulfide to H_2S, as shown in Equation (2), which is taken into the absorption cell with the help of a carrier gas:

$$\mathrm{S^{-2}(aq) + H_2SO_4(aq) \rightarrow SO_4^{-2}(aq) + H_2S(g).} \tag{2}$$

A schematic diagram of the glass reaction vessel (50 ml internal volume) used to produce H_2S is shown in Figure 1. The vessel was similar to that used by Winkler and Syty (*2*), with little change in its internal volume. Compared with 60 ml internal volume of that reaction vessel, the new design decreases the extent of dilution by carrier gas that a given amount of H_2S undergoes, which makes absorption signals better.

2. Results and discussion

In the present work, GPMAS has been used to assay sulfa drugs and to study the effect of concentration and time on the stability of sulfide solutions. Various factors such as volume and concentration of H_2SO_4, and pressure of nitrogen gas that can affect absorption, have been studied. Sulfur-containing compounds were fused with the sodium metal that gives sodium sulfide, which can be treated with mineral acids (such as hydrochloric acid, nitric acid and sulfuric acid) to liberate

hydrogen sulfide. Nitric acid produces nitrogenous oxides, whereas hydrochloric acid releases hydrogen chloride gas with hydrogen sulfide, which can cause interference in the absorption signal, thus making results inaccurate. Therefore, sulfuric acid has been used, which has produced hydrogen sulfide without producing any interfering compound.

The effect of the concentration of sulfuric acid has been studied. For equal volumes of sulfide solution each containing 40 μg/ml sulfide ions, 2 ml of sulfuric acid of different concentrations was used. It has been observed that the hydrogen sulfide absorption signal significantly increased as the acid concentration was increased up to 6 mol/l. After that, there was no significant difference in the absorption with concentration. Thus, 2 ml of 6 mol/l sulfuric acid is adequate to release maximum hydrogen sulfide.

The effect of the volume of sulfuric acid was investigated to get the maximum yield of hydrogen sulfide. Different volumes (0.5–2.5 ml) of 6 mol/l sulfuric acid were used for equal volumes of sulfide solution each containing 40 μg/ml of sulfide ions. It has been noted that the absorption signal was increased up to 2.0 ml of the acid volume. After that, instead of an increase, there was a slight decrease in the absorption signal. This can be attributed to the total volume of the solution in the reaction vessel which has increased enough to trap the hydrogen sulfide and not allow it to go to the absorption cell.

The effect of the flow rate of nitrogen gas on the absorption signal of hydrogen sulfide has been studied. Absorption increases with the flow rate of nitrogen gas, as more gas takes more H_2S molecules in the cell; however, this increase is up to certain limit, *i.e.* 2 cm difference in the mercury level filled in the limbs of the laboratory manometer. With further increase in the pressure of the nitrogen gas, the hydrogen sulfide will get diluted in terms of the ratio of H_2S evolved and the quantity of the carrier gas. In addition, H_2S will flush out quickly from the absorption cell, resulting in a decrease in the absorption signal.

2.1. *Effect of concentration on stability of sulfide solutions*

To study the stability of sulfide solutions, solutions of different concentrations were analyzed after different intervals by measuring their absorption at ideal conditions. As shown in Figure 2, with time the concentration of sulfide ions changes if placed in low-grade glass bottles and in

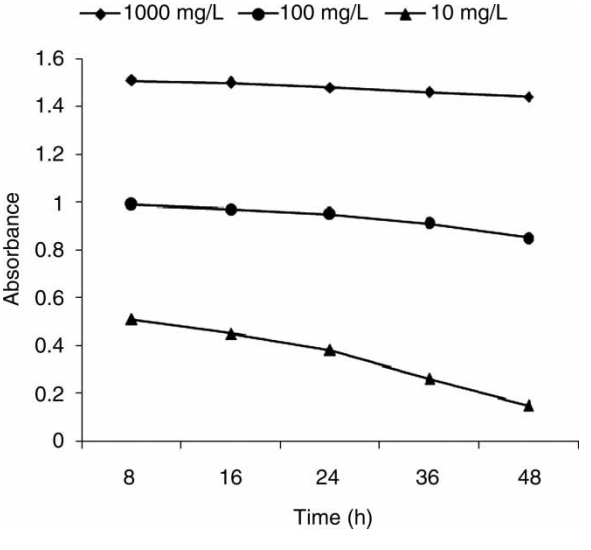

Figure 2. Effect of time on the stability of sulfide solutions of different concentrations.

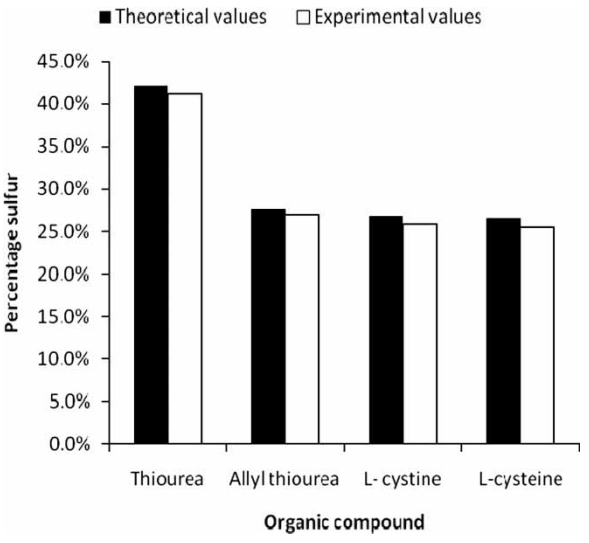

Figure 3. Comparison of percentage sulfur in organosulfur compounds estimated by GPMAS with theoretical values.

light. The loss of concentration was more pronounced in dilute sulfide solutions. Sulfide ions can readily react with the oxygen in air in alkaline conditions (use of metallic sodium makes media alkaline, as unreacted sodium reacts with water to produce NaOH on punching fusion tube in water) where sulfide solutions are unstable. Instability also becomes more pronounced in the case of light (*13*). Figure 2 reveals that the effect is less on 1000 μg/ml solution, and a significant decrease in absorption is observed for 10 μg/ml sulfide solutions. Therefore, in the present work, freshly prepared sulfide solutions were used.

2.2. *Calibration line and assay of sulfa drugs*

Calibration line (line equation: $y = 0.003x - 0.018$) has a correlation coefficient, R^2, of 0.99 (calculated by MS Excel 2003, chart options), marking that the technique is working efficiently under optimum conditions. Organosulfur compounds including thiourea, allyl thiourea, L-cystine and L-cysteine were tested, and the percentage sulfur obtained theoretically and experimentally is compared in Figure 3. The comparison marks close likenesses in values gained experimentally and theoretically. Standard deviation was calculated (MS Excel, 2003) by replicating thiourea solution, and was 0.63. The percentage sulfur in sulfa drugs obtained theoretically and experimentally is compared in Figure 4. Little difference is noted in this case; however, the results are satisfactory. The difference can be assigned to the complex existence of drugs; there might be some interfering ingredients. However, the results are dependable, as shown in Figure 4. It has been found in experiments that the technique can produce accurate results down to 2 μg/ml sulfide ion concentration.

It can be concluded that the present method can be used as a reliable technique for the estimation of sulfur in drugs at μg/ml level to yield satisfactory results.

3. Experimental

An atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 100) was used by replacing its flame assembly with a 10 cm long path glass cell having quartz windows on both sides.

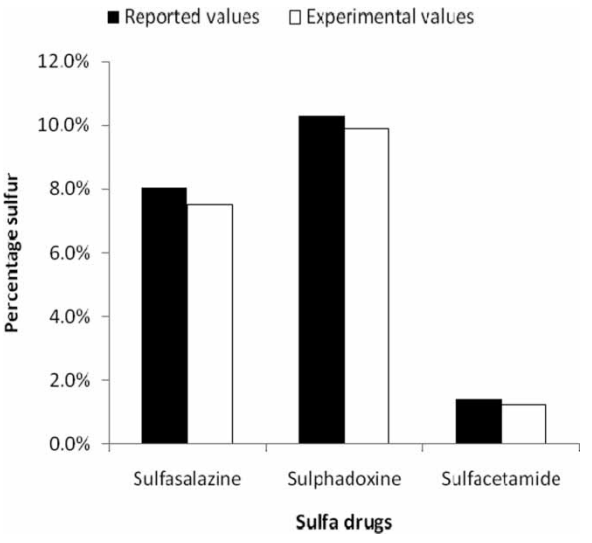

Figure 4. Comparison of percentage sulfur in sulfa drugs estimated by GPMAS with theoretical values.

A hollow cathode lamp of selenium was used as a source to produce light of wavelength 198 nm. A reaction vessel, as shown in Figure 1, was used to produce H_2S. A burette holds the sulfuric acid while the sample was injected through the injection port. Nitrogen (99.9%) was used to sweep hydrogen sulfide into the cell. A laboratory glass manometer was placed between the outlet of the nitrogen cylinder and the inlet of the reaction vessel to adjust the flow rate of nitrogen gas. A moisture trap was incorporated in the path of H_2S gas to remove water vapors before entering the absorption cell.

3.1. *Stock solution and standards*

A stock solution of sulfide (1000 μg/ml) was prepared by dissolving proper weight of acetone-washed and -dried sodium sulfide (Sigma–Aldrich) in 1000 ml double-distilled water. Standard solutions of concentrations 40, 80, 120, 160, 200, 240, 280, 320 and 360 μg/ml were prepared by successive dilution of this stock solution.

3.2. *Change of sulfur to sulfide*

The method used to convert sulfur to sulfide is similar to the Lassaigne method used to discover the presence of sulfur in organic compounds. Weighed quantities of sulfur-containing compounds or drugs were fused with freshly cut sodium metal in a fusion tube by heating on a Bunsen flame. Prior to this, sulfa drugs were powdered with the help of a pestle-mortar. The colored film of the tablet (if any) was also removed. As the tube becomes red-hot, it was punched into 5 ml distilled water taken in a small crucible. The contents were filtered and diluted up to 100 ml with distilled water and stored properly.

3.3. *Calibration and determination*

After optimizing the instrument, sulfide standard solutions and samples were added one at a time to the reaction vessel through the injection port. The nitrogen gas at an optimum flow rate was

constantly bubbling in the sulfide solution. Concentrated sulfuric acid was added abruptly with the help of a burette through the side arm of the vessel. The hydrogen sulfide evolved was swept into the long-path cell where the absorption was measured. A calibration line was plotted, and from the absorbance of samples, their corresponding concentrations were measured.

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