

THE DETERMINATION OF SULPHUR SPECIES IN PETROLEUM PRODUCTS BY
FLAME EMISSION SPECTROSCOPY

By

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ABSTRACT

The work in this thesis describes the determination of sulphur and sulphur containing compounds in petroleum products using cool-flame molecular chemiluminescence emission photometry combined with chemical generation of stable intermediate sulphur compounds. The introduction describes the properties and determination of sulphur species as well as the reasons for the importance of this element in petroleum products. The generation of sulphur compounds suitable for chemiluminescent photometric analysis is influenced by the nature of the compound and the product. The experimental section describes the investigation and optimization of methods for the generation of the same intermediate compounds: hydrogen sulphide and sulphur dioxide, from the different sulphur compounds found in petroleum matrices. The first method described is hydrogen sulphide generation by metal reduction of the species under different conditions, trapping and pre-concentrating the gas and subsequent liberation into the cool hydrogen-argon-air diffusion flame - permitting a degree of speciation of the sulphur compounds as well as their determination. The second approach described is the generation of sulphur dioxide, pre-concentration in sodium tetrachloro mercurate solution and liberation into the flame. This method permits the analysis of materials incompatible with metal reduction methods and also the determination of sulphur dioxide in air. An appraisal of the techniques and suggestions for future work form the conclusion.

ACKNOWLEDGEMENTS

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CHAPTER 1

Analytical Chemistry of Sulphur and its Compounds.

(1.1) Introduction.

Sulphur was one of the two non-metallic elements known to ancient civilisations, the other being carbon. It is one of the most plentiful elements in nature, ranking thirteenth in abundance in the earth's crust (1).

Elemental sulphur is a product of volcanic activity, and undoubtedly such sulphur was the source of supply of the element for ancient people as it is to a proportionally lesser extent today (2). Rall, et al., (14) say that sulphur is present abundantly in nature as metal sulphides and sulphates, such as FeS_2 (pyrite, the most common sulphide), Cu_2S , PbS , ZnS , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (the most common sulphate), BaSO_4 (barite), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite), and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Some sulphur always has been present in the atmosphere of the earth as hydrogen sulphide and sulphur dioxide, which are components of the exhalations of volcanoes. In addition, hydrogen sulphide is a product of the decay or putrefaction of dead plant and animal tissue. Organic compounds, such as sulphides, disulphides, thiophenes, thiocarbonates, thiols, and others are found in plants (3), foods (4), animal proteins (5) and petroleum (6).

(1.2) Sulphur in Petroleum:

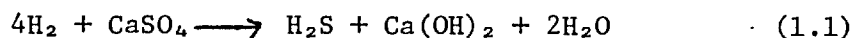
(1.2.1) Origin of Sulphur in Petroleum:

It is obvious that the biological remains that settled to lake and ocean beds and eventually produce petroleum certainly, while living, contained some sulphur and contained it, therefore, when deposited. It would seem axiomatic that geochemical processes, by whatever mechanisms they acted to produce the multitude of hydrocarbons constituting petroleum from the carbon and hydrogen of this biological debris, would, at the same time, include the element sulphur (also present in the debris) as a constituent of some of the chemical structures engendered (14).

This logic could apply as well to other hetero-atoms (nitrogen, oxygen, etc.) also present in the biological debris at the time of deposition. The quantity of these elements in petroleum range from essentially none to less than one per cent for nitrogen (7) and around half one per cent for oxygen (8). Thus the nitrogen and oxygen content of organic debris from which petroleum eventually was formed, was probably sufficient to account for the quantity of these elements in crude oils. However, for sulphur, it would appear that percentages of sulphur such as 13.95 in a Rozel Point, Utah, seep (9), and 9.6 in an Etzel, Germany, crude oil (10) would require a source of sulphur other than that contained in the organic matter from which the petroleum hydrocarbons were derived. Admittedly, the two crude oils cited are of maximum sulphur content and exceptional in this regard. However, crude oils of one to five per cent sulphur content (11) are more common. In addition, natural gases are known which

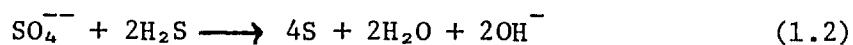
contain large percentages of hydrogen sulphide. Examples are those of Alberta, Canada, eighty-six per cent (12) and several Wyoming fields producing gases containing thirty to sixty-three per cent (13). However, the quantity of sulphur reported in biological material ranges only from about 0.14 per cent (human body and fish muscles) to 0.4% (plants), (14).

The biogenic reduction of sulphate has been mentioned in connection with the presence of sulphur over salt domes, and today, petroleum scientists, generally, believe that this mechanism also accounts for the major part of the sulphur in petroleum and natural gases. Starkey, (15), among many other investigators, has discussed the action of the microorganism, Desulphoribrio de Sulphuricans, on sulphates and proposed the general equation,



to account for the formation of hydrogen sulphide. The source of the hydrogen in this equation could be petroleum or similar organic materials.

Elemental sulphur would be produced in a non-biogenic process by the reaction of hydrogen sulphide (16) with sulphates:



The hydrogen sulphide also might react with compounds of the petroleum or of the formation (to yield inorganic sulphides), or remain in the gas cap of the reservoir. Elemental sulphur, where produced, could be precipitated in the formation (17), and, eventually, be dissolved by the crude oil. Here under geological conditions

of temperature, pressure, and time, reaction of elemental sulphur with hydrocarbons of the crude oil could occur to produce organic sulphur compounds and hydrogen sulphide (18). This mechanism would account not only for the sulphur compounds in crude oils, but also for the absence, or partial absence of sulphates (19) reported in many oil field brines.

(1.2.2) Quantity and identification of sulphur compounds in petroleum.

Because of the circumstances by which sulphur is incorporated into petroleum, it is doubtful whether any crude oil exists, or can exist that does not contain some sulphur. For the same reasons, it seems logical that the amounts of sulphur in crude oils should differ widely, as they do, depending upon the geological history of the petroleum.

Rall, et al., (14), pointed out that, in a very general way, the sulphur content of the crude oils correlates with specific gravity and per cent residue of the crude oils. This apparent interrelationship between sulphur content and specific gravity was observed by other petroleum investigators (20, 21). Another general trend has been observed, that is; oils from the deeper formations have lower sulphur content and lower specific gravity (22).

Table (1.1) lists a selection of crude oils varying in sulphur content. During the API research project 48 by the Bureau of Mines, 204 sulphur compounds were identified in four crude oils (14). In some naphtha, which was formed from residues by thermal cracking, significant amounts of hydrogen sulphide and traces of some disulphides were found (23). Coleman, et al.,

TABLE (1.1)Sulphur Content of Some Crude Oils.

Area	Average depth Feet	Sulphur Percent	Reference
America:			14
California	2,810	7.47	
Wyoming	3,570	3.28	
Texas	5,285	1.90	
Louisiana	10,000	0.26	
Canada:			34
Cold Lake	1,500	2.85	
Lloyd Minster	1,893	2.50	
Medicine River	7,326	0.80	
Iran:			35
Gach Saran	3,000	1.66	
Agha Jari	4,500	1.36	
U.S.S.R	---	0.4	36
Western Europe	---	0.1	36

identified (24) 44 individual thiols in a Wasson 111° to 150°C, distillate and stated that the most predominant thiols were 2-alkane thiols.

Another group of sulphur compounds in this distillate were reported as sulphides, 22 chain (25), 17 cyclic (26), and 4 alkyl aryl (28) sulphides.

Thiophenes represent a major class of sulphur compounds in petroleum. For example, 8 alkyl thiophenes (31), 22 alkylbenzothiophenes (29) were identified in some American crude oils.

The identification of thiaindans in petroleum has not been reported until 1966, despite their expected presence, because of a close similarity in structure to the relatively abundant benzothiophen (33).

Rall, et al., (14) reported the presence of quite large percentages of elemental sulphur (up to 1.0% where total sulphur was 2.17%) in some crude oils. Typical sulphur compounds identified in some crude oils distillate are listed in Table (1.2).

(1.2.3) Effects of Sulphur in Petroleum.

The interest of petroleum technologists and chemists in the compounds in petroleum originates in the practical problems and theoretical questions engendered by the presence of these compounds in crude oils.

From a point of view, this interest stems principally from the deleterious effects of sulphur compounds (37) on the metals used in processing crude oils and on the undesirable characteristics which sulphur compounds impart to the products derived from the crude oil. From the academic or theoretical point of view, the

TABLE (1.2)

Typical Sulphur Compounds Identified in Some Crude Oil Distillates.

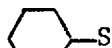
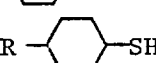
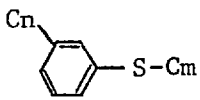
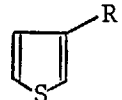
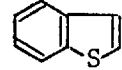
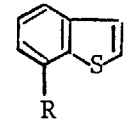
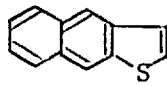
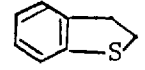
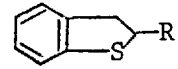
Compound Name	Structure	Reference	
Hydrogen Sulphide	H ₂ S	23	
Thiol:			
alkylthiol	straight chain branched chain	R-SH C₁ to C₇-SH	24
cyclothiol	cyclopentane- cyclohexane-	 	
alkyl-cycloalkylthiol			
Sulphide			
alkylsulphide	straight chain branched chain	R-S-R (C₁ to C₄)₂-S	25
cyclosulphide	thiocyclopentane thiocyclohexane	 	26, 27
alkyl-cycloalkylsulphide			

TABLE (1.2) (cont.)

Compound Name	Structure	Reference
alkylarylsulphide		28
Thiophene	 $m = 1 \text{ to } 4$ $n = 4 - m$	30
alkylthiophene		31
benzothiophene		32
alkylbenzothiophene		29
dibenzothiophene		34
Thiaindan		
1-thiaindan		33
alkylthianindan		
disulphide	$R-S-S-R$	23
elemental sulphur		14

interest in sulphur and its compounds have upon the origin, composition and the geochemical and geological history of petroleum (14). The corrosion of metals used to produce and refine crude oils is one of the most costly consequences of sulphur in petroleum. Nelson (37) indicated that in processing sulphur oils 1% of sulphur in the range of 0.5 - 1.0% probably results in a greater increase than 10% in cost. The cost of protection from sulphur corrosion as shown by these figures should not be confused with the cost of process equipment for the removal of sulphur or the treating of products. Livingstone, et al., (38) say that sulphur compounds in gasoline combine directly or indirectly with tetraethyl lead in the engine cylinder to reduce its anti-knock efficiency. The extent of this reduction in antiknock activity is greatest for the more reactive sulphur compounds such as hydrogen sulphide, sulphur dioxide, mercaptans, or disulphides. Less reactive sulphur compounds probably only effect the antiknock action of tetraethyl lead by contributing sulphur dioxide and trioxide to the burned gas formed on combustion. Analyses of combustion chamber deposits of engines operating on leaded sulphur-containing gasolines show lead oxysulphates are more common products than lead oxide or sulphate.

Thompson, et al., (39) investigated the changes in the oils during storage and reported their observations as follows: free sulphur, di- and polysulphide promote sludge formation; thiophenes, aliphatic mercaptans and aliphatic sulphides show little effect; thiophenol is a strong promoter of gum formation, and primary mercaptans have a small stabilising effect which can be caused by the relatively facile oxidation of the primary as compared to the tertiary mercaptans, the primary thus functioning as mild oxidation inhibitors.

It is suggested that (40) the length of time that lubricating oil compounding is effective in controlling wear and deposits, in car engines depends greatly on the sulphur compounds formed in combustion.

Catalytic poisoning is another effect of sulphur in petroleum. It was observed (41), during the formation of aromatic compounds from petroleum over a platinum-containing catalyst, that an increase in sulphur concentration in the feed stock has two principal effects, initial inhibition of aromatics formation and accelerated catalyst activity decline rate. This deactivation of the platinum on the catalyst is caused by the formation of a chemical compound between platinum and sulphur or by a chemisorption of hydrogen sulphide on the platinum surface. Heineman, et al., (42) have shown that organic sulphur compounds impair the dehydrogenation activity of the platinum-containing catalyst and sulphides and mercaptans appear to be more severe poisons than the other sulphur compounds tested.

It is fair to observe, however, that not all the effects of sulphur in petroleum are deleterious. Some sulphur compounds may be added in order to stabilise transformer oils by acting as an antioxidant (42). Kennerly and Patterson (43) stated that all of commonly used lubricating oil antioxidants are, in fact, peroxide decomposers (usually sulphur containing compounds). These peroxide decomposers act as antioxidants through catalytic decomposition of hydroperoxides initially present in a system or possibly formed as a result of the direct attack of oxygen on the substrate or on the inhibitor.

Because sulphur is a simple reagent capable of combining directly with lead oxide to form a protective film of lead sulphide, lubricants

containing sulphur can be used as copper-lead bearing corrosion inhibitors (44).

Some other beneficial actions resulted wholly or partially from sulphur in petroleum products have been reported, for example, thermal stability improver (39), additive for high-pressure lubricants and cutting oil improver (45).

(1.2.4) Removal of Sulphur:

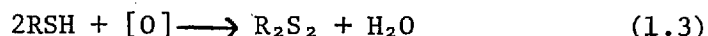
High sulphur content is generally considered to be harmful in most petroleum products and the removal of sulphur compounds or their conversion to less deleterious types has long constituted an important part of refinery practice. Of various types of sulphur compounds found in gasoline distillates, hydrogen sulphide and mercaptans are the most objectionable (38). Gasolines containing them are termed sour and the processes for their removal are called sweetening. By definition (46), a stock is sweet if it passes the "Doctor test" (the test sample is shaken with an equal volume of a sodium plumbite solution and a small amount of sulphur. If no dark discolouration forms at the interface, the sample is sweet).

Chemical sweetening methods most commonly used are of two types (47): those which oxidize mercaptans to disulphides (doctor, copper chloride, lead sulphide, inhibitor sweetening, and sodium hypochlorite methods) and those that remove mercaptans and hydrogen sulphide by alkaline extraction (alkali "solutizer" and alkali methanol methods).

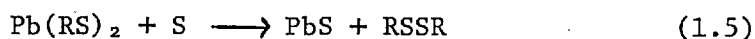
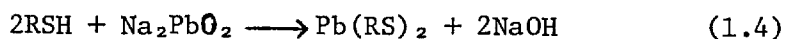
Other methods employed which both desulphurize and sweeten include vapour-phase treatment over solid catalysts, with or without presence of hydrogen, to convert the sulphur compounds to hydrogen

sulphide which is removed by alkali washing (47); treatment with metallic sodium has also been proposed (48).

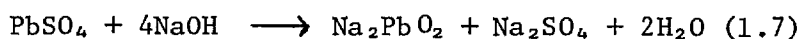
Hengstebeck (46) says that with the exception of the lead sulphide process, the overall reactions are the same in all sweetening processes:



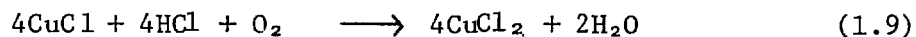
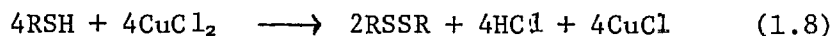
The oxygen may be supplied either as molecular oxygen or in an oxidizing agent. For example, in the Doctor sweetening process the reactions may be represented by:



Lead sulphide is converted back to sodium plumbite by air blowing the solution



and in the copper chloride method:



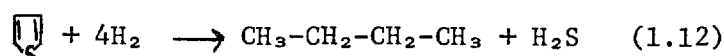
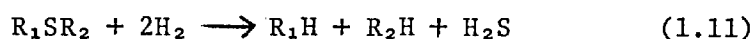
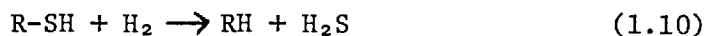
The alkali washing of sour distillates will remove hydrogen sulphide and to some extent a few of the lower alkylmercaptans (47). An organic sulphonylhalide along with an alkaline reagent, some ion-exchange materials or synthetic zeolites, metal phthalocyanine derivatives, humic acid salts and some other reagents have been used in sweetening processes too (53).

Another method of sulphur removal is catalytic desulphurization (49). The processes for catalytic desulphurization can be divided into two classes.

- (a) those employing extraneous hydrogen and resulting in a nett consumption of hydrogen.
- (b) those not using hydrogen or using hydrogen produced in the process itself.

In all hydrocatalytic desulphurization processes the main reaction is the elimination of sulphur in the form of hydrogen sulphide, which can then be easily removed from the product by distillation or washing with alkali solutions.

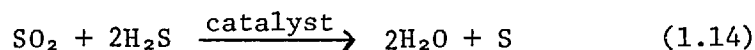
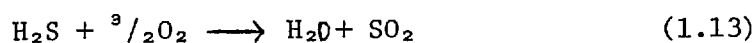
The chemical reactions of some sulphur compounds, in hydrocatalytic disulphurization process, are as follows:



The catalyst and process conditions are generally chosen so as to minimize any side reactions such as dehydrogenation, hydrocracking and aromatic saturation. These reactions therefore only occur to a very small extent in desulphurization processes consuming hydrogen. A large variety of catalysts can be employed for catalytic desulphurization using hydrogen, but the type most commonly used is a mixture of nickel, cobalt, molybdenum and alumina (50, 51, 52). However, there are some other alternative compounds, such as, sodium or sodium hydride, in the presence or absence of hydrogen (54) and

molecular sieve (55) (zeolites, which are hydrated crystalline sodium aluminosilicates) which have been employed. The autofining process employs no extraneous hydrogen but the benefits of hydrogen recycle and hydrogen partial pressure are obtained by dehydrogenation under controlled conditions of a small part of the feedstock itself (56). The process is particularly useful therefore in situation where no cheap hydrogen is available, e.g., when catalytic reforming is not practised or the hydrogen make is not sufficient.

An additional problem due to the presence of sulphur in petroleum is the undesirable effect on the environment by emitted sulphur compounds from combustion or refining of petroleum products. In petroleum refineries, the major emitted sulphur compound is hydrogen sulphide which is the product of the desulphurization process. Hydrogen sulphide can be converted to sulphur by the well known Claus process (57) using alumina-based catalysts. The basic chemical reactions are:



Bauxite catalysts (or alumina) are generally used in the Claus catalytic converters because of their high activity, durability and low cost. In the Claus reactor the hydrogen sulphide is first burnt in a limited supply of air so that a third is converted to sulphur dioxide. The resultant mixture of hydrogen sulphide and sulphur dioxide is then treated catalytically to produce elemental sulphur. For situations where further clean-up of tail gas, from

desulphurization, may be needed (only 97% of sulphur in tail gas can be converted into elemental sulphur in the Claus process) several processes are available (58).

Sulphur oxides emission is the most important process in air pollution-control. In the U.K. alone during one year (1974) about 2.64 million tons of sulphur dioxide were discharged into the air from combustion of petroleum and petroleum products (59).

Apart from combustion of low sulphur fuels, flue gas desulphurization is the most efficient technique for limiting sulphur oxides emission. This desulphurization process can be proceeded in several ways (59), e.g., Limestone-limewashing, magnesium regeneration method, the Gillo process and the Wellman-Lord process are sulphur dioxide removal techniques in which sulphur dioxide is removed from flue gases by washing with aqueous solutions or adsorption on metal oxide and carbon.

1.3. Uses of Sulphur Compounds. (60, 61, 62).

Most of the elemental sulphur, about 80% is transformed into sulphuric acid. It is well known that this acid plays an essential role in the chemical industry, e.g. fertilizers, synthetic fibres, white pigments, steel pickling. Hundreds of thousands of tons of bisulphites of sodium, of manganese, or of calcium are manufactured each year for the treatment of paper pulp. Sulphites are used in tanning, sugar refining, vegetable oil bleaching, and in coagulating latex. Sodium thiosulphate is used in photography. It forms soluble complexes of silver sulphites and has been used as preservatives in beverages (wine and beer) and in food. It has been charged with being noxious, but it has been proved that moderate doses are not dangerous. Specially prepared sulphur is used with success as a

pesticide for the protection of vines. It does not present any danger. Sodium sulphate is used in manufacturing of glass and ceramics. Minor amounts are used in textile dyeing and water treatment. High-performance lithium-sulphur cells are being developed for use in off-peak energy storage batteries in electric utility networks. The cells which operate at 400°C, consist of a lithium electrode, a sulphur or sulphide electrode, and molten LiCl-KCl electrolyte. The sodium-sulphur batteries satisfy the specific energy requirements for both automotive and utility load-levelling applications.

Polyphenylene sulphide is a commercial plastic which is characterised by good thermal stability, retention of mechanical properties at elevated temperatures, excellent chemical resistance, a high level of mechanical properties, and an affinity for a variety of fillers. It is produced from sodium sulphide and dichlorobenzene.

Molten sulphur is used to prepare a sulphur-coated urea fertilizer. Sulphur-coated urea is being tested in 54 countries, showing significant advantages with several crops.

The relatively low cost, high availability, and excellent physical properties of sulphur have justified considering it as a construction material. Its excellent bonding or adhesive qualities as well as chemical compatibility with many types of inorganic materials make it competitive for many applications which currently use cement or plaster binders. Its water repellancy makes it even more attractive for construction applications.

The addition of molten sulphur to hot-mix asphalt paving materials increases mixworkability so that the mixes may be placed

without roller densification. As the mix cools, the sulphur solidifies and imparts such a high degree of mechanical stability to the mix that high quality mixes may be produced from poorly graded aggregates and even one-sized sands.

Pure and modified sulphur can be used to impregnate, coat, and bond wood. Carefully prepared sulphur-wood joints have greater internal bond strength than whole wood.

Disulphides serve as polymerization catalysts, regulators in emulsion, polymerization, odorants in natural gas, plasticizers, modifiers in rubber, vulcanization accelerators, and flotation agents.

(1.4) Detection and Identification of Sulphur.

(1.4.1.) Organic Solution.

An ultramicro capillary method for the detection of organic sulphur compounds has been proposed (63). The test is performed in a simple capillary where the substance is oxidised by a mixture of cupric oxide and boron trioxide. The sulphur trioxide produced is in turn reduced to dioxide by vapours of mercury present in the capillary chamber. As revealing reagent pararosaniline-formaldehyde-hydrochloric acid is used. A blue violet colour is produced immediately, or after 20 seconds for small amounts of sulphur dioxide. Liquid samples must be evaporated in the same capillary sensitivity ranges between 20 to 40 mg of sulphur. Samples taken should be 0.1 to 1 mg.

Thiols are oxidised by sulphur in ammoniacal solution or with a trace of an amine, at room temperature. The aqueous layer assumes a yellow colour, probably because of the formation of ammonium polysulphide (64). This reaction is not given by organic sulphides.

and thiophenes.

It would appear to be a very specific test, at least with regard to other organic sulphur compounds. There are several other detection methods which are concerned with production of bubbles of nitrogen on addition of 1 to 2 drops iodide-azide solution (65).

(1.4.2) Inorganic Solution:

If barium ions are precipitated by adding sulphate to a solution also containing potassium permanganate, the barium sulphate includes permanganate in its lattice, consequently, the precipitate is violet. The permanganate thus retained by barium sulphate is quite resistant to all reducing agents that ordinarily attack it at once. The colour of the excess permanganate in the solution can be discharged by the addition of a drop of hydroxylamine hydrochloride solution (65). The test is not specific for sulphate because permanganate converts oxidizable sulphur-containing inorganic anions to sulphates. It has the advantage of eliminating the need for separate tests for S^{-2} , SO_3^{-2} , CNS , SO_4^{-2} , etc. Since they are obviously not present if the response is negative. Selenate and selenites interfere and must be removed by triple evaporation with concentrated hydrochloric acid before testing (66).

Benzoin is a reducing agent, when heated with elemental sulphur it produces hydrogen sulphide. The resulting hydrogen sulphide is sensitively detected by blackening of lead acetate paper. This effect has been employed for the detection of as low as 0.5 mg. elementary sulphur (67). However, the presence or absence of elemental sulphur also can be demonstrated by pyrolysis of the sample with mercuric cyanide; the resulting vapours, $(CN)_2S$, gives

a blue product when it reacts with the HNC reagent (68).

(1.5) Quantitative Determination:

(1.5.1.) Sampling:

Representative sampling of the material which is to be analysed for total sulphur is extremely important. The sampling of homogeneous gas and liquid sulphur-containing materials ordinarily is not difficult because the composition of any small part taken for an analysis will, to a high degree, be representative of the whole. Liquified petroleum gases constitute a special case because, although gases at atmospheric temperature and pressure, they are commonly transported, stored and sampled as liquids. The standard procedures for sampling liquified petroleum gases are described in ASTM standards (69).

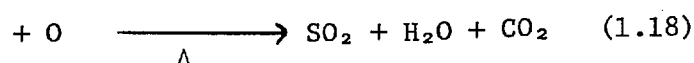
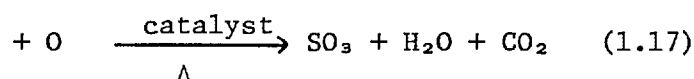
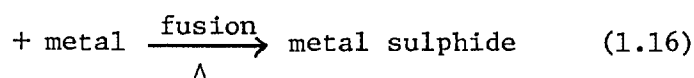
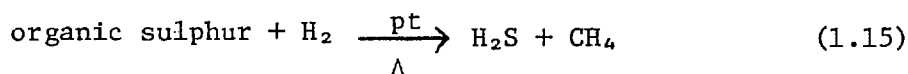
Liquid materials are best sampled after proper mixing, for example, it may be best to sample a tank car of fuel oil immediately after loading or just after it has arrived (70).

Two principal operations are involved in the sampling of many sulphur containing solids (71): (a) the collection of gross sample (b) the reduction of the gross sample to a portion small and fine enough for analysis in the laboratory.

(1.5.2.) Sample Treatment.

Many methods are available for the transformation of originally combined sulphur into an inorganic state that can be readily measured quantitatively. Oxidation, whether by lamp, bomb, tube or flask is the most important. Other methods, for example, catalytic reduction and metallic fusion, are used, but to a lesser extent.

Generally, the reactions for the conversion are (72):



The metals used in reaction (1.16) are magnesium, potassium, raney nickel, silver or calcium hydride. The oxygen in reaction (1.17) is supplied by nitric acid, perchloric acid, peroxides, nitrates, chlorates, oxygen, etc.

Cumbustion in an oxygen atmosphere in the absence of a catalyst results in the formation of sulphur dioxide.

The Carius wet combustion method (71), although slow and somewhat exacting is one of the oldest and most widely used procedures for the treatment of organic sulphur-containing materials. The sample is oxidized in a sealed glass tube containing concentrated nitric acid and sodium chloride at temperatures of 280 to 300°C. All of the sulphur is converted to sodium sulphate. The method may be used in semimicro work and is applicable to all types of organic sulphur compounds, both volatile and non-volatile (71). The inherent danger of an explosion with a sealed tube reaction can be significantly reduced by filling the reaction tube with oxygen before sealing and by reducing the amount of nitric acid used to only a few drops (73).

Perchloric acid is the most adaptable oxidant in general use for the wet oxidation of organic compounds, with added nitric acid, these combined oxidants serve to constitute the liquid fire reaction (74). Employing periodic acid in preferential applications, as a substitute for nitric acid, has marked advantages (74). The advantages attained are extended general applicability, low temperature requirements, and the noteworthy reactivity of periodic acid in downgrading heavy, complex organic molecules to fragments more readily soluble in perchloric acid used as companion reagent.

One of the simplest and most direct methods for the determination of total sulphur in organic materials is that of flask combustion. The procedure provides a rapid, economical, safe and accurate method for total sulphur without the use of costly and elaborate equipment (72). A temperature of about 1200°C is attained for a few seconds, which converts the sulphur to a mixture of its oxides. The oxides are absorbed and oxidized to SO_4^{2-} by the peroxide solution. Modifications in the procedure suggested by Belcher, et al., (75) permit the determination of sulphur in submicro quantities and the analysis of organic sulphur compounds containing nitrogen, halides, phosphorus or metals. Liquid samples can be handled in a gelatin capsule (71).

High temperature (tube) combustion and the lamp method which both are capable of converting sulphur compounds into sulphur dioxide quantitatively will be discussed in Chapter 5.

The determination of total sulphur in organic materials by means of the sodium peroxide bomb procedure is in common use. The sample is fused with a mixture of sodium peroxide, potassium chlorate or nitrate, and sugar in a bomb to form alkali sulphates that are water-soluble (71). This method is complicated by the large amounts of iron introduced by attack on the bomb and removal of the iron as the hydroxide is slow (74). A serious disadvantage of this fusion procedure is that the large amount of sodium in the extract of the fusion product interferes in the subsequent titration with barium perchlorate (76).

In the oxygen bomb method, the organic sample to be analysed is burned in a pressure bomb containing 30 to 40 atmospheres of oxygen (72). This procedure avoids the introduction of additional elements that might interfere with the determination of sulphate (77). This method is suspect if soot is found when the bomb is opened (74). The method is suitable for lubricating oils, greases, and like materials with sufficiently low volatility that they can be weighed accurately into an open sample container and samples containing no calcium, lead, iron, aluminum, silica and similar material that would produce residue other than barium sulphate (71). Such residues are acid-insoluble and would interfere in a subsequent precipitation step.

In the Wickbold oxy-hydrogen flame the sample is first combusted in oxygen; the combustion products are led into an oxy-hydrogen flame where the sulphur oxides are reduced to hydrogen sulphide and free sulphur (72). These products are absorbed in a basic solution and subsequently oxidized to

sulphate. Alternatively, the sample can be aspirated directly into the oxy-hydrogen flame. The resulting sulphur products are led into a hydrogen peroxide solution, where sulphuric acid is produced. The method has been used on as little as 0.002% sulphur in petroleum (78).

Reduction method, which will be discussed in Chapter 3, is another sample treatment procedure in which organic sulphur compounds are converted to hydrogen sulphide through the hydrogenation process or reducing sulphur compounds with sodium, magnesium, potassium or Raney nickel and acidifying the final products.

(1.5.3) Finishing techniques:

A) Spectrophotometric method:

Dasgupta, et al., (79) proposed a spectrophotometric sulphate determination method which relies upon the formation of insoluble 2-perimidinyllammonium sulphate by reaction of the sulphate ion with 2-perimidinyllammonium bromide on a glass fiber substrate. The excess bromide is removed by frontal elution chromatography with ethanol and the remaining organic amine, bound as the sulphate salt, is converted to highly coloured 2-amino-4,6,9-trinitroperimidine by treatment with concentrated nitric acid. The coloured compound may be monitored in acidic solution at 420 nm or in basic solution at 550 nm. For a 100 μ l aliquot the sensitivity is 1 ppm and the working range is 2-500 ppm sulphate. There are no known cationic interferences and among anions only oxalate and phosphate interfere.

Displacement barium chloranilate is an indirect method for sulphate determination which is based on the displacement of chloranilate from barium chloranilate by sulphate. Solid barium chloranilate, when added to a sulphate solution, precipitates barium sulphate and releases an equivalent amount of the hydrogen chloranilate ion, which has a purple colour and exhibits absorbance maxima in the visible and ultraviolet regions. Many cations, such as Ca, Cu, Zn, Pb, Fe and Al, interfere by forming insoluble chloranilates so that the removal of cations by a strong cation exchange resin in the hydrogen form is recommended (80).

Carlson, et al., (81) reported that increased sensitivity, in displacement-barium method, can be achieved for absorbance measurements at 530 nm by adjustment of the pH values of the solution to 1.8 after the removal of excess barium chloranilate. Sulphur in organic substances has been determined, in the range of 0.3 to 100 μg in samples weighing up to 3 mg, using this method (82).

Turbidimetric and nephelometric methods have been studied widely in the literature and found useful for quantitative estimations of sulphur. Sulphur already present as sulphate can be determined directly, whereas organic sulphur compounds must be converted to sulphate by wet or dry oxidation. Turbidimetric and nephelometric techniques are closely related and depend on the formation of a suspension and measurement of its capacity to absorb (turbidimetric) or scatter (nephelometric) light (72). Although nephelometric measurements are generally of low

precision, $\pm 1\%$ has been attained by exact control of the experimental conditions (83). In the method of Toenniec and Bakay (83), standard sulphate solutions are mixed with 40% ethanol-glycerol (to achieve a stable and reproducible suspension of barium sulphate), solutions and barium chloride solution is added.

The suspensions are allowed to stand for 15 minutes and the turbidity is measured as a function of the absorbance at 350 nm with a spectrophotometer. As little as 3 μg of sulphur with accuracy of 1% have been measured in this method. The sulphate is also precipitated with a solution of 4-amino-4'-chlorodiphenyl hydrochloride (84), and resultant suspension of amine sulphate is stabilised with gum ghatti and peptone. The optical density of the suspension is measured at 700 nm after 0.5 h. phosphate ions interfere and can be removed as magnesium ammonium phosphate beforehand. The addition of peptone and gum ghatti to the precipitant help considerably in the formation of stable and uniformly sized particles of the precipitate, but unfortunately the presence of these stabilisers have the effect of decreasing the sensitivity of the precipitation reaction, which, in turn, limit the sensitivity of the nephelometric procedure (85).

In order to improve the sensitivity an aqueous solution of 2-aminoperimidine hydrochloride is proposed as a reagent for nephelometric determination of sulphate ion (86). As little as 0.05 ppm sulphate can be detected by precipitation of the corresponding amine sulphate. Suspensions of the precipitate show remarkable stability and no colloidal stabilisers are needed.

There are some serious interferences from moderate amounts of halide and phosphate ions.

In general, the principal source of error in the conventional turbidimetric procedure is the lack of control over the conditions governing the formation of the precipitate and, therefore, the suspension resulting from particle distribution during mixing and stirring operations. This method usually results in a relative standard deviation of 10%, even when samples are concentrated before attempting the analysis. This is especially true whenever concentrations are less than 5 ppm (87).

Nephelometric procedures are generally more sensitive than comparable turbidimetric procedures in which the concentration of a suspension is measured by diminution of the incident light intensity (84). In nephelometric procedures the measurements must be made at a definite time after precipitation of the light-scattering particles and this is a disadvantage of these methods (72). Beswick and Johnson (88) have compared barium chloranilate displacement and barium turbidimetric methods and claimed that if inorganic ions are to be removed and high precision is not required the chloranilate method becomes laborious and unsuitable for routine work and the turbidimetric procedure may be used.

The methylene blue procedure is probably the most generally applied method for the colorimetric determination of hydrogen sulphide (72). The procedure is also applicable to the

determination of traces of metallic sulphides and other sulphur compounds which can be reduced and isolated as hydrogen sulphide solution with an acid solution of P-aminodimethylaniline in the presence of ferric iron. Although the reaction is not quantitative, the amount of methylene blue produced is quite reproducible if the conditions of colour development are adhered to (71). A study of the variables that may effect colour development has been made by Gustafsson (89), in preparation to applying the method to ultramicro determinations. Beers law is obeyed from 0.02 to 0.4 ppm of sulphide in this method. Total sulphur in natural gas has been determined by methylene blue procedure after conversion of all sulphur compounds present to hydrogen sulphide (90).

B) Gravimetric method:

In recent years gravimetric methods of sulphur determination have been replaced to some extent by instrumental methods. However, the time tested gravimetric procedure is still widely used and has a place in the repertory of the practicing analytical chemist. There are several reagents, such as barium, lead, silver and benzidine for the precipitation of sulphate. Many variations in the barium sulphate procedure have been offered (71). These include the precipitation of barium sulphate from either hot or cold solutions, the use of large or small volumes, and the addition of the sulphate solution to the chloride solution, a reverse order from that normally used.

Lead sulphate has a larger gravimetric factor than barium sulphate, which more than off sets the slightly increased solubility of the former (72).

The benzidine sulphate method has found only limited use in organic analysis. Although benzidine sulphate precipitates from acid solution to form easily filterable needles, the precipitate is sensitive to interferences from ions such as chloride and is fairly soluble in water (71).

It has been shown that oxides of sulphur react to form silver sulphate with silver in an oxidising atmosphere (92). A method for the microdetermination of sulphur in organic compounds based on absorption of sulphur oxides, products of organic substances combustion on electrolytic silver and gravimetrically weighing the electrolytic silver is described (93). Because silver reacts with both sulphur oxides and halogens, a separation by dissolving the silver in hot water is necessary when halide is present (72).

C) Titrimetric methods:

Titration of the sulphate ion with standard barium chloride using the indicator tetrahydroxy quinone (94) enables the determination of as little as 20 ppm sulphate. Because of an indistinct end point the method is not as accurate as gravimetric procedures but does offer an advantage in speed for routine analysis of large numbers of samples (71). Back-titration of excess of barium with standard sulphate solution, in presence of nitro-sulphonazo indicator is another titration method in which the

appearance of a faint pink colour in the blue solution indicates the end-point (95). The direct titration of small concentrations of sulphate with 0.005M barium perchlorate using thorin as the indicator is another simple and rapid titrimetric method with a sharp colour change from yellow to pink as end-point (96).

Sulphur in organic compounds and sulphate in fertilisers have been determined through a titrimetric method (97,98). The method involves the precipitation of the sulphate with barium chloride from an acidified ethylene diamine tetraacetic acid solution to prevent the co-precipitation of various ions. The precipitate is filtered off and dissolved in ammoniacal EDTA and the excess of EDTA titrated against standard magnesium solution with eriochrome black T as the indicator. This method is free of interference from nitrate and phosphate and does avoid some of the time-consuming details of the gravimetric method (71).

Iodimetric procedures provide the most widely used methods for the volumetric determination of hydrogen sulphide (72). Errors in this method were investigated by Bethge (99). In a proposed method by Honarkhah (100) the amount of sulphur in non-olefinic hydrocarbons were determined iodimetrically after the reduction of sulphur compounds with Raney nickel.

The sulphur dioxide produced in the oxygen combustion of organic sulphur-containing materials may be determined quantitatively by the iodimetric titration reaction (102). Karchmer (71) suggested that care should be exercised so that the sulphur dioxide

does not overrun the addition of iodate very much, since some sulphur dioxide will be lost to the air. When the approximate sulphur content of the sample is known, about 80% of the required iodate can be added at one time, minimising loss of sulphur dioxide. Chlorine and nitrogen, or their compounds, react adversely with the reagents used in the iodimetric procedure.

The sulphuric acid produced in the lamp, oxygen flask and high temperature combustion methods can be measured acidimetrically using methyl red or methyl purple as indicator (72). This direct finish is not satisfactory for samples containing significant quantities of nitrogen, halides or phosphorus. However, a simple evaporation step on a steam bath using purified air will separate nitric and halogen acids from sulphuric acid (71).

A great advantage of titrimetric methods is that they are an absolute method which do not require empirical calibration because of exact stoichiometry of the reactions (103). When micro quantities of material are titrated by visual methods, a low concentration of titrant is needed, making it difficult to detect the end point. To overcome this problem the end point can be detected colorimetrically, amperometrically, potentiometrically, or conductimetrically. The colorimetric titration is applicable to any of the methods using a colour indicator and is more sensitive and reproducible than the visual method (72). A colorimetric titration (104) of sulphate has been developed for the determination of the sulphur content of organic molecules after oxygen flask decomposition. The sulphate is titrated with barium perchlorate using thorin as the indicator. This titration method is subject to interferences from cations

(e.g., Sn, Fe and Cu) and is sensitive to pH changes. Among the anions, only PO_4^{3-} and higher concentrations of F^- cause significant errors.

Fensom, et al., (105) have used another colorimetric method for the determination of total sulphur in light petroleum distillate. In this method, nickel sulphide, after reduction of sulphur compounds with Raney nickel, was titrated with mercury acetate using dithizone as indicator. A mixture of propan-2-ol and water was used as the reaction solvent for the determination of total sulphur in the range 0.01 to 0.10 ppm with a precision of $\pm 10\%$ using a spectrophotometer to detect the end point.

In conductometric titrations, the sulphate ions are titrated with a solution of barium ions. The conductivity of the solution decreases, owing to precipitation of barium sulphate and replacement of the highly mobile sulphate ions by anions (attached to barium ions) of low mobility. After the equivalence point has been reached, excess of barium ion causes an increase in conductivity (106). Barium chloride, barium nitrate and barium acetate have been used as titrant, with the acetate providing an improved end point over the chloride or nitrate, due to the fact that mobility of the acetate ion is much less than that of nitrate and chloride (71). Phosphate and halide ions interfere and can be removed by addition of silver nitrate before titration (106). Cations such as calcium, magnesium, sodium, potassium and cations giving insoluble sulphates

interfere. These interfering cations can be removed by using an ion exchange column (107). The accuracy of the titration can be increased by titrating smaller volume of solution. This can be done using high-frequency micro-titration (107).

Sulphur in organic substances has been determined titrimetrically by means of potentiometric and amperometric end-point indication (71, 72). Different electrode pairs such as tungsten-calomel, platinum-tungsten or tungsten-molybdenum and indicator electrodes like mercury and glass have been used in potentiometric titrations of sulphur compounds (72). For the determination of nanogram amounts of sulphur in very small amounts of organic substances ($> 2 \mu\text{g}$), hydrogen sulphide, produced by hydrogenation, is determined argentometrically by means of potentiometric end-point indication, using silver sulphide electrode (108). Gildenberg (109) described an amperometric titration with lead nitrate of sulphate solution formed during a closed oxygen flask combustion of organic compounds. Increments of 0.5 or 1.0 ml of 0.01N lead nitrate are titrated into a 75% alcoholic solution (in order to suppress the solubility of lead sulphate) containing sulphate.

Three direct polarographic micro-methods are described for the determination of sulphur in organic compounds after oxygen flask combustion, followed by oxidation of products into sulphuric acid with hydrogen peroxide (110-111). The methods are based upon allowing the sulphuric acid to react with excess of barium chloride, iodate or bromate. In the case of using barium chloride, the unreacted barium ion is measured polarographically. Iodate ions liberated and bromic acid formed or

excess or bromate ions are measured respectively in the case of using iodate or bromate. In principle, the methods depend on recording the polarogram of a known amount of barium before and after precipitating a certain weight of the organic sulphur compounds. Maximum precision is attained when the amount of barium added in excess is kept small compared to that precipitated. The bromate method is superior to the iodate method being simpler and more rapid and results are correct to within ca. $\pm$ 0.5% (111). Phosphate, in high quantities interfere (110).

Two microcoulometric methods for the rapid determination of total sulphur in hydrocarbons are proposed (112). In both of these methods, the sample is pyrolysed to convert the sulphur to a form that can be automatically titrated in a microcoulometric cell. In the reductive method the sample is pyrolysed in hydrogen over a 10% platinum on an Alundum catalyst. The hydrogen sulphide formed is automatically titrated with silver ions. The reductive method suffers from nitrogen interference in proportion to the hydrogen cyanide formed in the pyrolysis. In the oxidative method, chlorine concentrations above 1000 ppm begin to interfere negatively. The oxidative system is simpler to operate. Both methods are suitable for the 0.2 to 1000 ppm sulphur range with an analysis time of typically ten minutes per duplicate analysis. The recovery for different sulphur compounds in kerosene are reported to be 73 - 87% (112). Cedergren (113) described a new oven construction in which the combustion conditions were selected to give a recovery of close to 100% for different sulphur compounds.

The recent introduction of a gas-sensing electrode which is selective for sulphur dioxide, makes possible the measurement of organic sulphur combustion products directly as sulphur dioxide in the absorbent. Krueger (114) described a method of collection and analysis of sulphur dioxide produced after burning the petroleum in a combustion lamp. The sulphur dioxide is measured directly in the absorbing solution using sulphur dioxide sensing electrode. Particulate and ionic by-products of the lamp combustion do not interfere.

D) Instrumental methods:

The sulphur content of petroleum and petroleum products is determined by various instrumental techniques. Kirkbright, et al., (115) reported the determination of sulphur by atomic absorption spectrometry in a nitrogen separated nitrous oxide-acetylene flame using sulphur microwave-excited electrodeless discharge lamp at the sulphur principal resonance line (180.7 nm). The preliminary study described in this report indicates that the nitrogen separated nitrous oxide-acetylene flame forms an efficient and transparent atom cell for the determination of sulphur and that the determination at 180.7 nm may be made with freedom from chemical and physical interferences. The electrodeless discharge lamp source even at the low power input suffers appreciable self-absorption broadening. They analysed oils which were diluted in methyl isobutyl ketone and sprayed into the flame. The results they obtained had errors relative to the standard of 13.9% to 0.5%. With the

arrangement and flame described above, a water-cooled demountable hollow cathode lamp was employed as a source in the determination of sulphur by atomic absorption spectrometry at its 180.7 nm line (116). The intensity of line emission, signal to background intensity ratio, and consequently the sensitivity and detection limit obtained with this hollow cathode lamp were improved compared to those of electrodeless discharge lamp. In addition, good long term stability and decreased source line broadening due to self absorption were achieved by using hollow cathode lamp.

A radiochemical technique has been combined with a high temperature combustion method to give a rapid method for the determination of sulphur in the range 1 to 10 ppm in organic substances such as purified light petroleum (117). The sulphate formed is precipitated with barium chloride labelled with barium -133. The active precipitate was washed free from excess of barium chloride reagent with small portions of anhydrous methanol until constant activities were obtained. The amount of barium sulphate obtained was determined by measuring its activity. A limitation is imposed on this method by the solubility of barium sulphate in water. Acid must be present to prevent the interference from carbonate, phosphate and silicate ions. In this work, the solubility limitation was overcome by evaporating to dryness after decomposing the carbonate with acid. The lowest detectable concentration of sulphur is dependent on the magnitude of the blank value.

X-ray fluorescence spectrography has been used to determine the sulphur content of petroleum (118). In X-ray fluorescence analysis, the sample is irradiated with high-intensity x-rays. The resulting energy changes appear as photons with wave-lengths characteristic of the atom. The frequency of occurrence of these fluorescent x-ray photons is proportional to the amount of element present. Bartkiewicz (118) details a rapid, 5 to 25 minutes, procedure for determining from 0.0005 to 10% sulphur in petroleum products ranging from gasolines through crude oils with precisions in the range 3 - 6%. Trace amounts of impurities (less than 0.15%) due to mass absorption, cause interference. Analysis time is less than 6 minutes per sample.

Although this technique is rapid and sensitive, but is sample matrix dependent and must be calibrated for each particular sample type (111). Also this technique involves high capital cost and requires considerable expertise if accurate results are to be obtained (116).

(1.5.4) Summary:

Observed difference effects and achieved working range for different methods used in determination of total sulphur in organic substances are summarized in Table (1.3). Except x-ray fluorescence and atomic absorption spectrometry, in which the organic sulphur compounds can be analysed directly, other methods can not be applied directly for organic sulphur determination. This is mainly because of matrix effects. In majority of methods phosphate and halide ions interfere.

TABLE (1.3)

Selected Determination Methods of Total Sulphur in Organic Substances.

Determination Method	Sample Treatment	Interfering Substance	Range of Sulphur	Precision	Reference
1 Barium chloranilate displacement	Nitric acid oxidation	P, Ca, Cu, Zn	0.03-3%	$\pm 2\%^a$	82
2 Acidimetric titration	Oxygen flask	halides, nitrate and phosphate ions	$>0.002\%$	$\pm 5\%^b$	101
3 Iodimetric titration	reduction with Raney nickel	olefins, sulphonides	0.01-100 ppm	$\pm 3\%^b$	100
4 Colorimetric mercury acetate titration	reduction with Raney nickel	olefins sulphonides	0.01-0.1 ppm	$\pm 9\%^a$	105
5 Colorimetric barium-thorin titration	Oxygen flask	Cu, Fe, Sn and PO_4^{3-} , F^-	$> 3 \mu\text{g}$	0.24^c	103
6 Conductimetric barium-perchloride titration	combustion in oxygen	Ba, Pb, K, Na and PO_4^{3-} , halides	0.4-50 ppm	$\pm 5\%^b$	106
7 Oxidative microcolometric titration	combustion in oxygen	halides, heavy metals	0.2-100 ppm	$\pm 3\%^a$	110

TABLE (1.3) (cont.)

Determination Method	Sample Treatment	Interfering Substance	Range of Sulphur	Precision	Reference
8 Turbidimetric	Oxygen flask	PO_4^{3-} , halide ions	10-300 μg	$\pm 2.3\%^d$	88
9 Nephelometric	hydrochloric and nitric acid oxidation		$> 0.7 \mu\text{g}$	$\pm 1\%^b$	83
10 methylene blue spectrophotometric	reduction on	heavy metals	0.02-0.4 ppm	$\pm 2\%^b$	90
11 Atomic absorption spectrometry			40-400 ppm	$\pm 7.2\%^c$	116
12 Radio chemical measurement	high temperature combustion	Co_3^{2-} , PO_4^{3-} , SiO_3^{2-}	1-10 ppm	$\pm 5\%^c$	117
13 X-ray fluorescence		impurities	0.005-10%	$\pm 6\%^a$	118

a = relative standard deviation

b = relative error

c = standard deviation

CHAPTER 2

Chemiluminescent Determination of Sulphur.

(2.1) Introduction:

Most metals can be determined by the techniques of atomic absorption and atomic fluorescence spectroscopy, including those that form molecular species with oxygen that do not readily dissociate except in strongly reducing flames. These techniques, however, are not suited to the determination of sulphur, phosphorus, oxygen or the halogens because their principal resonance lines lie in the far ultraviolet region of the spectrum, Table (2.1), where absorption by atmospheric oxygen and flame gases is high.

It is only recently that molecular emission in cool flames has been proposed to overcome these difficulties by using the emission of simple species such as S_2 (119), HPO (120) and $InCl$ (121). These are formed in an excited state by chemiluminescent reactions in cool flames and emit their characteristic band emission when they return to the lower electronic state.

Chemiluminescence arises when a chemical reaction produces an atom or molecule in an electronically excited state which then emits light as it returns to its ground state. Such reactions are common in biological systems where the phenomenon is called bioluminescence. In the latter part of the 19th Century it was found that rather simple organic (non-biological) compounds could also give rise to chemiluminescence. Thus, Radziszewski (122) found that lophine emitted green light when it reacted with

oxygen in alkaline solution. Today, many chemiluminescence systems are known, biological as well as non-biological, but despite intensive studies the detailed mechanisms involved are largely unknown.

Table (2.1).

Element	Main Resonance Line nm
F	95.5, 95.2
Cl	138.0, 134.7
Br	157.6, 148.9
I	183.0
P	178.8, 178.3, 177.5
S	182.6, 182.1, 180.7

The quantum yield of chemiluminescence, i.e., the number of emitted photons divided by the number of reacting molecules, is often very low. The development of sensitive photomultipliers has made it possible to follow very weak luminescence (123), even when the quantum yield is as low as 10^{-15} . The possibility of measuring small amounts of light also means that sensitive analytical methods based on luminescence can be developed. By using reactions where the quantum yield is high, of the order $\pm 0.01 - 1$, these analytical methods often attain exceedingly high sensitivities (124).

Chemiluminescence techniques are highly specific compared to conventional methods such as coulometry and colorimetry. For another molecule to be a positive interference, (in solution chemiluminescence) this molecule must react with the reagent added and the reaction must be exothermic and yield chemiluminescence. Furthermore, the resultant emission must overlap the spectral region of the analyte emission (125). A third body which quenches the emitting state is a negative interference. The predominant quenching agents in ambient air (gas chemiluminescence) are molecular oxygen and nitrogen which do not vary significantly in concentration and the quenching effect, if present, is generally constant (125).

Generally speaking, three conditions are required for chemiluminescence to occur: the chemical reaction must release sufficient energy to populate an excited energy state; the reaction pathway must favour the formation of a product in an excited state and the excited state product must be capable of emitting a photon itself or transferring its energy to another molecule that can emit.

The efficiency of chemiluminescence, Q_{CL} , can be defined:

$$Q_{CL} = \frac{\text{number (or rate) of photons emitted}}{\text{number (or rate) of molecules reacting}} \quad (2.1)$$

It is equal to the efficiency of excited state production (number of molecules formed in the excited state/number of molecules reacting) times the efficiency of emission (number of photon

emitted/number of molecules in excited state). Reactions can be used for chemical analysis by adjusting concentrations so that the chemiluminescence intensity I_{CL} (photons/sec) is related to the concentration of the reactant to be determined. At any time, t , I_{CL} is given by the expression

$$I_{CL} = Q_{CL} \times \frac{dc}{dt} \quad (2.2)$$

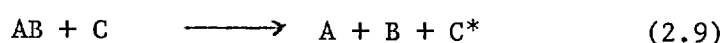
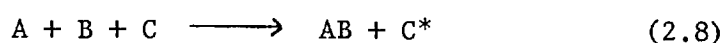
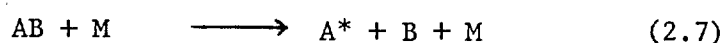
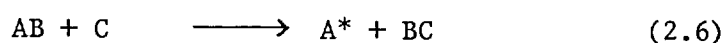
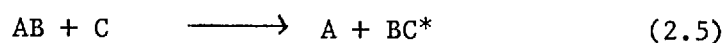
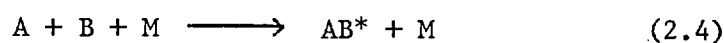
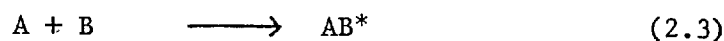
where dc/dt is the reaction rate for the starting material forming a product in an electronically excited state. I_{CL} can be measured as a function of time (kinetic analysis), or it can be integrated for a known time period. For chemical analysis, a convenient means of performing the integration is to carry out the reaction in a flow system observing steady state chemiluminescence intensity (126). Chemiluminescence offers three important advantages for chemical analysis.

This method can be extremely sensitive because it is easy to measure low levels of light emission against effectively a zero brightness background. In practice, however, sensitivity is usually limited by reagent purity, rather than by light-measuring capability.

For many of the available chemiluminescence reactions, response is linearly proportional to reactant concentration over several orders of magnitude (127). The methods can be made quite specific because of the nature of the chemiluminescence reactions (119-121).

(2.2) Flame Chemiluminescence of Sulphur.

Chemiluminescence can result from the recombination of species generated in a flame, e.g., C_2 , CH, CN, OH, etc. Generally speaking, the following reactions can be mentioned as chemiluminescent reactions (128):



The A, B, C and M stand for radicals or molecules as well as for atoms. Processes (2.3) to (2.7) may be termed chemiluminescence since the excited product is formed by the reaction. In processes (2.8) and (2.9), the excited product is a partner of the collision but is not chemically modified, it is action only to carry away the energy made available by the process. Such processes are termed induced chemiluminescence (128).

The most important analytical applications of flame chemiluminescence have been to determine sulphur and phosphorus by observing the molecular emission that occurs when sulphur and phosphorus compounds are introduced into a hydrogen-air diffusion flame. (119-120).

If a solution aerosol containing some sulphur species is introduced into a relatively low temperature, fuel-rich hydrogen flame, and a cold object near the flame core an intense blue emission is observed near the surface of the object (129). A similar effect occurs with phosphorus compounds, in this case resulting in a green emission (120). These emissions arise from the S_2 and HPO molecules formed in the flame gases, chilled by the relatively cold wall of the object.

Gilbert (130) has suggested that the enhancement of the HPO emission by a shield is due not to the action of the surface as a third body, but to the cooling effect of the wall or of an entrained inert gas. Syty and Dean (131) suggested that the third body can be either nitrogen or the shield wall. Veillon and Park (132) claimed that it would be expected that the cooling is not the only requirement, but that a third body (e.g., a cold wall) is necessary for the formation of S_2 . The magnitude of the signal from the flame photometric detector is determined by the emitted light intensity, I_E , which can be expressed (133) by

$$I_E = A M_s h\nu b K P_i \exp(E_s/kT) \quad (2.10)$$

where A is the probability of radiative transfer, M_s is the molecular mass, $h\nu$ is the energy of the emitted photons, b is the optical path length, K is a constant, E_s is the excitation energy, k is the Boltzmann constant, T is the absolute temperature, and P_i is the partial pressure of the species emitting light. At constant temperature, and for a given system, this equation may be written (134)

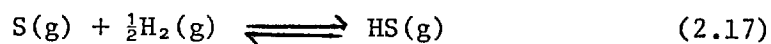
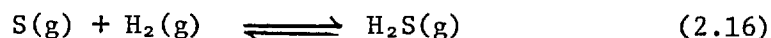
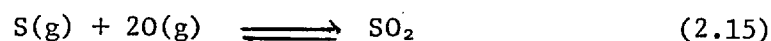
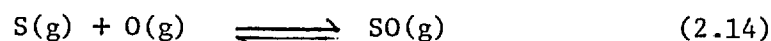
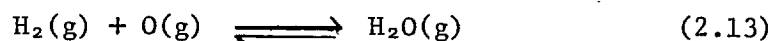
$$\log I_E = K' + \log P_i \quad (2.11)$$

from which it follows that the logarithm of the signal is a linear function of the logarithm of the concentration. If, in the case of S_2 , $P(S_2)$ is directly proportional to $[S]^N$ it follows that

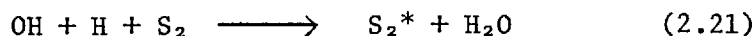
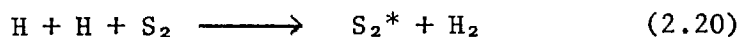
$$\log I_E = \text{const.} + N \log[S] \quad (2.12)$$

which means that if the logarithm of the intensity is plotted against the concentration of sulphur in the sample, a straight line with slope N is obtained. The value of this slope will be discussed later.

The mechanism of S_2 formation and excitation of the S_2 to the excited state is not fully understood, but conditions for the maximum formation of gaseous S_2 can be understood by considering the following reactions (134).



It is also suggested that an overexcitation origin has been attributed to S_2 emission (135).



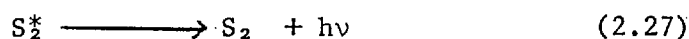
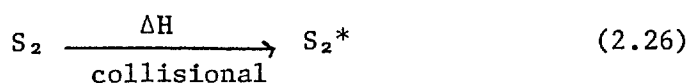
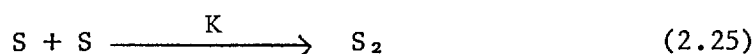
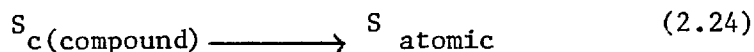
Reaction (2.20) probably dominates. It offers an excitation energy of 4.5 eV from reaction (2.21).

The formation of S_2 takes place according to the following equilibrium



After the deactivation of the excited state, S_2 is oxidised in the upper part of the column of flame gases to the final equilibrium from SO_2 that is found in the burnt gases.

It is also claimed that the following reactions probably are, in part, responsible for the formation and excitation of S_2 (136).



2.3: Particular problems in flame chemiluminescence determination of sulphur.

Although flame chemiluminescence has been found to be useful for the determination of sulphur, there are a number of difficulties associated with the technique.

1) The S_2 emission intensity is not linearly proportional to the concentration of the sulphur compound, instead, the relationship between intensity of the S_2 emission and the concentration is given by the equation:

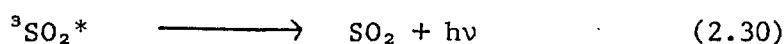
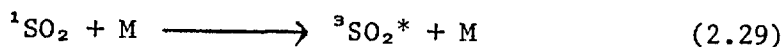
$$I_{S_2} = I_0[S]^N \quad (2.28)$$

where I_{S_2} is the observed intensity of the molecular emission due to the S_2 species, $[S]$ is the concentration of the sulphur atoms, and I_0 and N are both constant under given experimental conditions. Although the value of N is usually assumed to be equal to 2, this exact square relationship is not always obtained. The value of N has been repeatedly reported to vary from $N \approx 1$ to $N=2$ (137-140).

In general, the N values reported have been between 1.5 and 2. One of the primary and also most disturbing reasons for this experimental variation in N , is that its value depends upon the flame conditions (140, 141).

Eckhardt, et al., (140) have found that the gas flow rates for hydrogen, nitrogen oxidant as well as the oxidant to fuel ratio drastically affect the exponential proportionality factor N . Calculations have shown that there is a maximum in the formation of S_2 for $\alpha = 0.52$ ($\alpha = 2F_{O_2}/F_{H_2}$, F denotes the flow rate) compared with experimentally found values of 0.56 (134). The discrepancy between the theoretical and experimental results for α might, apart from the effects of wrong estimates of temperature, depend on the emission from sulphur dioxide.

Sidebottom, et al., (142) proposed that the sulphur dioxide molecule absorbs light with resultant excitation to a singlet and triplet state, which de-excite, according to the following scheme:



Consequently, the only way to actually maintain any degree of analytical accuracy or precision would be to adjust exactly all of the flame parameters and to ensure that they remain constant.

It has been also demonstrated that the exponential proportionality function is different for different sulphur compounds (139, 143, 144). The reason for this is probably due to varying degrees of decomposition for different parent sulphur-containing molecules in the flame (145).

2) Each sulphur compound has a different emissivity. Many workers (146, 147, 148) have noted the difference in S_2 emission obtained with different compounds. Shiffman and Frank (148), observing that the S_2 emissivity of thioacetamide was twice that of thiourea. Dagnall, et al., (119) reported the order of emissive response for sulphur-containing groups to be



The emission is very dependent on the strength with which each sulphur atom is bound in the molecule and, because of the low temperature of the analytical cool flames, there is a limited amount of energy available for dissociation of the sample molecules. For this reason, there is very little S_2 emission from compounds containing carbon-sulphur double bonds or mercaptan groups (131).

The problem of different response for different sulphur compounds can be overcome by converting the organic or inorganic sulphur compounds into hydrogen sulphide prior to sample introduction into the flame. This can be achieved in several ways which will be discussed later (Chapter 3).

Another method for overcoming this difficulty is to separate the sulphur-containing species from the matrix and from each other prior to the flame photometric determination, as in gas chromatographic measurements using molecular emission as the detection system (150). This method requires that standards of all of the sulphur-containing species be available so that calibration curves can be prepared.

3) The emission behaviour of the common cool flames are quite dissimilar (137, 149). In the Brody-Cheney flame photometer (150), the analytical curve for a specific sulphur species is approximately quadratic at all concentrations except the lowest, where it is linear. This is exactly opposite to the behaviour of other burner designs. Brody and Cheney's data show that the response for their

design is only proportional to the approximate square of the sulphur concentration from about 0.05 $\mu\text{g/L}$ of sulphur of equivalent air up to about 3 $\mu\text{g/L}$, and below 0.05 $\mu\text{g/L}$ the analytical curve becomes almost linear. For oxygen to hydrogen flow ratio (α) = 0.33, the range of linearity of the calibration curve is larger than that for α = 0.52. The reason for this is that for small values of α the partial pressure of hydrogen is changed only slightly when the amount of sulphur introduced is increased under equilibrium conditions (134).

The range of linearity of the calibration curve is restricted to sulphur concentration axis.

Greer and Bydalek (138) have attributed this curvature to self-absorption and corrected for it using the expression

$$\log R = \log C + \log (S)^2 - \alpha K (S)^2 \quad (2.31)$$

where R is instrument response, C and K are constants and α is the absorption coefficient. Firstly, $\log R$ vs. $\log (S)^2$ is plotted and $\log C$ calculated from the intercept; αK is then calculated from the points on the calibration line where curvature is observed and a mean value found. A corrected curve, $(\log R)_{\text{corr}}$ vs. $\log (S)^2$ is then plotted, where

$$(\log R)_{\text{corr}} = \log R + \alpha K (S)^2 \quad (2.32)$$

This should then give a straight line of gradient unity and intercept $\log C$. This treatment was applied with some success

by Everett, et al., (159) and suggested that between 0-10 ppm, the signal intensity is proportional to S^2 ; the major cause of curvature is self-absorption between 10-40 ppm, but self-quenching above 40 ppm.

4) The temperature at the centre of the cool flame is about 398°C and is believed to be most suitable for formation of S_2 (119). It is, however, already well known that such a flame does not supply the energy or the optimum temperature for the determination of sulphates via S_2 emission. For instance, Dagnall, et al., (119) obtained a relative response ratio of 600:1 for SO_2 and H_2SO_4 in cool flames. Furthermore, they reported that the optimum height for S_2 emission from sulphates was higher up in the flame, thereby indicating that sulphates require a higher temperature for their ultimate dissociation and subsequent S_2 production. For example, the relative decomposition temperatures of some sulphates are (151): $MnSO_4$ 755, $FeSO_4$ 537, $CoSO_4$ 708, $NiSO_4$ 675, $CuSO_4$ 598, $ZnSO_4$ 646, $CdSO_4$ 816, $PbSO_4$ 803, $MgSO_4$ 895, $CaSO_4$ 1149 and $SrSO_4$ 1374 C.

If the temperature of the flame is made high enough for SO_4 decomposition, then the majority of the flame cone will be above the temperature at which the S_2 molecule dissociates, (the bond energy of S_2 is about 4.5-5.1 eV) (135, 152) and so no S_2 molecules will be formed.

5) Another serious complication concerns the interferences caused by hydrocarbons. Generally, even the presence of traces

of non-sulphur containing organic compounds in either the carrier gas or in the sample causes a decrease in the response of the detector (143, 153).

Sugiyama, et al., (154) suggest that the magnitude of the interference caused by organic compounds on the molecular emission due to the S_2 species increases exponentially with the concentration of volatile organic compounds. The decrease in the intensity of the S_2 molecular emission is based on the deactivation of the excited S_2 species by combination or collision with an organic compound and/or its degradation products. This intensity decrease is independent of wavelength, is not due to the absorption of light by the organic compound, and the S_2 emission decreased almost uniformly over the complete 320 to 440 nm wavelength range and is not due to the temperature rise in flame which results from the presence of organic compounds.

Veillon and Park (132) found that the S_2 emission signal in organic solvents, nebulising solution directly into the flame, was considerably lower than that obtained in aqueous solvents. This they attributed to the increase in flame temperature caused by the combustion of the organic compounds or by the presence of organic radicals quenching the emission. Based on experimental results, Fredriksson and Cedergren (134) suggest that the formation of the thermodynamically stable gaseous CS is probably responsible for the decrease in the cool-flame signal from S_2 in the presence of hydrocarbons. On addition of carbon monoxide carbon dioxide and nitrogen, the decrease

in the S_2 signal is largest for carbon monoxide and this might be a result of a local dissociation of carbon monoxide to free carbon and carbon dioxide.

In order to minimize the effect of hydrocarbons, Rupprecht and Phillips (155) introduced a combined oxidizer and detector burner. They reported that 20-100 ppm of sulphur in organic liquids could be measured successfully.

Patterson, et al., (156) described a dual-flame photometric detector. By use of this construction the quenching of the S_2 emission can be decreased but not eliminated. Joonson and Loog (157) suggested that improvements with respect to interference from hydrocarbons are obtained if the sample is mixed with hydrogen before introduction into detector. By using controlled conditions, different sulphur compounds can be quantitatively converted to a single sulphur compound (sulphur dioxide or hydrogen sulphide, will be discussed later) which means that a single calibration curve can be used independently of the type of sulphur compound to be determined and the signal is completely free from the interferences caused by hydrocarbons.

6) Any further attempts to reduce the noise level of the commercial flame photometric detectors are severely restricted since the flame noise predominates over other low-level noise in the important signal-to-noise ratio (158). Although the S_2 emission is detected above the actual flame, the background signal is

still largely due to the flame noise. This background noise current obtained with a cool-flame is about 2×10^{-9} A, which is an order of magnitude greater than the normal photomultiplier dark current (137, 159), consequently, the flame noise for a typical cool-flame is equivalent to the signal corresponding to an SO₂ concentration of about 5 ppb.

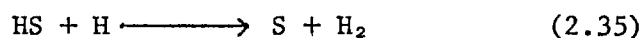
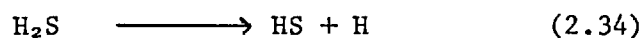
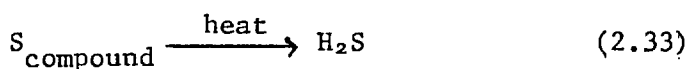
Grice, et al., (160) have reported a detection limit for sulphur of 0.2 ng or 0.035 ng/sec with the flame photometric detector.

- 7) The emissive intensity of many compounds is dependent on the hydrogen ion concentration of the sample solution (119).
- 8) The evaporation of the solvent and the vaporization of the sample are very inefficient processes under low temperature conditions.

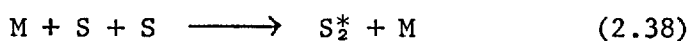
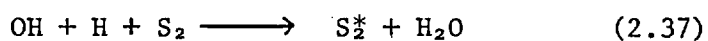
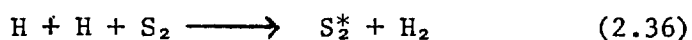
(2.4) The Flame.

It is assumed that the flame serves three vital functions in the overall mechanism of sulphur chemiluminescence (145, 146).

- 1) The hot region of the flame decomposes the sulphur-containing molecules.
- 2) The products from this decomposition of the parent molecules are believed to produce sulphur atoms directly or indirectly by



3) The cool centre region of the flame results in the formation of excited S_2 molecules possibly by the following set of reactions:



where the recombination of atomic hydrogen, the formation of H_2O and three-body collision supplied the excitation energy for S_2 respectively.

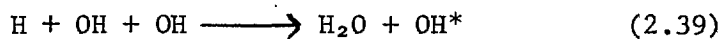
The highly reducing nature, limiting quenching action and low incidence of molecular or atomic oxygen in the air/hydrogen diffusion flame are contributing factors in the production of the intensely emitting molecular species. Atmospheric oxygen, which supports the flame combustion, diffuses only a little way toward the centre of the flame, and for this reason the molecular emission is observed only within the central region. It is important therefore, to reduce flame turbulence and prevent the available oxygen from reaching the centre, because this would tend to quench the molecular emission and also increase the temperature of the flame.

Dilution of the fuel gases with an inert gas, such as argon or nitrogen reduces the temperature and background emission of the air/hydrogen diffusion flame and also restricts the ingress of oxygen (119, 161).

The temperature of the centre of the flame is a function of the burner diameter for diffusion flames and temperatures closer to optimum for S_2 emission can be achieved by utilising a relatively wide (10 mm) tube as burner (162, 163).

The use of argon instead of nitrogen as diluent gas is preferred due to the argon having no vibrational levels available to quench the excited state of the S_2 molecule. Pinches (136) found a three-fold enhancement of emission from an Ar/H_2 flame compared to an N_2/H_2 flame.

The air/hydrogen flame is practically non-luminous in the visible region. Normally impurities such as sodium and calcium give flickers of orange coloration. The only radiation from the pure air/hydrogen flame due to the OH bands which is however much weaker than that from the inner cones of hydrocarbon flames (161). Charton and Gaydon (164) say the OH radiation appears to be due to some chemi-excitation of OH by the reaction



The excitation will vary as the cube of the concentration of free radicals, and it dies out rapidly higher in the flame as the excess radicals recombine.

Dagnall, et al., (119) claimed that the signal obtained from the direct introduction of ammonium sulphate solution into a

pre-mixed air/hydrogen flame burning inside a borosilicate glass tube, which is cooled to prevent dissociation of S_2 species produced in the hotter part of the flame, was about 30 times greater than in the hydrogen-nitrogen diffusion flame, while the emission from a sulphur dioxide solution was virtually identical.

The sheath dimensions were found not to be critical (132). Very little difference in signal levels were obtained when sheaths of borosilicate glass, fused silica and copper were used. Cooling of a fused silica sheath even further with air or a water jacket had little effect. On the other hand, Crider (165) notes that the response from 1 ppm sulphur dioxide in an unshielded diffusion air/hydrogen flame was about three times that from the shielded flame.

(2.5) Sample introduction and determination:

Apart from the flame two other parameters, sample introduction and signal recovery, are very important in cool flame work. Because the emission from S_2 is banded sensitivity is lost if a monochromator instrument is used, measuring the emission over a narrow wavelength region (119). To increase the sensitivity of this determination a simple filter photometer has been constructed, such as that has been used for the gas-chromatographic detection, which improves the detection limit of sulphur about 100 fold, compared with a monochromator (163). The effect of emission from the species should be increased as compared with the monochromated system. With equimolar amounts of sodium,

potassium and zinc present this was found to be so, the percentage decrease in peak height being of the order of 80% compared with ca. 30% for the monochromated system (146). The spectrum of sulphur and the transmission curve of filter (the superimposed) are shown in Figure (2-1). Liquid gas-phase samples can be introduced into the cool-flame in several different ways.

With liquid samples, introduced as aerosols to the diffusion flame, there are several problems. With direct nebulisation of sample into the flame in organic solvents, the S_2 emission was considerably less than that obtained with aqueous solutions. With the alcohols, the sensitivity decreased by about 4 fold, while in n-butyl acetate it decreased by about 30-fold (132). Dagnall, et al., (119) found that above 10-fold excess, orthophosphoric, nitric and hydrobromic acids caused a decrease in the S_2 signal, while acetic and oxalic acids caused an increase in signal, probably caused by viscosity and surface tension.

The emission signal per unit sulphur is over 10 times smaller for nebulised liquids than for vapour phase samples, even when ultrasonic nebulization is used to produce a finely divided aerosol. The sensitivity increases with increasing volatility of the compound being analysed: alkali metal sulphides and sulphites giving approximately a hundred-fold increase in signal upon acidification to produce a volatile species (127).

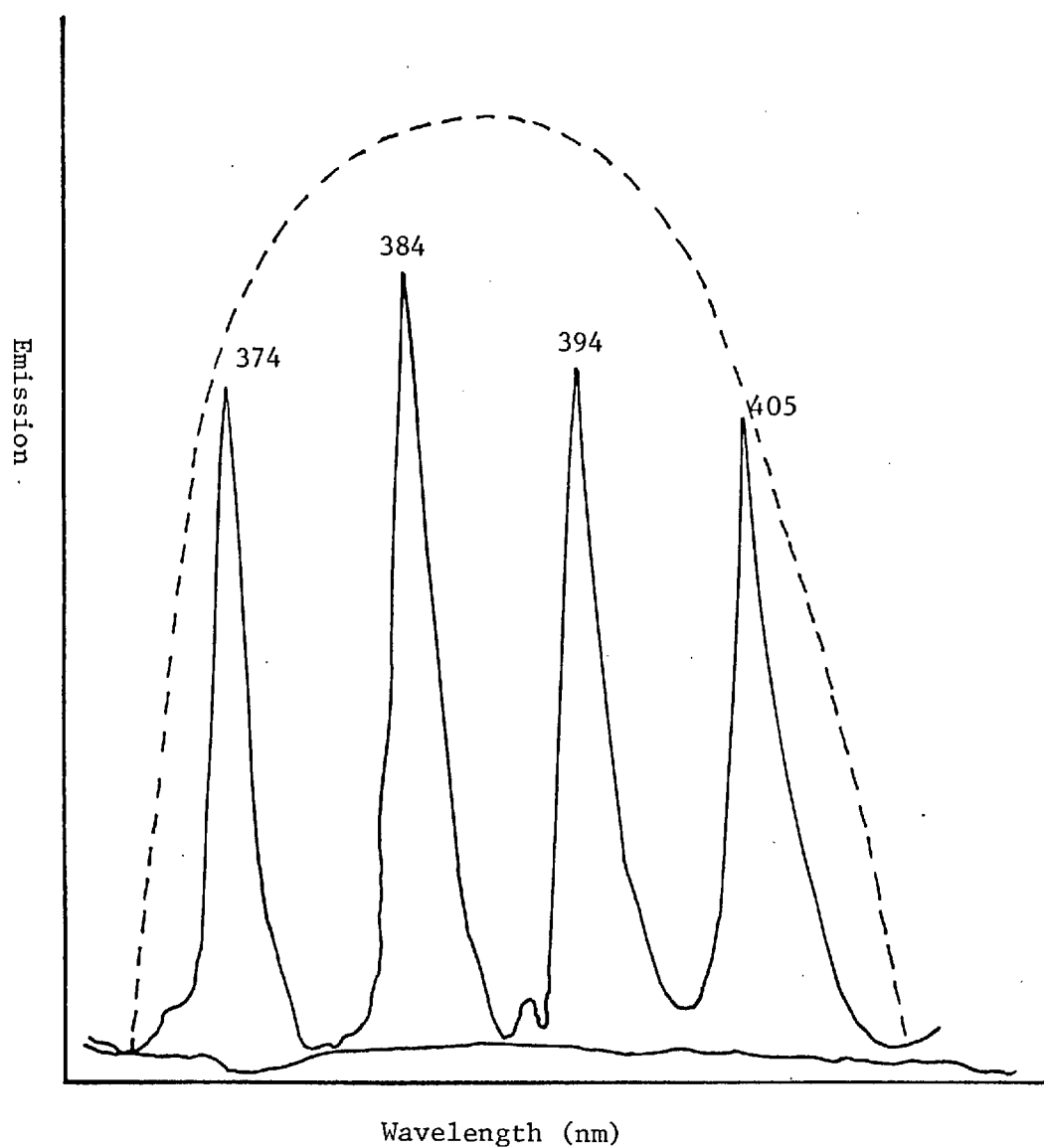


Figure (2.1)

Spectrum of sulphur in a H_2/Ar flame.

Superimposed is transmission characteristic of filter used.

Conventional atomic absorption nebulizers give droplets that are too large to be readily vaporized in the central cool regions of the flame, an extremely fine aerosol is preferable. Most pneumatic nebulizers are only 3-7% efficient in transporting sample to the flame and so, with the low atomisation efficiency, this method of sample introduction is poor.

Two modifications (163) have been developed in an effort to overcome these drawbacks. For sample volumes of less than about one ml a heated injection manifold system was used (162). This gave increased sensitivity when compared with a conventional pneumatic nebulisation system and was most suitable for sample volumes up to 10 μ l.

For sample volumes greater than about one ml the introduction of a heated nebulizer chamber gave the lowest detection limits. The increase in flame background and noise that accompanied the increased sample input offset the expected increase in sensitivity. These modified methods suffer from matrix and organic compound interference effects. All metal cations interfere to some extent, usually depressing the emission and organic solvents completely quench the emission (156). By using using a modified Wickbold apparatus in conjunction with a filter flame photometer a complete determination of sulphur in organic solvents could be carried out in 5 minutes for samples containing more than 0.5 ppm of sulphur (163). This method involves the initial burning of the hydrocarbon in an oxy-hydrogen flame at low pressure. The combustion products are scrubbed by passing the gases up through an absorber column containing hydrogen peroxide solution which converts

the oxide of sulphur into sulphate. The sulphate produced was nebulised directly into the flame photometer. One way of overcoming the problems associated with the introduction of aerosols into the cool flame is by preliminary thermal decomposition of the sulphur compounds to gaseous products. The first to use this approach were Scaringelli and Rehme (166) who slowly heated and vaporized the sample in a furnace prior to introduction into the flame. Roberts and Lander (167) placed a filter paper section between two stainless steel strips and rapidly vaporized the sulphur compounds by capacitor discharge. Husar, et al., (168) have applied this technique to the determination of sulphur in filter samples collected in plumes by aircraft. The sample vaporization was performed by capacitor discharge across a tungsten boat, resulting in resistance heating to 110°C . The vaporized gaseous decomposition products of sulphur compounds were carried to the flame photometric detector in a stream of clean, charcoal filtered air at a flow rate of $2\text{ cm}^3/\text{sec}$. Neither matrix nor organic compound interference effects were eliminated in this method.

Another method of sample introduction into the flame is the method of Everett, et al., (169). In this method, emission from the S_2 molecular species was excited in a hydrogen-nitrogen diffusion flame burning on the sheathing-gas box of an unenclosed carbon filament atomiser (170). A calibration curve was obtained for the concentration range 0 to 10 ppm. The continuum radiation emitted by the glowing filament at intermediate

temperatures interfered a little but the interference effect of cations and anions were serious. Almost all metals depress the S_2 emission except Cu and Mo. There was no interference on the S_2 emission from ten-fold amounts of chloride, nitrate, acetate, perchlorate depressed the emission by 15% and 45% respectively. There were some problems encountered when applying this method to the determination of sulphur in oils, quenching of the chemiluminescence by organic fragments from the oil matrix, a scatter signal from the smoke given off by the oil and loss of sulphur in the preheating cycle. It was therefore necessary to dry the oil prior to atomisation by carefully heating the oil at the lowest possible temperature to drive off the bulk of the solvent without loss of sulphur. To remove the scatter signal it was necessary to remove the maximum amount of oil matrix without loss of sulphur. Calibration curves from 0-10,000 ppm and 0-200 ppm sulphur were constructed from SAE 10 base oil and petroleum ether solutions respectively.

A technique of flame emission analysis called MECA (molecular emission cavity analysis) has been employed for measuring sulphur molecular emission in a cool flame (179). This technique employs a small cavity at the end of a rod into which the samples are deposited. The cavity is introduced into a fuel-rich hydrogen flame, cooled by addition of nitrogen or argon and the resulting emission is recorded. Samples of a few microlitres of the sample is injected into the cavity which can be reproducibly positioned into the flame in line with the

detector. The cavity is introduced into the flame pitched at slight angle downwards to optimize contact with the flame gases. The flame serves the double function of heating the cavity to vaporize the sample and of providing the radicals which maintain the molecular emission. The time that elapses between introducing the cavity into the flame and the appearance of maximum intensity was found to be characteristic of the sulphur compound; it is related to its vaporization and decomposition temperatures and thus the rate of heating. The peak intensity and, more particularly, the time integral of the emission, are related to the quantity of sulphur placed in the cavity. It has been shown that MECA can be used to determine sulphate, sulphide, metalbisulphite, thiosulphate, thiocyanate, and peroxodisulphate ions, on the basis of their S_2 emission measured at 384 nm (172).

Sulphuric acid gives a good emission response whereas the equivalent amounts of the more refractory compounds such as Iron(II) manganese(II) and sodium sulphates give little or no response under these conditions. Ammonium sulphate gives about 50% of the response of the equivalent amount of sulphuric acid. Addition of phosphoric acid, which is the least volatile acid and forms the most refractory salts, was found to have the same effect on Iron(II), manganese, sodium and ammonium sulphates. All give intense peaks of identical area to sulphuric acid under the same conditions. The detection limit under these conditions was about 1 ppm S.

As with sulphate, the presence of sodium ions decreases and delays S_2 emission from sulphite compared with that from sulphurous acid. Again, however, the addition of phosphoric acid markedly enhances sharpens and speeds up the response. The limit of detection is only ca. 10 ppm S. under the conditions used. Potassium metabisulphite behaves similarly to sodium sulphite, except that the responses of the former in the presence and absence of phosphoric acid are slightly faster than those of sulphite under the same conditions.

In the presence of phosphoric acid, the response due to potassium peroxidesulphate is very similar to that of sulphate ions.

Potassium thiocyanate gives a broad, multi peaked response when present alone. Addition of phosphoric acid increase the emission intensity.

Addition of phosphoric acid in the case of sodium sulphide and sodium thiosulphate is not feasible because of loss of hydrogen sulphide and decomposition of thiosulphate in acidic media. Since some of the sulphur-containing anions show appreciable differences in evaporation time, they give separate emission peak in their binary mixtures, and can be therefore be differentially determined (173). Even three-component mixtures can be determined under certain conditions, for example, the components of a mixture of sulphide, thiocyanate, and sulphate have been determined after treatment with an ammonium phosphate buffer (174). On using the MECA technique the curves show the sulphide, thiocyanate, and sulphate emission in the form of well separated peaks in the sequence indicated.

The saccharin content of cold drinks has been also successfully determined from the emission of S_2 molecules. The sample is treated with hydrochloric acid and extracted with ethyl acetate, an aliquot of the extract is transferred to the cavity, and the S_2 radiation measured (175).

In the MECA method, the slope of the linear portion of the log-log calibration plot varies between 1.6-1.7 for emission of sulphate and persulphate to 2.2 for emission of sulphide. The variation reflects the instantaneous concentrations of sulphur in the cavity obtained from various sulphur compounds (172) so, in the case of total sulphur determination this method requires that standards of all of the sulphur-containing species be available so that calibration curves can be prepared.

The hydrogen/air flame has seen widespread use in gas chromatography as a specific detector for sulphur or phosphorus-bearing compounds. The most widely used version of this detector, was first described by Brody and Chaney (150) who employed a diffusion flame in which a mixture of the gas chromatography effluent and air was conveyed to the centre orifice of a flame tip, and an excess of H_2 was introduced from the periphery of the flame tip.

Several advantages of sample introduction into a flame via gas chromatography over nebulization of sample have been reported (176) e.g., loss in sensitivity due to a rather large variation in droplet size and cooling effect from the vaporization of the solvent which is subsequently greater than the cooling effect from the introduction of the non-combustible

carrier gas.

Several workers have described the application of gas chromatography flame photometry technique to the separation and determination of organic and inorganic sulphur compounds in air and petroleum products (177, 178, 179). Pearson and Himes, (177) used three columns to achieve separation and determination of the sulphur compounds from each other and from interferences in gases and hydrocarbon streams. They reported the lower detection limits of 0.2 ppm for COS and CS₂; 0.4 ppm for SO₂ and 0.8 ppm for H₂S.

Total sulphur in gasoline was determined by this method (178). In this case 0.1-0.4 µl of sample was injected by syringe and in 3-5 minutes the peak area was printed out on the integrator.

A special chromatographic column combined with FPD has been used for separation and determination of H₂S, SO₂ and CH₃SH in air (179). Most of the known limitations of the FPD gas chromatography method of sulphur determination can be related to the fact that a single flame is used to both decompose samples and produce the desired sulphur emissions. Samples in the effluent can include compounds of complex molecular structure, and such compounds can change the flame environment and adversely affect the production of light (145). Rupprecht and Phillips (155) stated that the detector must be calibrated for each compound separately and results should be interpolated on a calibration graph. The problem of the flame extinguishing and how to overcome it has been noted by

Burgett and Green (180) and the quenching effect of hydrocarbons on molecular sulphur emission has been studied by other workers (177, 178).

The hydrocarbon quenching problem can be reduced by separating the region of sample decomposition from the region of optical emission, this being accomplished through the use of a dual-flame burner. Van der Simissen (181) employed an optically transparent Smithells-type (182) chimneys to achieve two longitudinally separated hydrogen/air flames. Rupprecht and Phillis (155) also described the use of a dual-flame burner for the analysis of sulphur in hydrocarbon streams. In this case an initial oxygen-rich flame was used to oxidize incoming hydrocarbons and sulphur compounds. S_2 emission was then generated and detected in a second hydrogen-rich flame located downstream of the oxidizer flame.

Some disadvantages of this dual-flame burner have been reported (156). The requirement for an optically transparent chimney in the Van der Simissen burner meant that the burner was constructed of heat-resistant glass which typically has a low thermal conductivity and contains significant alkali impurities. Consequently, hot flames in this dual-burner generally exhibited background coloration due to alkali impurities outgassed from the hot glass walls, even with a cooling water jacket surrounding the chimney.

A major disadvantage of Rupprecht and Phillips dual-flame burner was the requirement of an elaborate ignition sequence in order to achieve successful ignitions of both the oxidiser and detector flames. Like the Van der Simissen

burner, this burner was also constructed of glass, and alkali emissions were a source of interfering light in the flames (156).

Patterson, et al., (156) described the design and performance of a new dual-flame burner as detector for sulphur measurement. This dual-flame burner is constructed mostly from metal consequently, interfering emission from alkali impurities are largely eliminated. In addition the volume between the two flames is kept small so that excellent sulphur sensitivity is still maintained when emission in the second flame is viewed. Sulphur compounds that have been analysed with this dual-flame detector and found to have a pure square-law dependence include the following: carbon disulphide, thiophene, hexanethiol, dodecanethiol, hydrogen sulphide, sulphur dioxide and methyl mercaptan (156). A good application of the dual-flame operation is shown to be the analysis of sulphur compounds in gasoline (183). Patterson (183) compared single and dual-flame photometric detectors and stated that dual-flame detector operation may not be as sensitive as single-flame operation in some cases. However, dual-flame operation will generally provide more uniform response to samples, irrespective of sample composition or concentration.

(2.6) Conclusion.

The observed interference effects and achieved detection limits for different sample introduction methods are summarized in Table (2.2). As it can be seen from this table, cations, anions and organic compounds interfere in organic and inorganic sulphur compound determination.

Cation interference effects can be removed, using cation-exchange resins or by adding phosphoric acid. Organic compound effects can be decreased by using a dual-flame detector.

Although the individual sulphur compound determination can be performed down to low detection limits, total sulphur determination is associated with problems which are mainly due to the fact that flame molecular emission intensity of different sulphur compounds are different.

Table (2.2)

Detection Limits and Interference Effects in Different Sample Introduction.

Sample Introduction Method	Sulphur Compound	Sample	Detection Limit ppm	Interference	Reference
1) Nebulisation	H ₂ SO ₄	aqueous solution	3	A, C	1
2) Heated nebulisation chamber	H ₂ SO ₄	aqueous solution	0.08	A, C	48
3) Heated injection manifold	H ₂ SO ₄	aqueous solution	0.1	A, C	48
4) Direct injection	CS ₂	organic solvent	20	O.C.	48
5) Capacitor discharge decomposition	(NH ₄) ₂ SO ₄	aqueous solution	0.06	-	53
6) Carbon filament reservoir	H ₂ SO ₄	aqueous solution	0.5	A, C	54
7) MECA	t.butylsulphide	petroleum ether	.5	O.C.	30
	sulphate	aqueous solution	1	C	57
	sulphite	aqueous solution	10	C	57
	saccharin	soft drinks	2	-	60
	(benzoic sulphinamide)				
8) Chromatography/FPD	total sulphur	gasoline	20	O.C.	63
	H ₂ S and SO ₂	air ;	0.005	-	64
	CH ₃ SH	air	0.015	-	64

A ≡ anion C ≡ cation O.C. ≡ organic compounds

EXPERIMENTAL

CHAPTER 3

Hydrogen Sulphide Determination

(3.1) Introduction:

The reported analytical use of S_2 band emission was reviewed in Chapter 2. A number of difficulties were noted in this study. Most of these difficulties are the direct result of the low temperature necessary for the formation of the chemiluminescent S_2 species. There are two basic methods for overcoming these difficulties. The first is to separate the sulphur-containing species from the matrix and from each other prior to flame photometric determination, as in gas chromatographic measurements using emission as the detection system. This method requires that standards of all of the sulphur containing species be available so that calibration curves can be prepared. The second method is to convert all of the sulphur in the sample to a single intermediate and to remove this intermediate from the interfering matrix. This is the method that is the subject of this investigation.

Hydrogen sulphide, subject of present chapter, is a well known intermediate compound used in total petroleum sulphur content determination methods.

Reduction of petroleum sulphur content into hydrogen sulphide can be divided into two methods: hydrogenation and metal

reduction. A high temperature catalytic hydrogenation suitable for petroleum hydrocarbon samples was developed (184). In this method, the sample was heated in a hydrogen stream and passed over a nickel catalyst at 1200°C . Halogens, nitrogen, phosphorus and arsenic do not interfere at concentrations normally found in petroleum. Average recovery on a variety of sulphur types was found to be 99%. This hydrogenation method was compared with other common sulphur methods on typical petroleum samples. Decreasing accuracy was obtained with samples containing proportionately greater amounts of heavy materials such as residue. Schluter, et al., (184) say that in an analysing especially heavy samples back-up of part of the sample in the cool upstream zone could not be prevented even with the 300 ml/min hydrogen flow rate. For this reason difficulty is encountered in analysing samples with heavy sulphur-containing materials.

Farley and Winkler (185), say that in the case of using larger sample size the nickel-on-quartz catalyst, as used by Schluter (184) has a very short life time. Twelve successful runs were made by them and was found that after which a gradual decline in sulphur recovery was experienced and no conversion was evident in the 19th run. Because of this they proposed a new hydrogenation method in which a 2 ml sample was vaporized in a hydrogen stream, pyrolyzed in a hot zone, and passed over a platinum-on-quartz catalyst at 1200°C . It was shown that the catalyst has an exceptionally long life time

for the relatively large samples. Hydrogen flow rates controlling was found to be critical (185). The lower hydrogen flow rates resulted in severe deposition in the catalyst zone, while the higher flow rate of 1200 ml/min showed no deposition in the catalyst zone but included downstream deposition of carbon and hydrocarbons on the cool part of the reaction tube. The downstream deposits contained sulphur. It was claimed by these workers that this hydrogenation procedure is faster and has greater precision than the Wickbold technique in the low parts per million range. However, Watson, et al., (103) say that one of the biggest problems with the hydrogenation technique is the removal of impurities (oxygen and humidity) and blanks from the gas stream. For this purpose, hydrogen and nitrogen must be purified very carefully.

One of the well known metal reduction procedures is the Raney nickel reduction method which was proposed by Granatelli (186) for the determination of microgram quantities of sulphur. Organically bound sulphur present in non olefin hydrocarbon solutions was reduced to nickel sulphide by heating the mixture of sample and propanol in presence of Raney nickel. The addition of acid liberates hydrogen sulphide. Average recovery achieved, on 24 standards covering the concentration range of about 1 to 355 ppm of sulphur, was found to be $99 \pm 1.6\%$. The method requires about 1.5 hours for a completed analysis and is reliable for the analysing of samples containing as little as 0.1 ppm sulphur.

Reed (187) presented some modifications in Granatelli's method in order to improve the percentage recovery from elementary sulphur and carbon disulphide. The modifications deal with the temperature at which the Raney nickel is activated, the detailed instructions for washing the activated catalyst and the immediate use of the catalyst after its preparation.

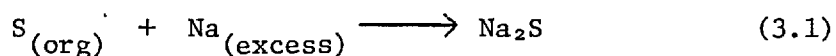
Fensom, et al., (105) claimed that for the analysis of purified petroleum distillates containing about 1 ppm of sulphur the method gave erratic results. Increasing the amount of sample taken to improve the sensitivity only resulted in a lower recovery of sulphur. Good recoveries, 97%, were obtained over the range of 0.01 to 4 ppm sulphur when a definite amount of water equivalent to 5% of the added propanol was present during the reduction. However, according to Granatelli (186) olefins interfere in the reduction reaction and compounds such as sulphoxides or sulphones are reduced with difficulty or not at all.

In proposed method by Shiffman and Frank (148) magnesium was used as reducing metal. In this method, organic samples containing sulphur was heated at 600°C for one hour in the presence of the magnesium. Upon the acidification of the magnesium sulphide, liberated hydrogen sulphide. Sampling times were between 80 to 90 minutes. Mean deviation of replicate samples were in the range $\pm 10\%$. This method has the advantage of using samples in solid state,

making it useful for samples whose physical properties preclude the use of solution techniques. Considerable handling of the sample is required however, and this is a decided disadvantage. In addition, both the precision and accuracy of the technique are subject to improvement by modification of the experimental procedure and sophistication of the sampling apparatus (148).

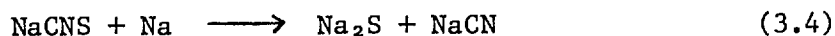
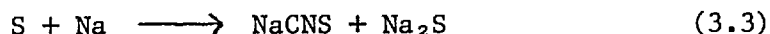
In another investigation, the organic samples were heated with potassium in a sealed tube at $480^{\circ} \pm 20^{\circ}\text{C}$ for 20 hours in a metal block (188). The hydrogen sulphide obtained on acidification of the fusion mixture the controlled fusion procedure ensures that reproducible conditions are used.

In the work of Alder, et al., (189) it was shown that a modified Lassaigue sodium fusion method could be employed for the rapid, quantitative determination of sulphur in oils and fuels. In this method the product was fused with sodium and the hydrogen sulphide liberated in the subsequent hydrolysis of sodium sulphide formed was passed into a cool argon-hydrogen diffusion flame. The relevant reactions being:



Excess sodium must be added to effect complete reduction of any intermediate sulphur products such as thiocyanates, according

to the following reaction (190).



This method provided a rapid but rather imprecise method for the determination of sulphur. It was supposed that the reasons for the imprecision lay mainly in the loss of volatile sulphur species and consequent poor recovery of sulphur from the samples, later estimated to be 50-60% and the poor control of heating and fusion procedures. The present study was concerned with estimating the recovery of the sulphur from the samples by this method and subsequent optimisation of the condition of pretreatment in order to maximise recovery and improve both precision and accuracy.

(3.2) Apparatus and reagents:

Hydrogen sulphide was generated, initially, in the hydride generation cell as shown in Figure (3.1).

The original form of burner assembly employed a copper tube as the burner port, however after some use an increase in background and random flickering was noted. This was due to CuH (136) emission; hydrogen chloride carried over from the hydride generation vessel reacted with the copper burner port to form copper chloride which formed the emitting species in the flame.

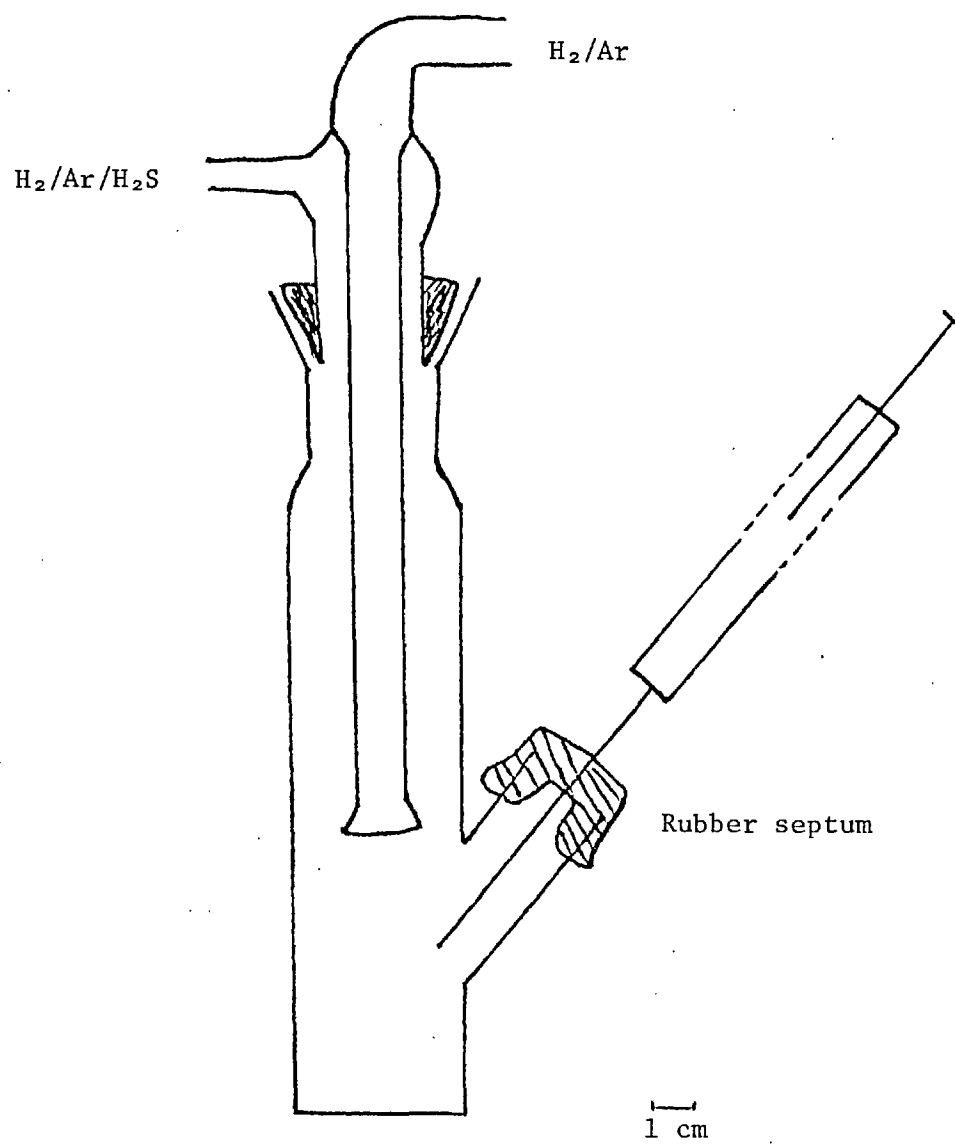
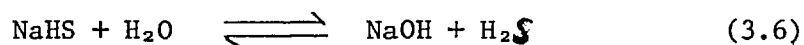
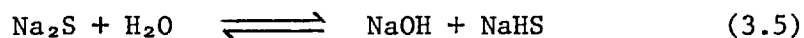


Figure (3.1)

Generation cell

This difficulty was overcome by locating a silica tube (10 cm x 2 mm, i.d.) inside the copper tube, as shown in Figure (3.2). The emitted radiation was passed through a circular variable wavelength filter (Barr and Stroud, Glasgow) with a band pass of about 20 nm at 384 nm. The filtered light was focussed onto an E.M.I. 9781A photomultiplier and the signal passed via an amplifier and backing-off unit, as shown in Figure(3.3), to a strip chart recorder. Sample introduction was effected by a variable volume (50-250 μ l) ejection pipette (Finpipette, Jencons Ltd.). Aqueous standards were prepared from analytical reagent grade Na_2S , $9\text{H}_2\text{O}$ (B.D.H. Ltd.) and organic standards from t-butyl-disulphide (Aldrich Chemical Co. Ltd.) made up in either liquid paraffin (B.D.H. Ltd.) or white spirit.

It was found that sodium sulphide solution is not stable due to this fact that sodium sulphide dissolved in water with the evolution of hydrogen sulphide, according to the following equation (192).



The rate of hydrogen sulphide evolving depends highly on pH values, acidic solutions are unstable and alkaline solutions are stable. The sodium sulphide solution was stabilised initially with a pH 11 borate-NaOH buffer but a better method

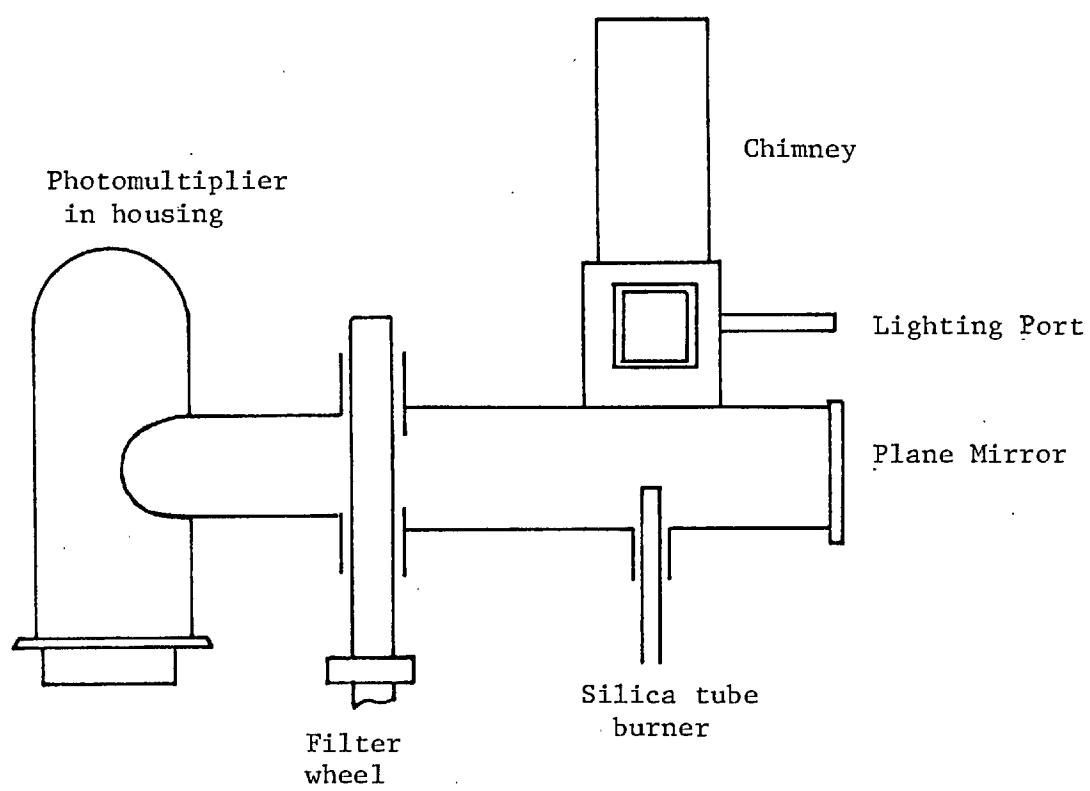


Figure (3.2)

Burner assembly

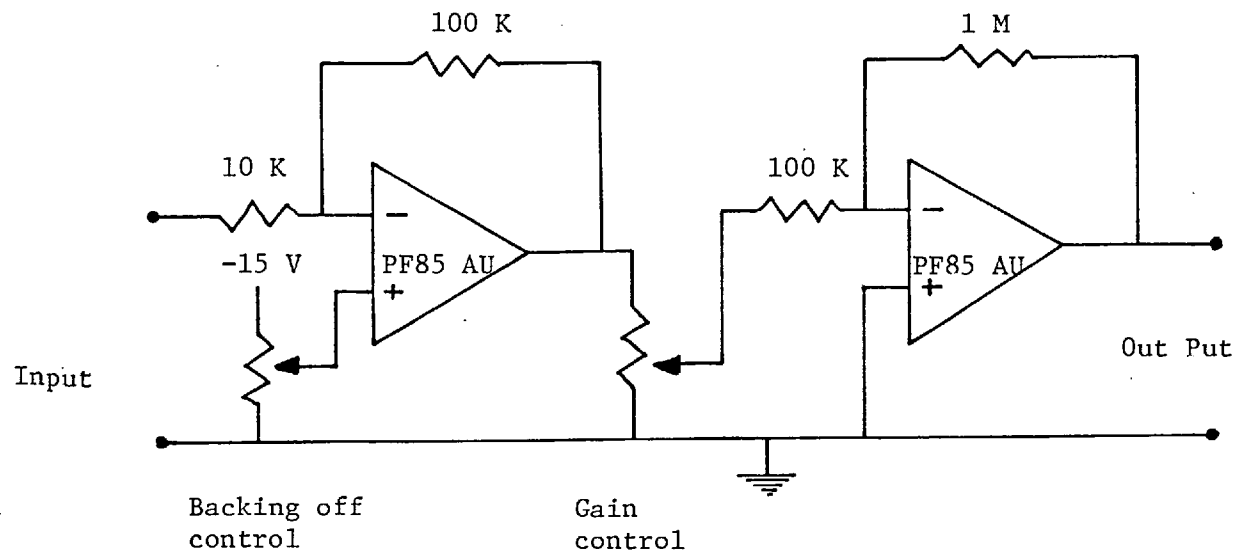


Figure (3.3)

Circuit diagram of the backing off and d.c. amplifier

Resistance values in Ohms.

was found to be the use of 20% w/v aqueous NaOH. Addition of sodium hydroxide could minimise the formation of hydrosulphide in reaction (3.5) besides enhancement of pH values. The stock 1000 ppm solutions thus made up were stable for up to one week, Table (3.1), and were standardised iodimetrically before use (191).

Table (3.1)

Stability of aqueous standard solutions

(100 ppm sulphide initial concentration)

a) In aqueous solution	ppm S $\pm$ S.d.
after 8 hours	89 $\pm$ 1
after 24 hours	75 $\pm$ 1
b) In 20% NaOH	
after 3 days	99.5 $\pm$ 1
after 7 days	99.0 $\pm$ 1

Organic solutions were found unstable, Table (3.2) and because of that they were prepared fresh daily.

Table (3.2)

Stability of Organic Standard Solution.

a) In liquid paraffin		
S added (ppm)	S found (ppm) $\pm$ s.d.	
	fresh	24 hours old
260	262 $\pm$ 1	202 $\pm$ 2
195	194 $\pm$ 2	160 $\pm$ 1
130	129 $\pm$ 2	107 $\pm$ 2
b) In white spirit		
260	257 $\pm$ 2	202 $\pm$ 2
195	192 $\pm$ 2	152 $\pm$ 2
130	129 $\pm$ 2	140 $\pm$ 1

(3.3) Optimisation of gas flows and stirring.

The argon flows through the cell and into the flame and the hydrogen flow were controlled via a special device as shown in Figure (3.4). This device helped us to prevent the flame to be extinguished while we wanted to wash the cell after each sample injection. The argon flows through the cell and into the flame and hydrogen flow were optimised using a continuous steady stream of hydrogen sulphide generated by a small crystal of sodium sulphide decomposing in dilute hydrochloric acid, Figure (3.5). It can be seen that the flow rates are quite critical for maximum emission intensity from the flame. A total argon

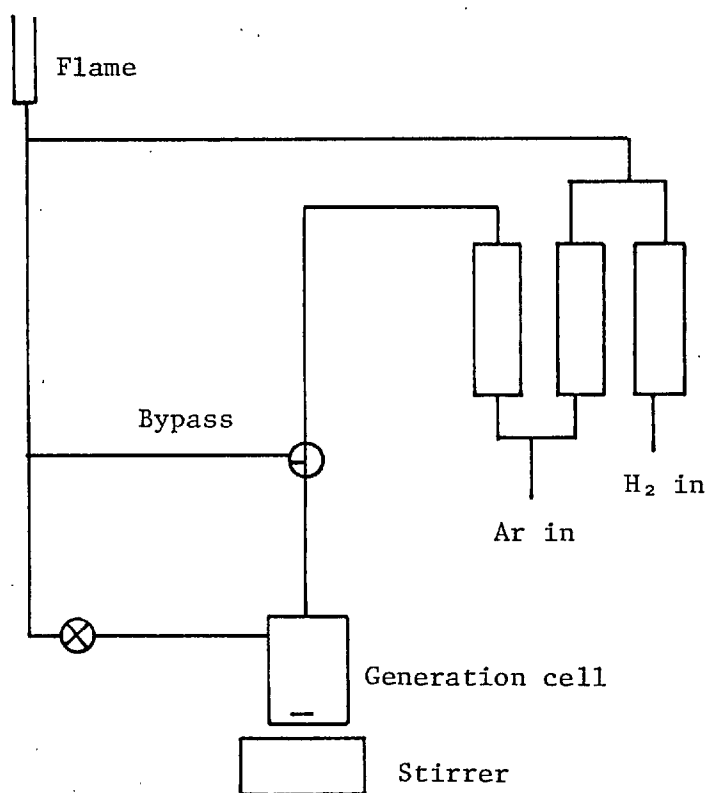


Figure (3.4)

Schematic diagram of sample introduction system

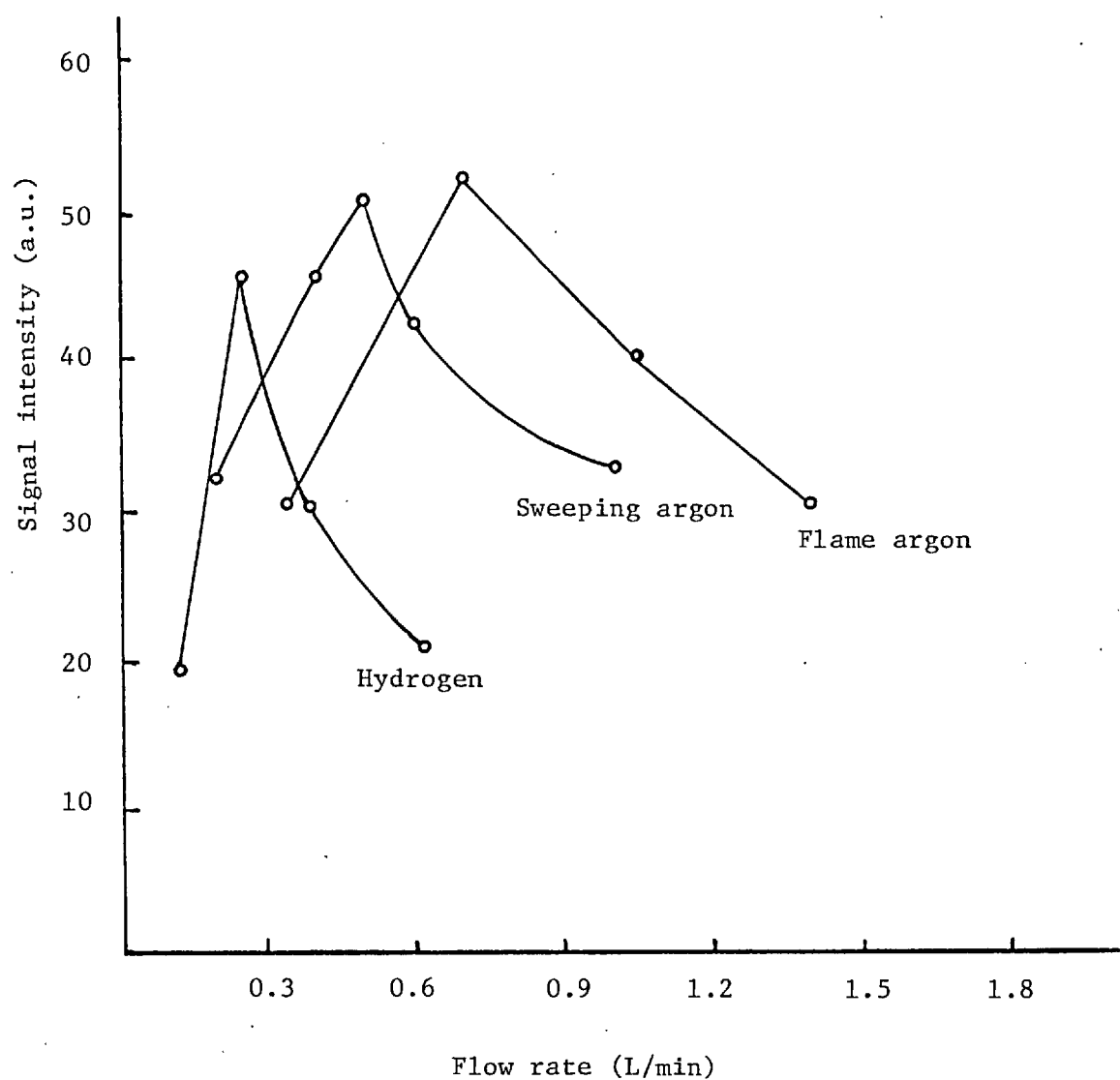


Figure (3.5)

Optimisation of flow rates (H_2 pressure 1 p.s.i., Ar pressure 1.5 p.s.i.). When one curve was being obtained the other flow rates were at their optimum settings.

flow rate greater than 2.2 L/min caused the flame to be extinguished. The least noisy flame was obtained with the hydrogen flow rate at its minimum.

These optimised flow rates gave a flame that was colourless except for occasional flashes seen when foreign bodies were inadvertently entrained in the flame. This was most noticeable at the top of the flame well from the emitting zone. At optimum flow rate the pressure of the argon and hydrogen were varied to give maximum emission intensity Figure (3.6), why the pressure influenced the signal intensity in this way is not understood. Operating conditions are shown in Table (3.3).

Table (3.3)

Experimental parameters.

Emission wavelength	384 nm
hydrogen flow rate	0.25 L/min
argon flow through the cell	0.5 L/min
argon flow into the flame	0.7 L/min
argon pressure	1.5 p.s.i.
hydrogen pressure	1 p.s.i.

The rate of stirring of the mixture in the gas generation cell was found to be critical, Figure (3.7) (this curve was obtained using injection of sample into the cell and subsequent acidification with HCl (see below)). The rapid fall off in

emission intensity above the optimum stirring speed is due to the onset of splashing in the stirred solution. The stirring affects the rate of mixing of the analyte solution and the hydrochloric acid in the vessel and the subsequent generation and release of hydrogen sulphide. Not only did the signal intensity increase towards the maximum but so did the precision of the method. The precision of the method also was affected by the controlling the injection of sample with pipette. Rapid injection causes sudden change in pressure of gas in the cell (which is directly connected to the flame) and enhances the hydrogen sulphide evolving rate.

(3.4) Improvement of sample treatment.

The fusion process is influenced by a variety of factors including sample size, heating time, fusion temperature and the state of the sodium before addition of sample.

It was found that if sodium was freshly cut, placed in the fusion tube and heated alone, a white powder most probably Na_2O_2 formed on the surface. If the heating was continued it became covered in a black powder thought to be Na_2O which is known to be the reduction product of Na_2O_2 and Na (190). The different sensitivities obtained by addition of sample to the two different forms and to molten sodium which had not been treated is shown in Table (3.4). The results obtained in this respect were consistent for the open tube fusions, but no significant improvement could be obtained with the reflux reduction method (see later).

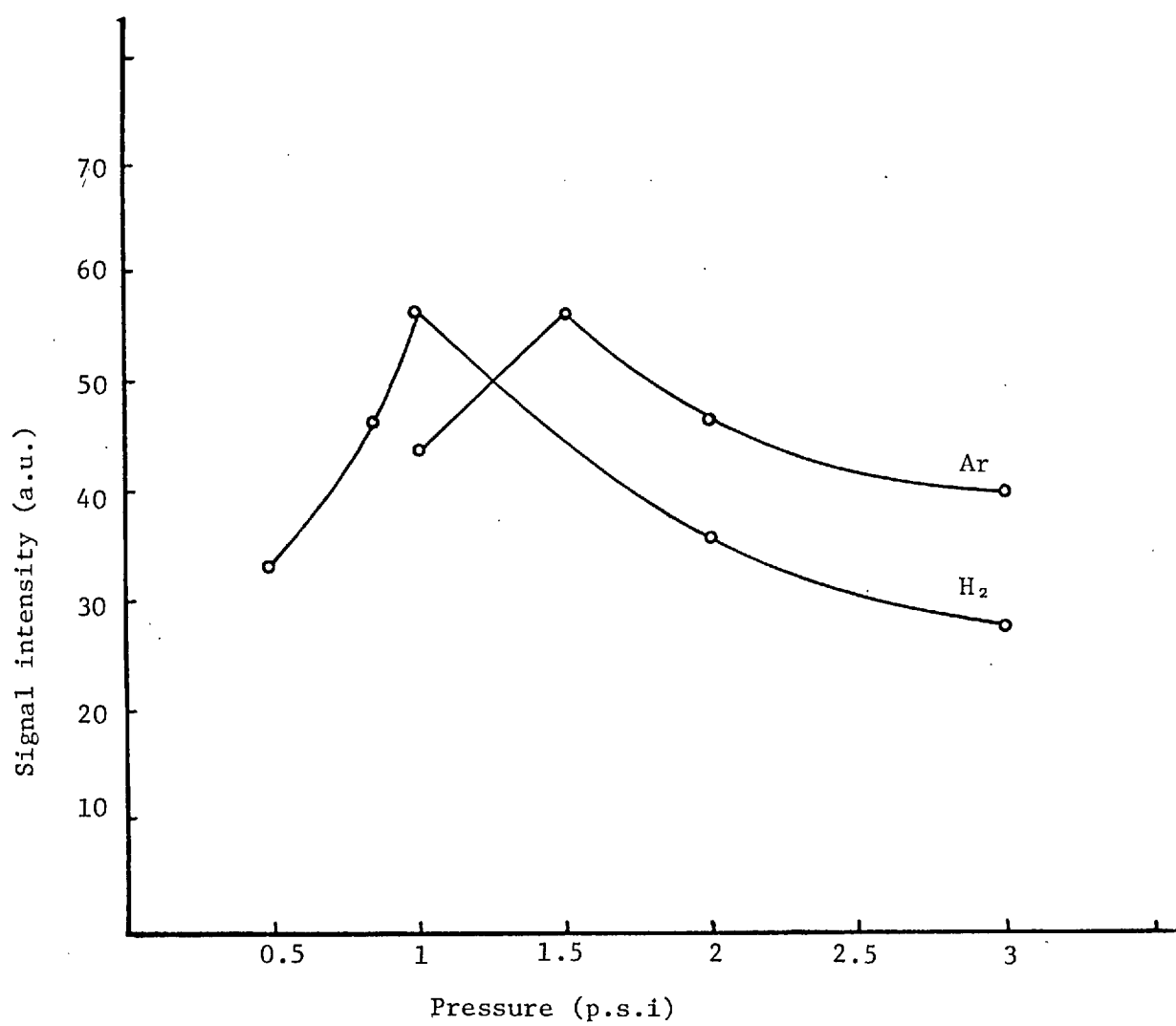


Figure (3.6)

Optimisation of Argon and Hydrogen pressure (obtained under optimum flow conditions).

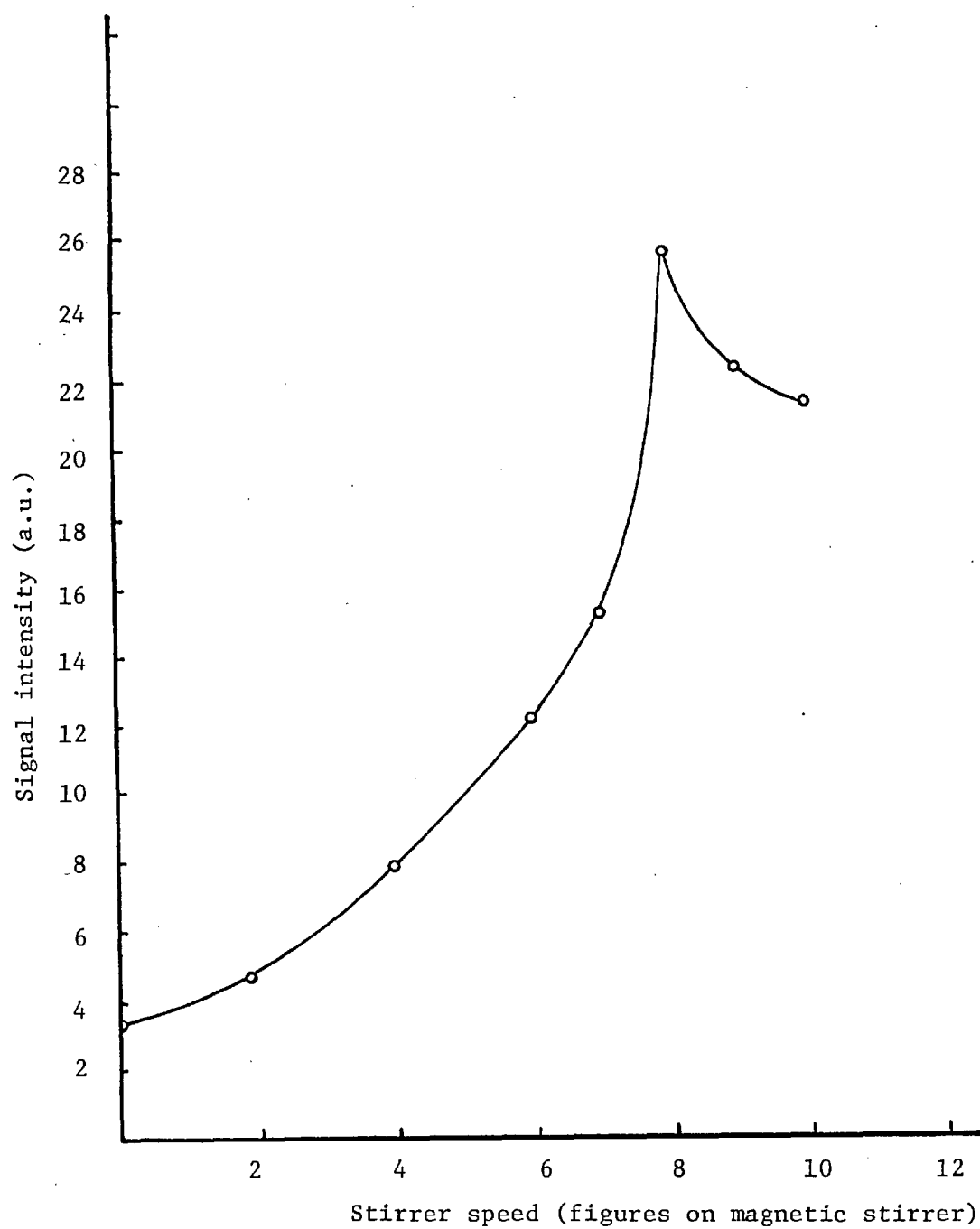


Figure (3.7)

Effect of stirring speed on signal intensity

Table (3.4)

The effect of different sodium pretreatment on sensitivity.

Form of Sodium	Sulphur found (ppm) $\pm$ s.d. (34 ppm added)
Molten	24.5 $\pm$ 0.5
White coating	27.3 $\pm$ 0.5
Black coating	22.1 $\pm$ 0.2

The reproducibility of heating of sample and sodium together was improved by the use of a metal block bored with holes just wider than the test tube sitting on a hot plate, the tubes being placed in the block for the required time. The duration and temperature of heating were optimised by preparing solutions containing known quantities of t-butyl disulphide in liquid paraffin and white spirit. The solutions were heated over the range 80°-210°C for periods of 2, 4, 8 and 20 hours; blanks were treated in the same manner. The signal due to sulphur was compared to that obtained from the same weight of sulphur as Na₂S analysed in aqueous solution and hence the recovery of sulphur from the liquid paraffin by the sodium fusion method calculated, Table (3.5). All aqueous sulphide solutions were standardised iodimetrically before dilution (191).

Table (3.5)

Optimisation of Heating Duration and Temperature.

Temperature °C	Heating Duration (Hours)	Sulphur Recovery (%)	
		<u>Liquid Paraffin</u>	<u>White Spirit</u>
210	20	20	-
	16	20	-
	8	25	-
	4	30	-
	2	43	-
170	20	20	-
	16	25	-
	8	25	-
	4	32	-
	2	45	-
130	20	65	30
	16	69	30
	8	80	40
	4	70	60
	2	64	55
100	20	60	45
	16	59	65
	8	40	80
	4	40	70
	2	30	64
80	20	-	20
	16	-	20
	8	-	15
	4	-	20
	2	-	20

The best sample size was determined by heating 0.2-1.5 ml aliquots of t-butyldisulphide in liquid paraffin at 130°C for eight hours, Table (3.6).

The final procedure adopted for this approach was therefore to place a 2 mm cube of sodium, which had been freshly cut into pieces, into a test tube (10 x 75 mm) and warm it gently at about 90°C until it was covered in white powder.

A 0.5 ml aliquot of sample is added to the sodium and mixture heated at 100°C for white spirit and 130°C for liquid paraffin over 8 hours. The excess solvent is then carefully removed by vaporisation in a flame and the residue is carbonised at dull red heat for 15 seconds. The tube is then wrapped in 40 mm Whatman No. 50 filter paper, mechanically crushed into 5 ml 2% aqueous sodium hydroxide and filtered.

Table (3.6)

Sample size optimisation.

Sample size (ml)	Sulphur recovery (%)
0.2	65
0.5	80
1	70
1.5	57

A 100 µl aliquot of this solution is placed into the hydride generation cell which is flushed with argon under

optimum conditions of flow rate and stirring speed and the solution then rendered acid with 200 μ l 35% HCl. The H_2S liberated is swept into the argon-hydrogen flame and the peak height of the signal due to the S_2 emission recorded. This pretreatment approach, although yielding information about sulphur recovery was not adequate to give good reproducible analyses and further modifications were necessary.

(3.5) High temperature sodium reduction.

The changes in recovery efficiency under the various conditions of temperature and heating duration are due to the conflicting processes of reaction rate and sample vaporisation. Above $130^{\circ}C$, for liquid paraffin samples, the duration of heating can be shortened but the recovery is lower, the same characteristics can be seen too for the white spirit samples. In order to reduce the duration of heating process a reflux method was devised. The apparatus comprised of a 10 ml three neck flask filled with nitrogen purge. The condenser was a single surface Liebig type 10 cm long with a delivery tube at the exit which passed the purge gas into a 10 ml round bottom flask containing the absorbing solution.

A 1 ml aliquot of sample is placed in the reflux flask with a freshly chopped-up 2 mm cube of sodium. The flask is fitted to the condenser and the delivery tube immersed in 8 ml 5% sodium hydroxide in the collector flask. The whole system is purged with nitrogen at a rate of 4 ml/min. The

contents of the flask are refluxed under predetermined temperature and time conditions on a calibrated temperature isomantle. The reflux is stopped and the flask allowed to cool then removed and the contents transferred to a 25 ml beaker (to remove the possibility of explosion). The contents of the absorber flask are diluted to 10 ml with 5% NaOH and used to rinse the reflux flask; the washings are then transferred to a separating funnel, shaken for 1 min and allowed to stand until the lower (aqueous) phase is clear. The lower layer is transferred to a 10 ml graduated flask. The sulphide concentration is then measured in the usual manner.

Purging the reflux systems ensures complete removal of any H_2S formed, or present in the sample, from the condenser and it is then trapped in the sodium hydroxide. The amount of sulphur trapped in the sodium hydroxide is small. Two samples of a light distillate were refluxed in this manner and the contents of the absorber flask analysed by standard addition; the results are given in Table (3.7).

Table (3.7)

Concentration of hydrogen sulphide in absorption flask after refluxing.

Sample (light distillate)	S concentration in sample * (ppm)	S concentration in absorption flask (ppm)
8136	300	2
7956	260	1
* Data supplied by B.P. Research		

(3.6) Optimisation of reflux conditions.

Duplicate 1 ml sample aliquots were refluxed as described above at 272, 345 and 380°C for liquid paraffin solvent and 157, 173 and 190°C for white spirit solvent, for 20, 30 and 40 min periods. After subtraction of the solvent blank signal, the recorded S₂ emission signal intensity was compared with that obtained from aqueous samples containing the same original sulphide concentration and the recovery calculated (Table 3.8). As can be seen there is little difference between 345°C and 380°C and 173°C and 190°C for the liquid paraffin and white spirit recovery figures respectively. In both cases, therefore, the lower temperatures were chosen to carry out the analyses so as to minimise loss of volatile sulphur species.

The preliminary heating of sodium in order to obtain the white powder coating did not give any improvement in recovery in the reflux method and was not therefore carried out.

(3.7) Calibration curves.

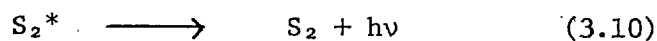
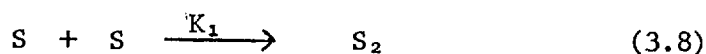
Calibration solutions were made up from t-butyl disulphide in white spirit and liquid paraffin to represent low and high-boiling petroleum products respectively and from sodium sulphide in 20% NaOH. The solvent blanks were 1.5 and 0.5 ppm S for the white spirit and liquid paraffin respectively. These were subtracted before plotting.

Table (3.8)

Optimisation of Temperature and Duration of Refluxing.

	Temperature (0°C)	Heating Duration (min)	Sulphur Recovery (%)
Liquid Paraffin			
	380	20	63
		30	95
		40	70
	345	20	61
		30	94
		40	70
	272	20	15
		30	50
		40	47
White Spirit			
	190	20	67
		30	89
		40	73
	173	20	66
		30	90
		40	74
	157	20	30
		30	60
		40	40

Calibration curves, plotting I vs. C and $\log I$ vs. $\log C$, where I is the emission intensity and C the mass of sulphur, were constructed for aqueous sodium sulphide solutions (Figure 3.8 and 3.9). The slope of calibration ($\log I$ vs. $\log C$) was ca. 2, this lends support to the concept that the chemiluminescent emission occurs in four basic steps;



Assuming $(S_2^*) \approx (S_2)$, $(C_s) \approx (S)$ and $(S) \approx (S_2)$ the equilibrium of equation (3.8) may be described by

$$K_1 = (S_2^*) / C_s^2 \quad (3.11)$$

The intensity of the emission is given by

$$I = K_2 [S_2^*] \quad (3.12)$$

Therefore combining equations (3.11) and (3.12)

$$I = K' C_s^2 \quad (3.12)$$

Where $K' = K_1 \times K_2$

$$\text{or} \quad \log I = \log K' + 2 \log C_s \quad (3.14)$$

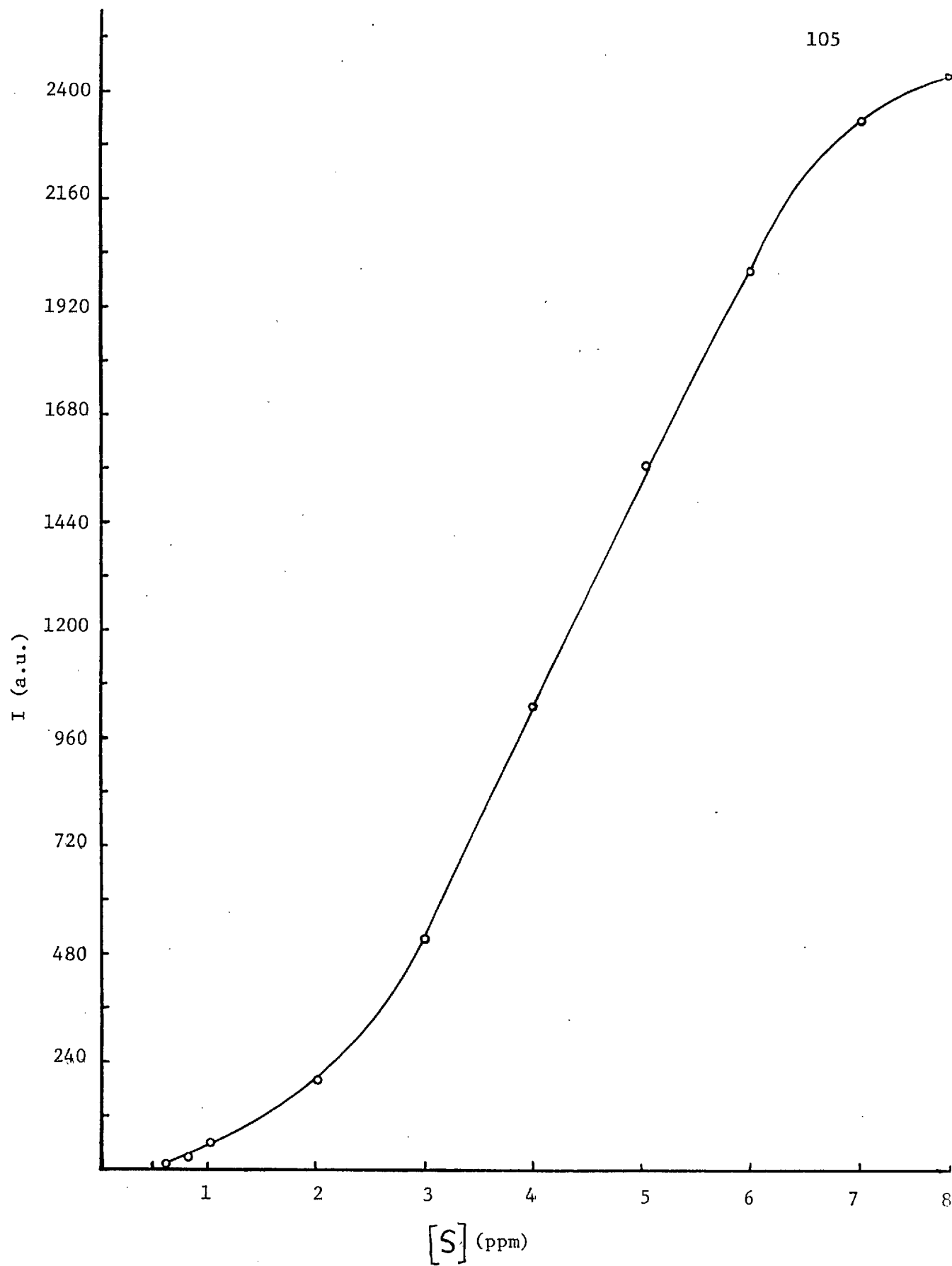


Figure (3.8)

Calibration curve for aqueous solution.

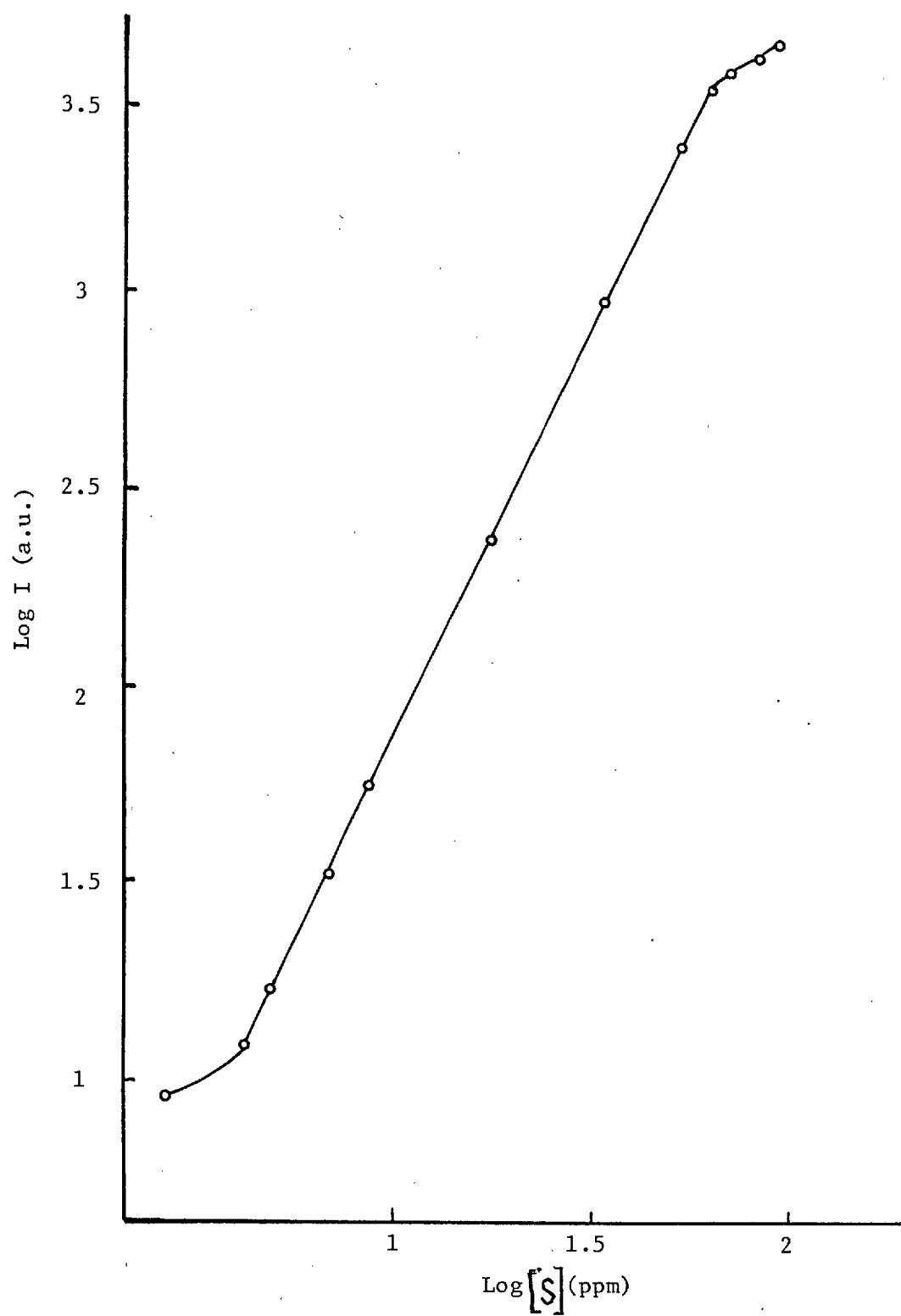


Figure (3.9)

Calibration curve for aqueous solution

As may be seen from Figure (3.8) above $0.7 \mu\text{g S}$ the calibration (I vs. C) curves toward the concentration axis and in the range 0.3 to $0.6 \mu\text{g S}$ the emission intensity is approximately linear with concentration. The linear portion of $\log I$ vs. $\log C$ calibration is between about 0.5 and $7 \mu\text{g S}$ and at higher sulphur levels even this breaks down and a limit on the signal seems to be reached.

As the origin of the emission is chemiluminescent, it is not easy to say what causes the non-linearity but it may be due to ^{kinetic} quenching effects in the lower region where the $S + S$ recombination may be incomplete; these points have yet to be investigated however. The calibration curves, for sulphur in organic samples are shown in Figure (3.10). The linear portion of the curves was between about 5 and 70 ppm in the original sample (corresponding to 0.5 and $7.0 \mu\text{g}$ sulphur in the $100 \mu\text{l}$ aliquot taken). The shape of the curves is similar to those obtained by other workers (146); the curves do not coincide because of the different recoveries of sulphur. The relative standard deviation of the method and recovery compared to aqueous solutions on 10 replicate analyses of samples containing 150 ppm were, for liquid paraffin solvent 95% recovery and 7% r.s.d.: for white solvent 90% recovery and 8% r.s.d.

However, the reproducibility of the method (in aqueous solutions analyses) was calculated as the percentage relative standard deviation of the signal obtained for 10 replicates

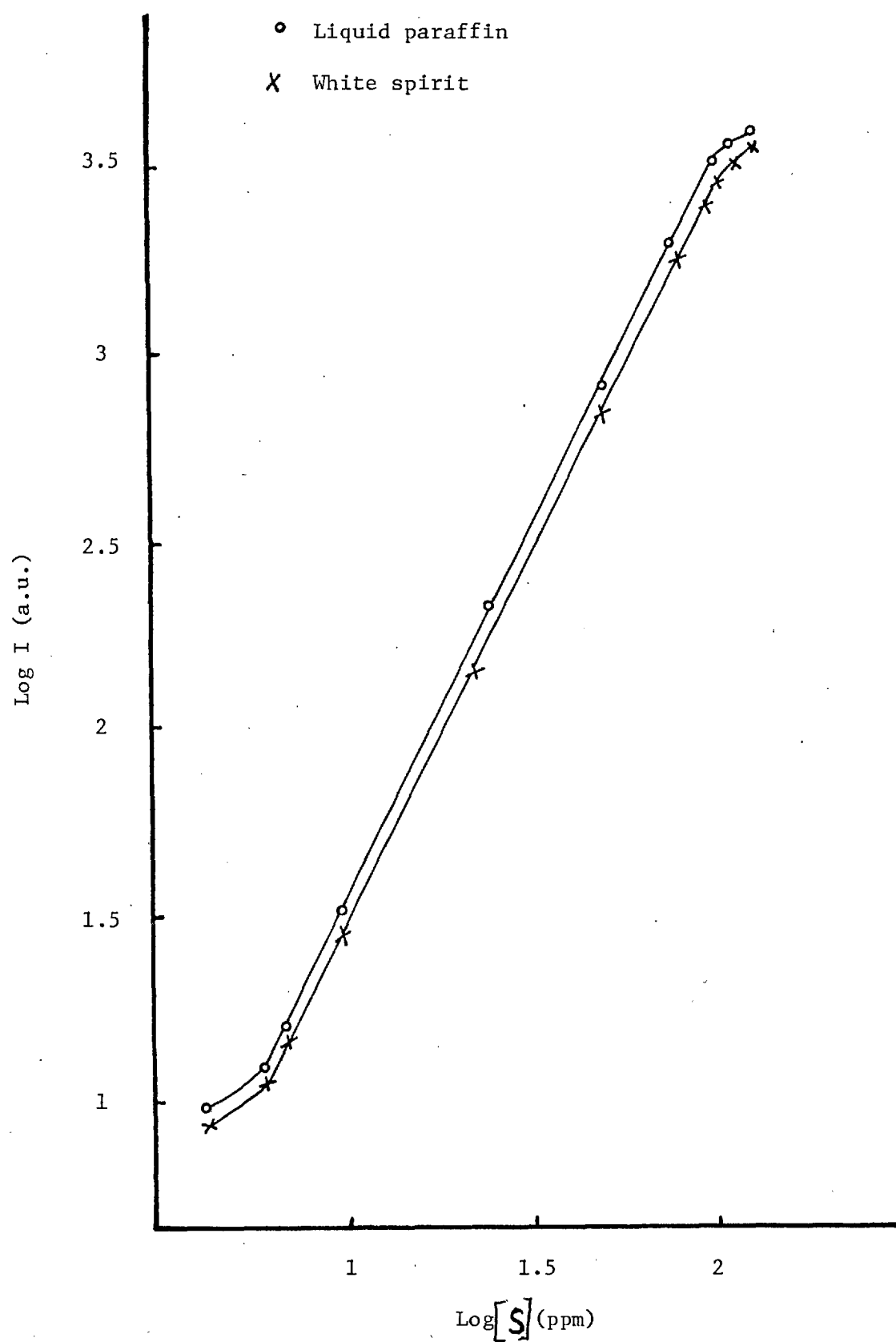


Figure (3.10)

Calibration curves for organic solutions.

of 100 μ l of 15 ppm S. This was found to be 4%. The minimum measurable signal was due to 0.001 μ g S.

(3.8) Petroleum product analysis.

Samples provided by B.P. Research Ltd., and previously analysed by X.R.F., were analysed by the reflux method. The samples had to be diluted with white spirit for the light distillates and liquid paraffin for the waxy residues, to bring the final solution into the correct concentration range, (Table 3.9). The results compare most favourably with those obtained by X.R.F.

The precision could be improved by controlling the speed and the pressure of injection, e.g., using an automatic device for injection. Low results were possibly due to fusion of sulphide into the ignition tubes or its occlusion onto the resulting charred carbon.

(3.9) Conclusion:

Conditions for the determination of sulphur in petroleum products, by sodium reduction, sulphide generation and chemiluminescent emission determination, have been optimised. An improved method of reduction involving refluxing of the product with sodium is described.

It has been shown that this approach to total sulphur analysis can provide both accurate and quite precise determination of the element in petroleum products. It is likely that the method can also be applied to other organic matrices containing sulphur and its sensitivity opens up a wide field of application for the technique.

Table (3.9)

Real Sample Analysis

	Sample	% S found $\pm$ s.d.	% S given*
Light Distillate	8014	0.01 $\pm$ 0.002	0.01
	7935	0.02 $\pm$ 0.015	0.24
	8136	0.025 $\pm$ 0.002	0.03
	7914	0.18 $\pm$ 0.01	0.2
	7956	0.2 $\pm$ 0.025	0.26
	9143	1.05 $\pm$ 0.06	0.95
	9142	0.14 $\pm$ 0.01	0.11
Waxy Residues	9246	0.63 $\pm$ 0.02	0.62
	9245	0.79 $\pm$ 0.065	0.75
	8630	3.65 $\pm$ 0.3	3.73
	8634	1.5 $\pm$ 0.1	1.39
	7990	2.29 $\pm$ 0.15	2.24
	7927	2.2 $\pm$ 0.18	2.11
	8635	3.3 $\pm$ 0.2	3.33

* Data supplied by B.P. Research

CHAPTER 4

Di- and Polysulphide Determination

(4.1) Introduction.

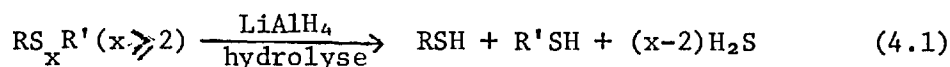
Disulphides and polysulphides play many very important roles in the wool, synthetic polymer, rubber, petroleum and protein industries. The S-S bond in these compounds imparts many properties, most of which are based on its role as a cross-linking agent. Thus, in wool (71), the disulphide bonds serve as the cross-links for the main polypeptide chains, and these cross-links impart the desirable properties that differentiate wool from other protein fibers. In some cases the properties imparted to materials by S-S bond are undesirable. The various processes used in petroleum refining are largely concerned with the effects of disulphides or polysulphides as undesirable impurities on product quality (71). Polysulphides and disulphides in petroleum distillates result in a loss in octane number and a lowering of lead susceptibility, they are even more detrimental, in the order named, than the corresponding mercaptans (194). Reactivity of the S-S bond is considered here as a partial background for purposes such as the proper selection of methods from available procedures; the modification of tests

or methods for new situations arising in the same overall sample matrix, or, most important, development of new tests or methods. The stability of disulphides and polysulphides for the purposes above is important, since their response behaviour to the analytical test conditions, chemical or physical, must be known. The analytical reaction most commonly used is the reduction of the S-S bond. In this reaction the electronic structure of the S-S bond is a critical factor. Polysulphides, when subjected to heat, either decompose by random processes involving C-S and S-S bond fission or disproportionate (71). Disulphides are more stable than polysulphides (70 versus 39 Kcal/mole bond strength) but less stable, in the order named, than sulphides, thiols and thiophenes (195).

The analytical difficulties which arise in the determination of disulphides and polysulphides arise more from the type of samples encountered, than from the measurement techniques available (196). There have been many different quantitative methods reported for the determination of disulphide and polysulphide in the presence of other sulphur compounds. These can be largely divided into chromatographic separations and determinations by TLC and GC (197, 198), and metal reduction followed by chemical separation and determination (199).

Sulphur-sulphur bond reduction with lithium aluminum hydride (reaction 4.1) forms the basis of a method for

determining (a) the proportions of di- and polysulphides and (b) the average sulphur chain length in the polysulphides, (200).



Complete analysis of a mixture of sulphides, $a\text{RSR}' + b\text{RS}_2\text{R}' + c\text{RSyR}'$ (where a, b, c are mole fractions, $y \geq 3$, and R and R' are alkenyl or alkyl), can be achieved by: a) determination of the overall composition of the mixture by elemental analysis and molecular-weight measurement; b) determination of $(b + c)$ and $C(y-2)$ by measurement of the amounts of thiols and hydrogen sulphide, respectively.

However, Porter, et al., (200) found that the method is not generally applicable to diallyl sulphides or sulphides containing tert.alkyl S groups. Wronski (201) claimed that lithium aluminum hydride reagent is inconvenient and even dangerous in daily analytical application and introduced a new method, which is the most recent chemical separation and metal reduction method, is based on the conversion of disulphides by sodium aluminum bis(2-methoxy ethoxy)dihydride in benzene solution into hydrogen sulphide and thiols which can either be directly titrated, after dilution with alcohol, or separated by extraction and determined in the presence of each other by selective masking with acrylonitrile. This is a simple and sensitive method; sulphur at the 0.1 ppm

level in hydrocarbons can be determined with a relative standard deviation in the range of 0.5-1.5%. By application of the photometric method using dithio fluorescein complex or the titration with tetramercurated fluorescein the estimation of even lower sulphur contents may be possible. The recovery for di-tert.butyl disulphide is however only 75% and compounds containing active hydrogen interfere in the reduction by decomposing the sodium aluminium dihydride. Stahl and Siggia (202) say that lithium aluminium hydride reduce part of the disulphide to hydrogen sulphide and cause high results on disulphide determination. They presented a method in which organic disulphides were reduced to the mercaptan with sodium borohydride in presence of aluminum chloride and titration of the mercaptan with silver nitrate. The precision and accuracy of the method are within $\pm 1\%$. Sulphides do not interfere with the procedure. In determining the disulphide content of a sample which contains mercaptan, the mercaptan must be determined on an unreduced sample and subtracted from the value obtained after reduction. The mercaptan is unchanged by reduction and titrates with the reduced disulphide. However, the reducing agent will interfere with the titration unless it is completely decomposed and the decomposition of the hydride presented a problem because sodium borohydride can readily be decomposed only by the addition of acid

which causes a rapid evolution of gas and loss of mercaptan (202).

Quantitatively the metals used for reduction of di- and polysulphides, have been almost either zinc or sodium, with the latter almost always as the amalgam and the former with about equal frequency, either as the bulk metal or amalgamated (71). These methods suffer from poor reduction efficiency for tertiary disulphides, except for the zinc reduction under reflux conditions which is expected to yield 85-90% recovery for di-tert.butyl disulphide. This recovery is, however, only achieved by heating and purging the sample for 3 h and 1.5 h respectively. Elemental sulphur, however, was reduced to the extent of 50 to 60% to hydrogen sulphide.

In the present study the metal reduction method was modified in order to differentiate between some of the various species of sulphur found in petroleum products and to permit their determination by chemiluminescent flame photometry.

(4.2) Apparatus and Reagents.

The hydrogen argon diffusion flame and burner assembly and generation cells have been described elsewhere (Chapter 3). Aqueous standards were prepared from Analytical Reagent grade Na_2S , $9\text{H}_2\text{O}$ (B.D.H. Ltd.) and organic standards from tert-butyl-disulphide (Aldrich Chemical Co. Ltd.), diphenyl sulphide,

ethane thiol, benzene potassium sulphonate, dimethyl sulphoxide, diphenyl disulphide, diphenyl trisulphide and 1,3-dithiane, all of which were of the highest purity available, made up in white spirit or liquid paraffin.

(4.3) Determination.

The reduction conditions using sodium (as described in previous Chapter) are so drastic that all organic sulphur containing compounds appear to be converted to sulphides. Whereas total sulphur is a very useful quantity in many applications, particularly where the petroleum product is to be used as a fuel, there are many cases where more discerning methods for sulphur determination are required. One of these is the determination of disulphide and polysulphide, which play an important role in lubricant and polymer technology.

A number of reducing agents were therefore studied for their suitability as specific reductants for the disulphide and polysulphides links.

After preliminary experiments, described later, to obtain the best conditions for each reducing agent a series of comparative tests were carried out; the results are summarised in Table (4.1).

Using the apparatus shown in Figure (4.1), 100 mg of the metal was placed in the reflux flask and 1 ml of solution

Table (4.1).Results From Different Reducing Agents.

Reducing Agent	Signal Intensity (a.u.)
Mg (fine powder)	unsuccessful
Zn (powder)	19
Zn (granulated)	79
Zn (foil clippings)	81
Zn-amalgam	81
50% Zn: 5% SnCl ₂	10
Cu (foil clippings)	23
Devarda's Alloy (50% Cu, 45% Al, 5% Zn)	100*

Sample 0.032% S as tert-butyldisulphide/liquid paraffin

* normalised to 100.

Note: The normalised data for 0.032% S as tert-butyldisulphide
are intercomparable between Table 4.1 to 4.5.

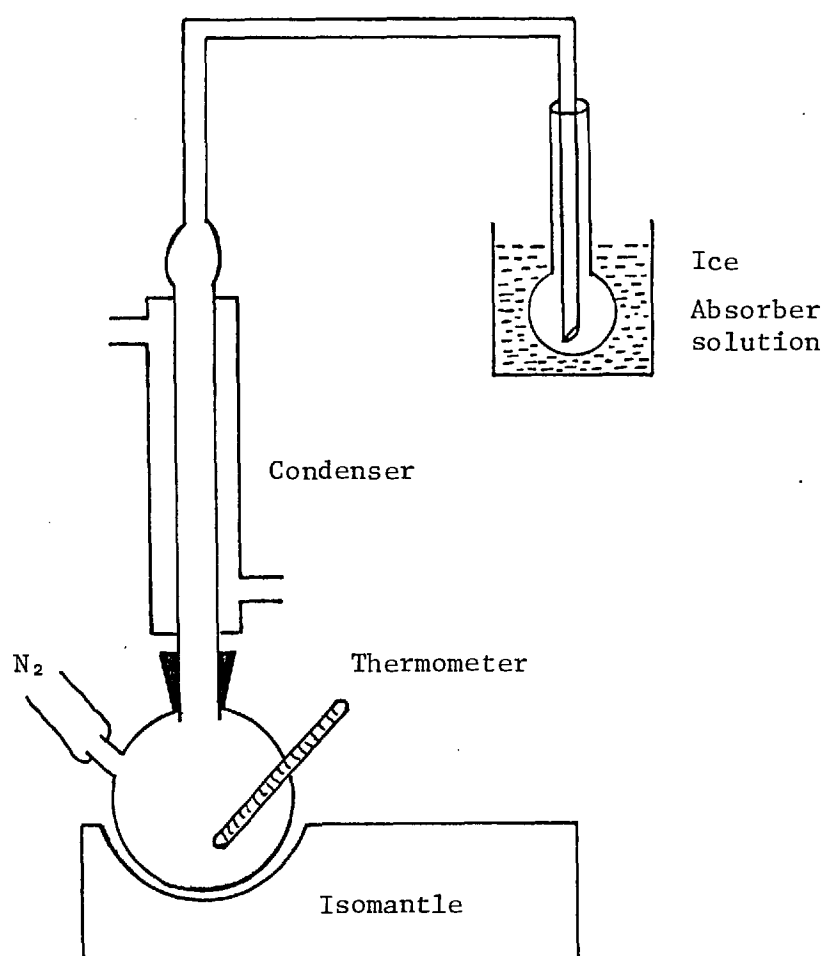


Figure (4.1)
Reflux apparatus

of tert-butyl disulphide, 0.032% S w/v in liquid paraffin was added. The flask was purged with nitrogen (4 ml/min) and the contents heated to 320°C on a calibrated isomantle for 40 mins. The flask was cooled and to the contents were added 2 ml conc. HCl. The contents were heated again under reflux for 20 mins at 120°C. The liberated H₂S was collected in 10 mls of cooled 5% w/v sodium hydroxide solutions. A 0.1 ml aliquot of this sample was taken and treated as described previously (Chapter 3) to liberate H₂S in the generation cell and pass it into the cool hydrogen diffusion flame. The signal due to the S₂ chemiluminescent emission was recorded and compared to that from standardised aqueous sodiumsulphide solutions to obtain the amount of sulphide (as S) in the sample.

(4.4) Results and Discussion.

Reducing Agents.

Magnesium: Commercially available magnesium powder was employed (B.D.H. Ltd.). The addition of conc. HCl to the flask after the initial reduction step resulted in an uncontrollably vigorous reaction. To overcome this 10% HCl was added instead and this gave a more moderate reduction, but the recoveries obtained were so low as to be not useful.

Zinc: As can be seen from Table (4.1), powdered zinc gave rather low recovery and was not studied further.

Granulated zinc was much better and gave similar results to the zinc amalgam and zinc foil. (The amalgam was made by grinding granulated zinc in liquid nitrogen, washing with water, 2% HgCl_2 . The amalgam was stored under water). The 1:1 $\text{Zn}:\text{SnCl}_2$, which is a powerful reducing agent, gave rather poor results.

Copper and Devarda's Alloy.

Copper clippings (<40 mesh) gave low results but Devarda's alloy (50% Cu, 40% Al, 5% Zn) was most efficient and was this reagent which was used in the subsequent work. Different weights of the alloy were employed in the reduction of 1 ml of the sample solutions and it was found that 100 mg was the optimum.

A) Temperature and duration of heating.

The conditions of reduction particularly in the first part with the alloy alone and then in the presence of hydrochloric acid are quite critical. In the first step the reduction is thought to proceed via partial reduction of the S-S bond and formation of metal sulphides.

Extending the duration of the heating at 320°C during the first step of the reduction results in increased recovery up to about 40 mins (Figure 4.2). Beyond the 40 mins, the formed metal sulphides will be mixed with organic solvent which prevent, partly, the evolution of hydrogen sulphide

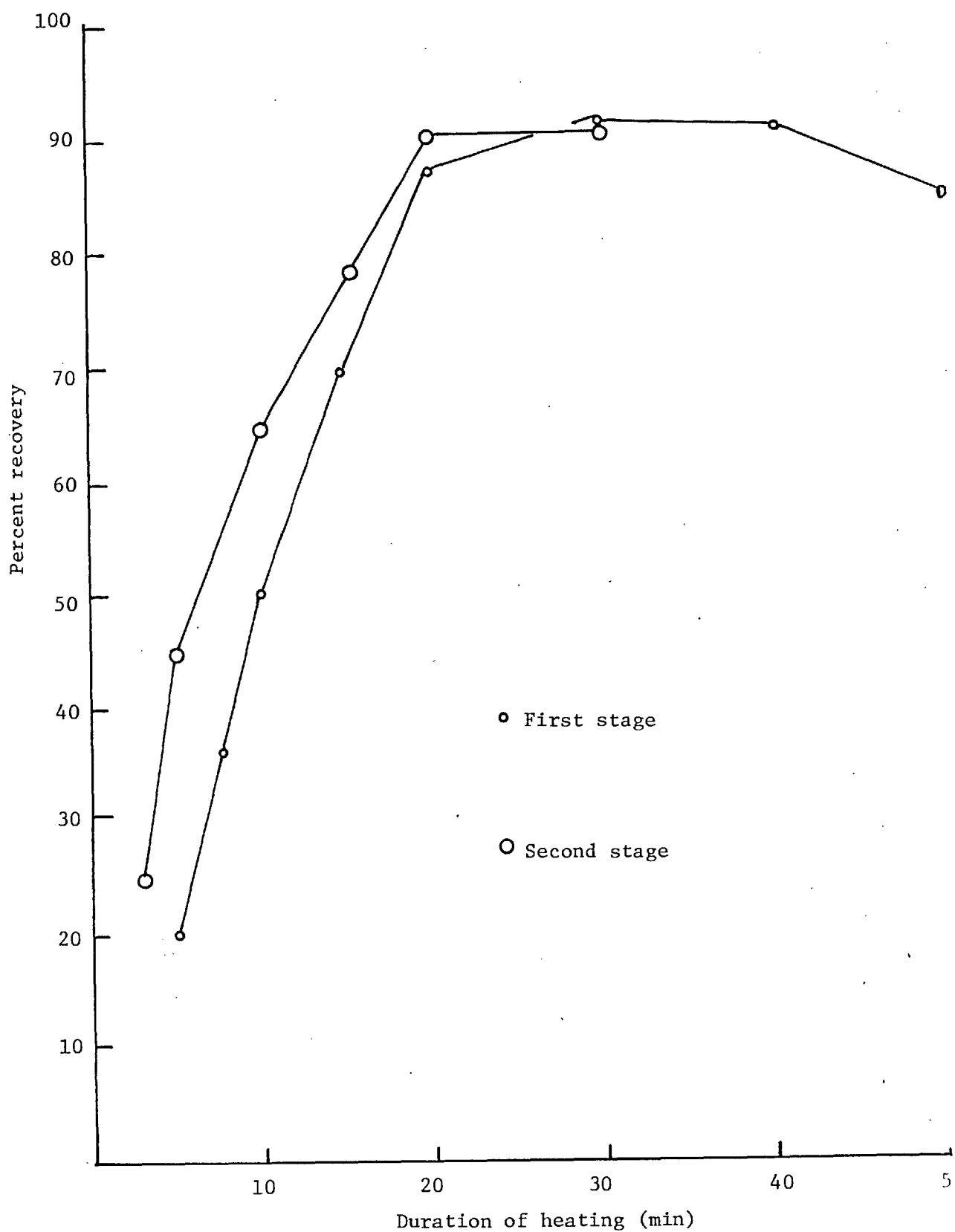


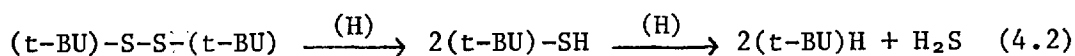
Figure (4.2)

Effect of duration of heating on sulphur recovery

in the second stage.

To obtain optimum duration of the heating in the first part, the heating time during the second stage was kept constant at 20 mins.

The second stage of reduction which involves the alloy and hydrochloric acid is thought to occur through two processes: decomposition of metal sulphides and also reduction of some S-S and S-H bonds by hydrogen (71):



The optimum period of heating the solution during the second stage was determined in the usual way (the heating time during the first stage was kept constant at 40 mins) and found to be 20 mins at 120°.

The temperature of the reflux is influenced by the boiling point of organic sulphur compounds, unless the boiling point of the solvent is lower than that of sulphur compounds.

The efficiency of reduction of S-S bond and formation of metal sulphides were found to be influenced by temperature of heating (Figure 4.3). In the second stage of reflux, hydrogen formation (due to the hydrochloric acid/metal reaction) is more affected by temperature than the decomposition rate of the metal sulphide. Optimum temperatures were determined at constant temperature of one stage (100° and 320°) (Figure 4.3).

At a temperature higher than 320°C (in the second step) some organic vapour was found in the absorbing solution. This

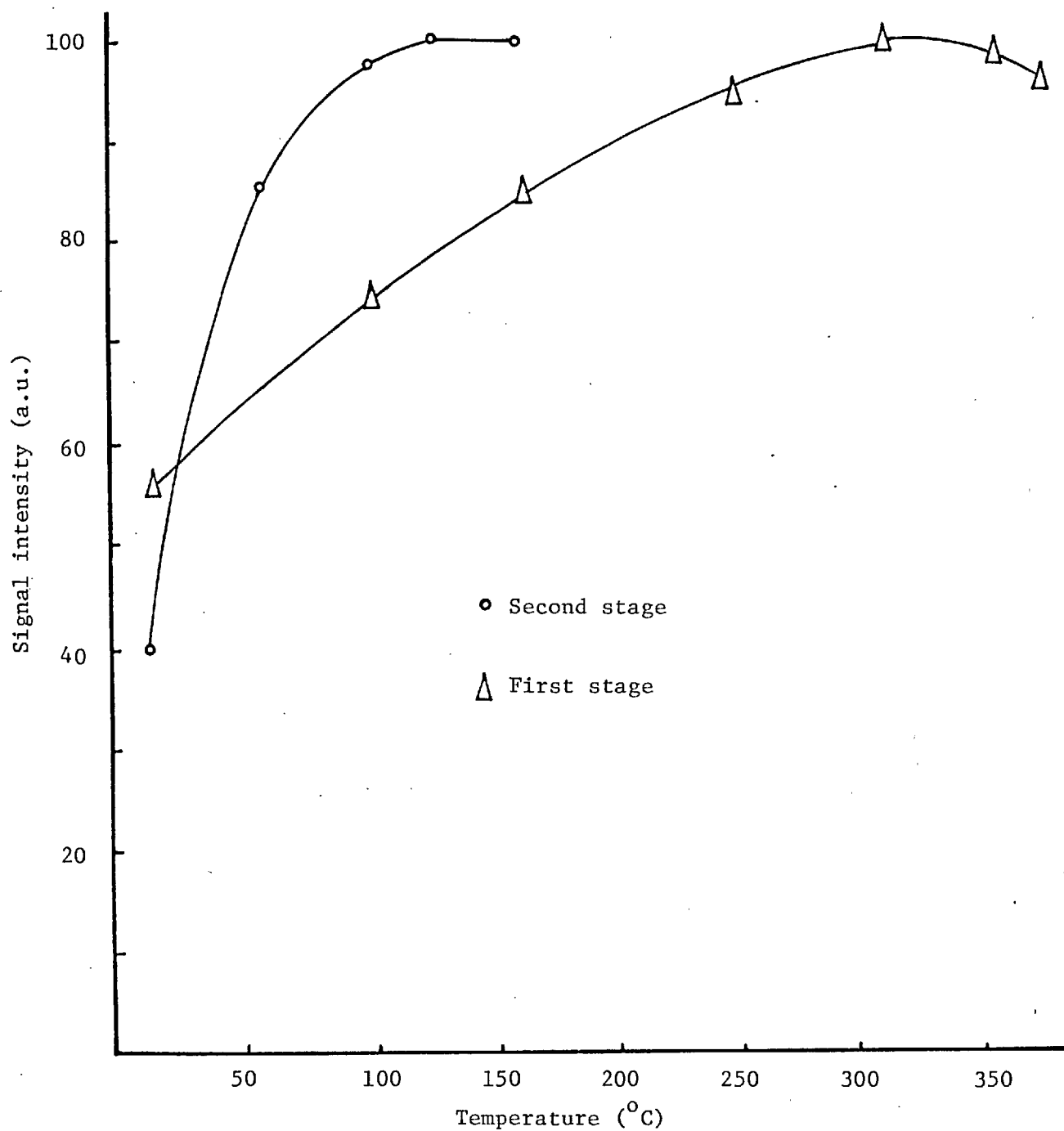


Figure (4.3)

Effect of temperature of heating on signal intensity

probably is due to the high rate of organic vapour formation and the inefficiency of the small condenser employed. However, employing temperatures higher than 320°C results in decreased signal intensity (Figure 4.3). At a temperature higher than 120°C (in the second step) the reaction of acid and metals was found to be uncontrollable. The amount of concentrated hydrochloric acid employed in the second step was varied in order to obtain the optimum recovery of S (Table 4.2). Adding a large amount of hydrochloric acid results in decreased recovery due to the absorption of escaped hydrochloric acid by the absorbing solution (Table 4.2.).

Many different solutions have been proposed as hydrogen sulphide absorber; the most popular seem to be buffered or ammonical solutions of zinc or cadmium salts, or sodium hydroxide solution. Although Zimmermann (203) obtained satisfactory results with buffered cadmium acetate as the absorbent, its use has been criticized (72) because cadmium sulphide is insoluble and light sensitive.

Sodium hydroxide, recommended by Bethge (99), readily absorbs sulphides and oxidation to sulphate does not occur if air is excluded and the solution is strongly alkaline (188).

However, due to the insolubility of zinc and cadmium sulphide, in the present work, only using sodium hydroxide was found to be practical.

The concentration of sodium hydroxide solution in the absorber was varied in order to optimise the conditions. The

concentration of sodium hydroxide does not want to be too high as the solution must be rendered acid in the subsequent step and the minimum concentration compatible with good recovery is best. The outcome of these experiments was using 2 ml concentrated hydrochloric acid and 10 ml 5% w/v sodium hydroxide in the absorbing flask (Table 4.2).

During the course of the heating process the sodium hydroxide solution becomes warm as the purge nitrogen passes through. This leads to loss of hydrogen sulphide (about 5-7%) by decomposition of the sodium sulphide and was to be minimised. The flask was therefore kept cool in an ice bath throughout the experiment and this alleviated the problem.

Table 4.2.

Effect of Amount of Acid and Concentration of NaOH in Absorbing Solution.

Amount of HCl (ml)	Intensity a.u.		
	H ₂ O absorber	2% aq. NaOH absorber	5% aq. NaOH absorber
0.5	24	24	24
1.0	29	56	24
1.5	16	86	87
2.0	6	95	100
2.5	3	85	100*

Sample: 1 ml 0.032% S as tert-butyl disulphide/liquid paraffin

*normalised to 100, all other signals referred to this.

B) Optimisation of Other Parameters.

It was found that if nitrogen was bubbled through the solution in the flask, lower recoveries (about 5%) were found, possibly due to more rapid removal of the hydrogen from the solution. The purge gas was therefore passed over the surface of the liquid and this effected an improved recovery.

The order of addition of the reagents in the reduction process was also investigated as well as the effect of having no Devarda's alloy there at all. Four experiments were carried out and the results obtained shown in Table (4.3).

Table 4.3.

The Effect of Order of Addition of Reagents on Obtained Signal Intensity.

Experiment	Intensity (a.u.)
1	<2*
2	8
3	19
4	100**

- 1) 0.032% TBD/liquid paraffin sample, 1 ml + 2 ml conc. HCl : heat 60 mins.
- 2) 1 ml sample + 100 mg Devarda's Alloy + 2ml conc. HCl : heat 60 mins.

- 3) 1 ml sample + 2 ml acid: heat 20 mins; add 100 mg alloy and heat further 40 mins.
- 4) 1 ml sample + 100 mg alloy: heat 40 mins; add 2 ml acid and heat further 20 mins.

* NaOH absorbing solution became acid

** Signal normalised to 100 and others referred to it.

It can be seen that the last method is by far the most efficient and underlines the role that the reducing alloy plays in the initial reduction of the S-S bond.

To check whether any hydrogen sulphide passed through the absorbing flask a second flask was put in series containing the same 5% sodium hydroxide solution; no sulphide was detected in this flask.

(4.5) Interference Studies.

A number of other sulphur containing organic compounds were analysed by this method. The compounds were dissolved in liquid paraffin, where possible, to give solutions containing 0.032% S. The results are summarised in Table (4.4). It was found that thiols, sulphur (and of course, dissolved hydrogen sulphide) interfere. In view of the proposed mechanism of the reduction of the S-S bonds it is not surprising about the effect of thiols.

The elemental sulphur interfering effect can be due to its reduction by hydrogen to hydrogen sulphide (194) in the

second step of heating, according to the reaction:



The thiols can however, be easily removed by previously shaken 5 ml of the analyte solution with 5 ml M silver nitrate aqueous. The silver mercaptide precipitates, is centrifuged out and can be determined separately if required.

Table (4.4)

Potential Interference of Sulphur Containing Compounds on Disulphide Determination.

Species	Intensity a.u.
Liquid paraffin	<1
tert-butyl disulphide	100*
Ethylmercaptan	110
diphenyl trisulphide**	95
diphenyl sulphide	<1
dimethyl sulphide	2
dimethyl sulfoxide	0.03
benzene potassium sulphonate**	2
1,3 dithiane**	1

With the exception of liquid paraffin, all species were present at a level of 0.032% sulphur by weight calculated on their molecular formula, and made up in liquid paraffin.

* The signal for tert-butyldisulphide was normalised to 100 and all other signals referred to that.

** Dissolved first in a little benzene and then diluted with liquid paraffin.

The elemental sulphur can be removed by then shaking the solution with mercury (2g to 10 ml sample) which forms mercury sulphides; this too can be readily centrifuged out and determined separately. Recovery test of disulphide from solutions containing other sulphur compounds are shown in Table (4.5).

Table (4.5).

Recovery of Disulphide Sulphur in Presence of 100 Fold Excess of Interfering Compounds.

Species	Intensity a.u.
tert-butyl disulphide (TBD)	100*
Ethyl mercaptan + TBD	>350
Ethyl mercaptan + TBD washed/AgNO ₃ **	110
diphenyl sulphide + TBD	130
dimethylsulphide + TBD	145
dimethylsulphoxide + TBD	96
benzene potassium sulphonate + TBD	96
1,3 dithiane + TBD	100
Elemental sulphur* + TBD	>350
Elemental Sulphur* + TBD shaken with Hg***	98

In each case tert-butyl disulphide was present at 0.032% S and the other species at 3.2% S levels.

* The signal from tert-butyl disulphide is normalised to 100

** 5 ml of sample washed with 5 ml M AgNO₃ prior to analysis.

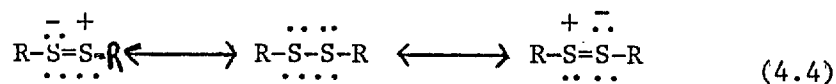
*** 10 ml of sample shaken with 2 g mercury prior to analysis.

• Dissolved first in a little aniline and then in liquid paraffin.

The Determination of Disulphide in the Presence of Monosulphide.

In order to test the applicability of the method for the determination of the disulphide species in the presence of monosulphide, solutions of 32 ppm S as tert-butyl disulphide were made up in liquid paraffin in the presence of 320-4000 ppm S as dimethyl sulphide and diphenyl sulphide. The effect of the recovery of S is illustrated in Figure (4.4). It can be seen that there is only a modest interference by these other species on the disulphide determination. It may be due to the impurity of the monosulphide used.

Reactivity of the S-S bond is considered as a partial background for purposes such as the proper selection of methods from available procedures for specific problems involving sample matrices and components (di- and polysulphides) to be determined (71). The analytical reaction used in this study was the reduction of the S-S bond (equation 4.2). For di- and polysulphide compounds this means cleavage of S-S bond. Polarization is one of the principal ways the bond may be activated. Resonance polarization of the S-S bond may be represented as below (71):



It can be seen that in any of these three structures there is a high electron density about the S-S bond which makes it a good target for electrophilic agents, such as hydrogen.

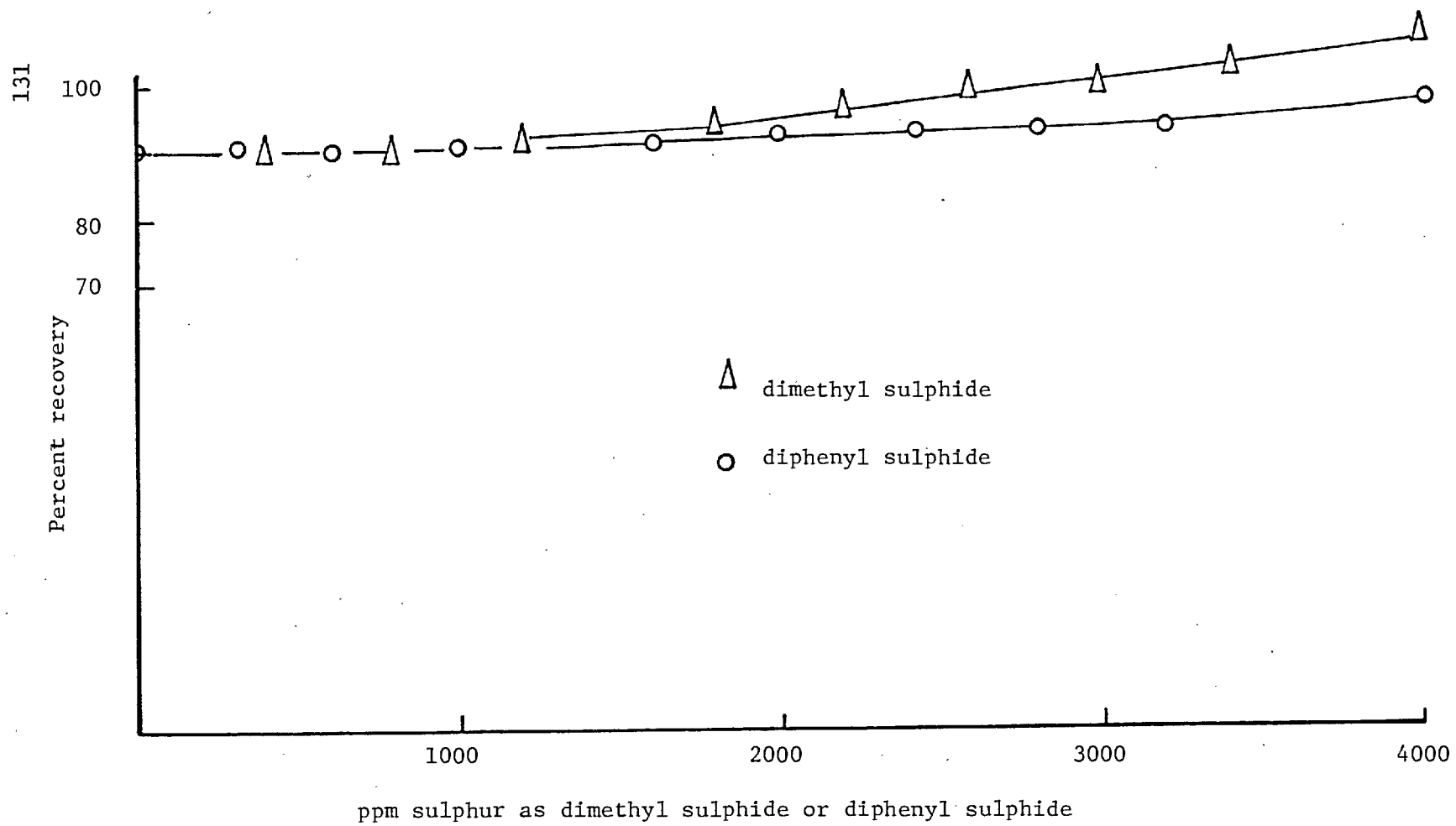


Figure (4.4)

Interference of monosulphide on disulphide determination.

Therefore, it can be said that the absence of S-S bond in monosulphide is probably the main factor which prevents monosulphide to interfere.

(4.6) Recovery From Light Distillates.

Recovery tests were carried out on tert-butyl disulphide and diphenyl-trisulphide light distillate fractions diluted with white spirit to bring their sulphur levels down to between 300 and 1000 ppm. These samples had previously been analysed for total sulphur by BP using X.R.F. and in this laboratory (Table 3.9, Chapter 3). The samples were first shaken with M silver nitrate and then mercury to remove any mercaptans or sulphur. As can be seen from Table (4.6), the recovery is good for both the disulphide and trisulphide species.

(4.7) Conclusions.

This work has shown that the combination of metal reduction of sulphur compounds to sulphides in petroleum products coupled with release of hydrogen sulphide into a cool flame and measurement of the S_2 emission provides a useful method for the separate determination of sulphur species. The method is capable of good precision and accuracy as well as versatility. With selective separation of the species, mercaptans with acrylonitrile (201), hydrogen sulphide with silver nitrate and sulphur with mercury these species could all be analysed separately and thus provide S, -SH, H_2S (S_2 and S_n) in the same sample.

Table (4.6).Recovery Tests From Light Distillates.

Original Sample	S in diluted sample* (ppm)	tert. butyl disulphide		diphenyltrisulphide	
		added ppm	recovery %	added ppm	recovery %
7866	400	320	90	320	89
7914	800	420	92	410	90
7956	520	250	91	240	92
7957	330	200	93	200	92
8110	450	180	90	180	91
9142	300	150	90	150	91
9143	950	120	91	120	90

* Light distillates diluted with white spirit.

CHAPTER 5

Sulphur Dioxide Determination.

(5.1) Introduction.

The determination of sulphur by generation of hydrogen sulphide, sulphur dioxide or a sulphuric acid aerosol into a cool flame and measurement of the consequent S_2 band emission is well known (132, 149). Work described in Chapter 3 and elsewhere (189) has shown this to be a useful technique for the analysis of sulphur in petroleum products giving a sensitive, selective and quite precise determination. Much of the previous work has been carried out using hydrogen sulphide as the intermediate and this has certain attractive features; storage of the gas in sodium hydroxide permits pre-concentration; the low solubility of hydrogen sulphide in acid solution ensures good and rapid recovery from the storage solution; formation of hydrogen sulphide by metal reduction can impart selectivity to the method permitting a degree to specialization (Chapter 3).

Sulphur dioxide has the following properties which cause it to be of interest;

- 1) It has a high S_2 emissivity
- 2) It is a gas at room temperature and is therefore easily removed from the matrix. It also requires no energy for solvent evaporation or sample vaporization.

3) There is, to some extent, a linear relationship

between S_2 emission intensity and S_2 concentration.

The use of sulphur dioxide as intermediate does offer certain advantages over hydrogen sulphide in particular applications.

For determinations where the matrix is reactive, for example, fatty acids or long chain esters, the use of sodium or acid/zinc as reductant to liberate hydrogen sulphide is precluded due to the formation of soaps.

Combustion of the sulphur compounds to sulphur dioxide by the lamp method (101), or in a stream of purified oxygen (high-temperature combustion) (204, 205) are widely used in the determination of total sulphur in petroleum and related materials.

Combustion of sulphur-containing samples leads to the formation of both sulphur dioxide and trioxide (in the high-temperature method (204)). Conditions must, therefore, be chosen such that the highest possible yield of sulphur dioxide is obtained. The amount of sulphur dioxide formed must be independent of the form in which the sulphur is present in sample.

Killer and Underhill (206) say that the combustion of sulphur compounds (in an atmosphere of oxygen) to sulphur dioxide depends on the conditions in the combustion tube and is mainly a function of temperature, but also depends on the type of tube, oxygen flow and rate of cooling of the emerging gases. Sulphur dioxide may be oxidised to sulphur trioxide in the presence of oxygen according to the equation:



The high temperature combustion method (204) is widely used in the determination of total sulphur in petroleum products such as fuel oils, lubricating oils with or without additives and asphalts. The method is applicable to materials of low volatility that contain not less than 0.06% sulphur. The sample is burned in a flow rate of 300 to 700 ml/min purified oxygen and at a high temperature (1315°C using induction or resistance-type heating) about 97% of the sulphur is converted to sulphur dioxide.

White (205) has described an interesting combustion system (based on the combustion of samples in quartz tube and in the absence of any catalyst) which gave close to a 100% yield of sulphur dioxide. He carried out the high-temperature combustion in a separate chamber followed by dilution of the combustion gases with helium and cooling to 700°C . He also used a minimum of oxygen, about 3% by volume, in the combustion equilibrium zone to favour the formation of sulphur dioxide. This however, limits the injection speed to $0.1\ \mu\text{L}/\text{sec}$ which raises the limit of detection and requires the use of a special injection device.

The lamp method (101) is a recommended procedure for the determination of total sulphur in gasoline, kerosine, naphta and other petroleum products that will flow through and can be burned completely from a wick. Modifications (71) in the technique and apparatus also permit the burning of highly volatile liquified petroleum gases, samples of very high or very low sulphur content, samples of high aromatic content and samples with too high a boiling point to flow

through a wick without dilution. In the past, the instability of sulphur dioxide solutions and the unavailability of interference-free methods for sulphur dioxide measurement have made it more convenient to use a hydrogen peroxide absorbing solution and to measure the sulphate formed (114).

Recently, Kruger (114) introduced a method in which the sulphur was measured directly as sulphur dioxide in the absorbing solution using a gas-sensing electrode after the combustion of the organic sample in an atmosphere of air in a lamp. The results obtained by him indicated that sulphur combustion products are almost completely in the form of sulphur dioxide.

In the present study, the generation, storage and release of sulphur dioxide as an intermediate in the determination of sulphur in petroleum products was investigated along with the optimisation of burner design.

(5.2) Experimental.

(5.2.1) Apparatus.

The flame photometric apparatus employed for this work is shown schematically in Figure (5.1). The generation cell is the same as described in Chapter 3, but the gas inlet tube came very close to the bottom of the cell to permit bubbling through the solution. The cool-flame burner design is shown in Figure (5.2). In order to keep the flame burning during washing of the cell, the gas flow system illustrated in Figure (5.4) was used.

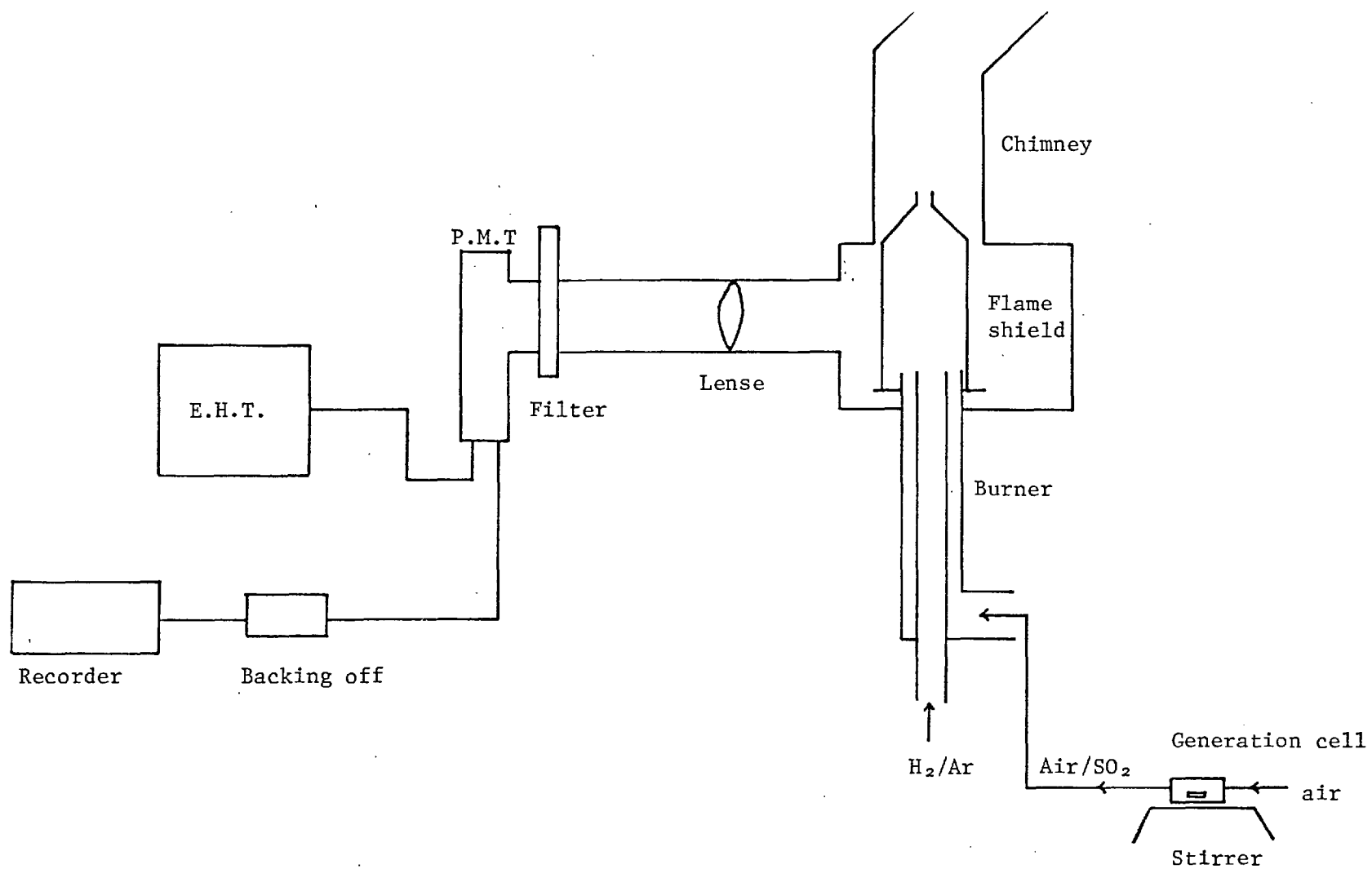


Figure (5.1)

Schematic diagram of apparatus used.

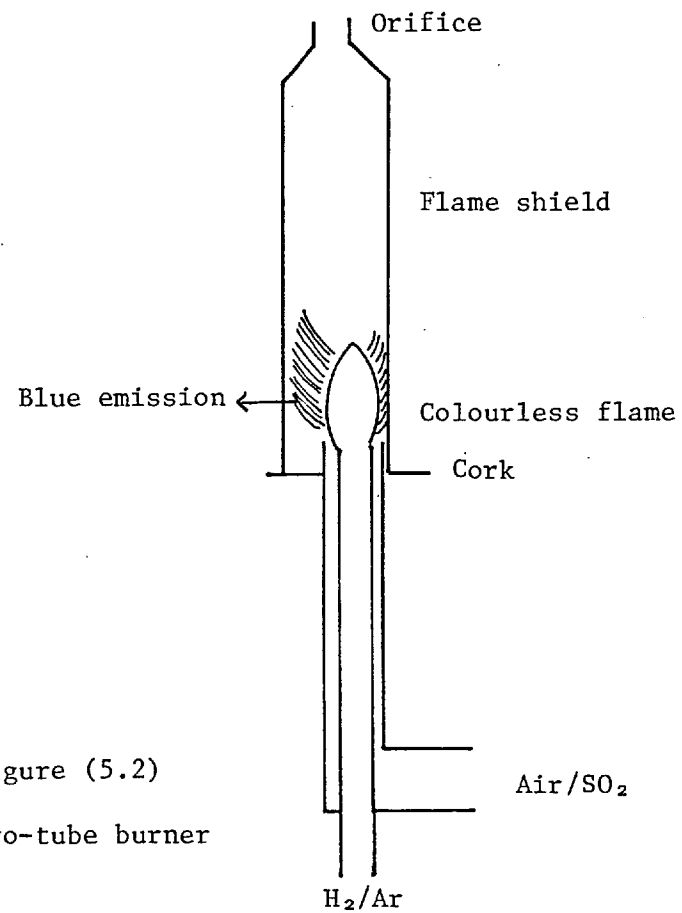


Figure (5.2)

Two-tube burner

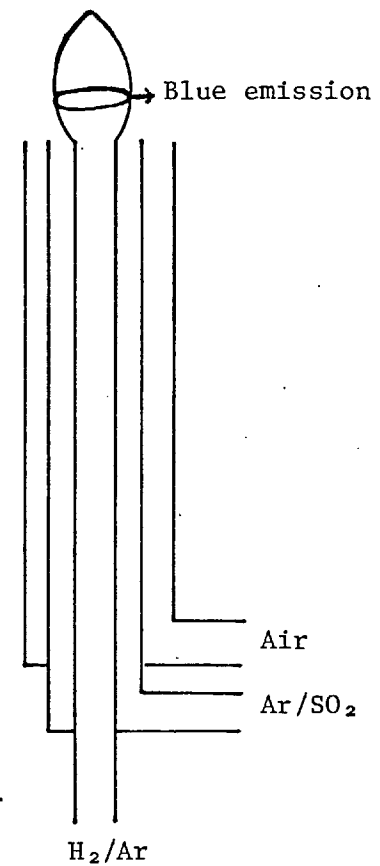


Figure (5.3)

Three-tube burner

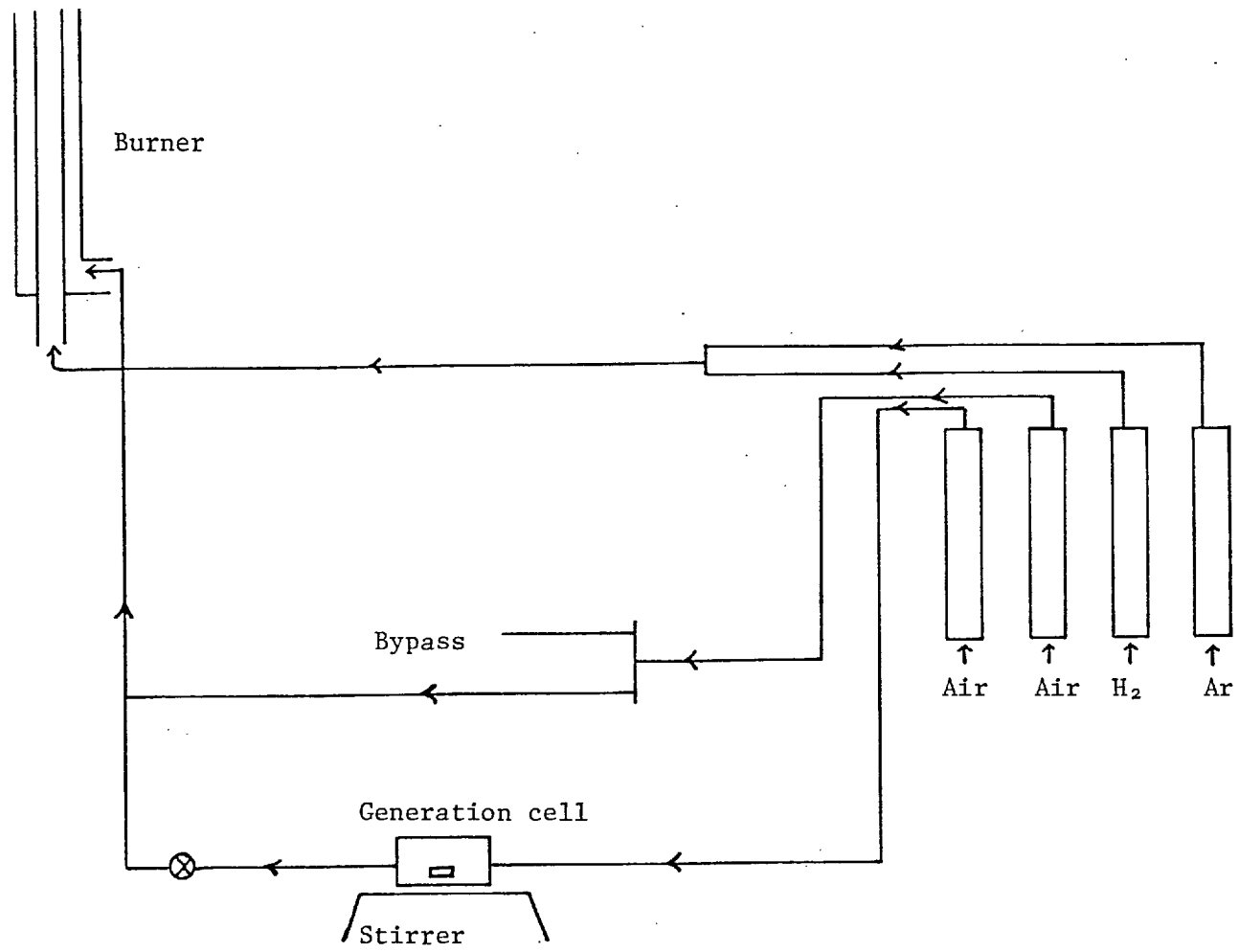


Figure (5.4)

Schematic diagram of sample introduction system.

The burning of light distillates to produce sulphur dioxide was performed using a standard lamp apparatus (Townson Mercer Ltd.). The generated sulphur dioxide was swept out of the cell into the flame via the outer tube of the burner (Figure 5.2) with air. Filter, photomultiplier, backing off unit and strip chart recorder were the same as described in Chapter 3.

(5.2.2) Standard Sodium Sulphite Solutions.

Sodium sulphite solutions alone are unstable due to oxidation of sulphite by oxygen, catalysed by traces of heavy metals (207), particularly copper and iron. A solution of sulphite in absolutely pure water would be unaffected by the presence of oxygen, but even the use of the purest conductivity water fails to reduce the speed of oxidation to zero. The oxidation will only proceed in the presence of minute traces of catalysts, e.g., copper and iron which will always be dissolved from the walls of the containers to produce a measurable speed of oxidation (207). The following experiment verified these points. Four samples of sodium sulphite solutions of different sulphur concentrations (60, 30, 12 and 6 ppm) were analysed according to the analytical method, described later, over 4, 8, 16, 24 and 48 hour periods. Results are shown in Figure (5.5).

Sodium sulphite solution alone can, however, be stabilised by sodium tetrachloromercurate (STCM) in the presence of ethylenediamine tetraacetic acid (EDTA) at pH between 5.0 and 7.3 (208, 209). At

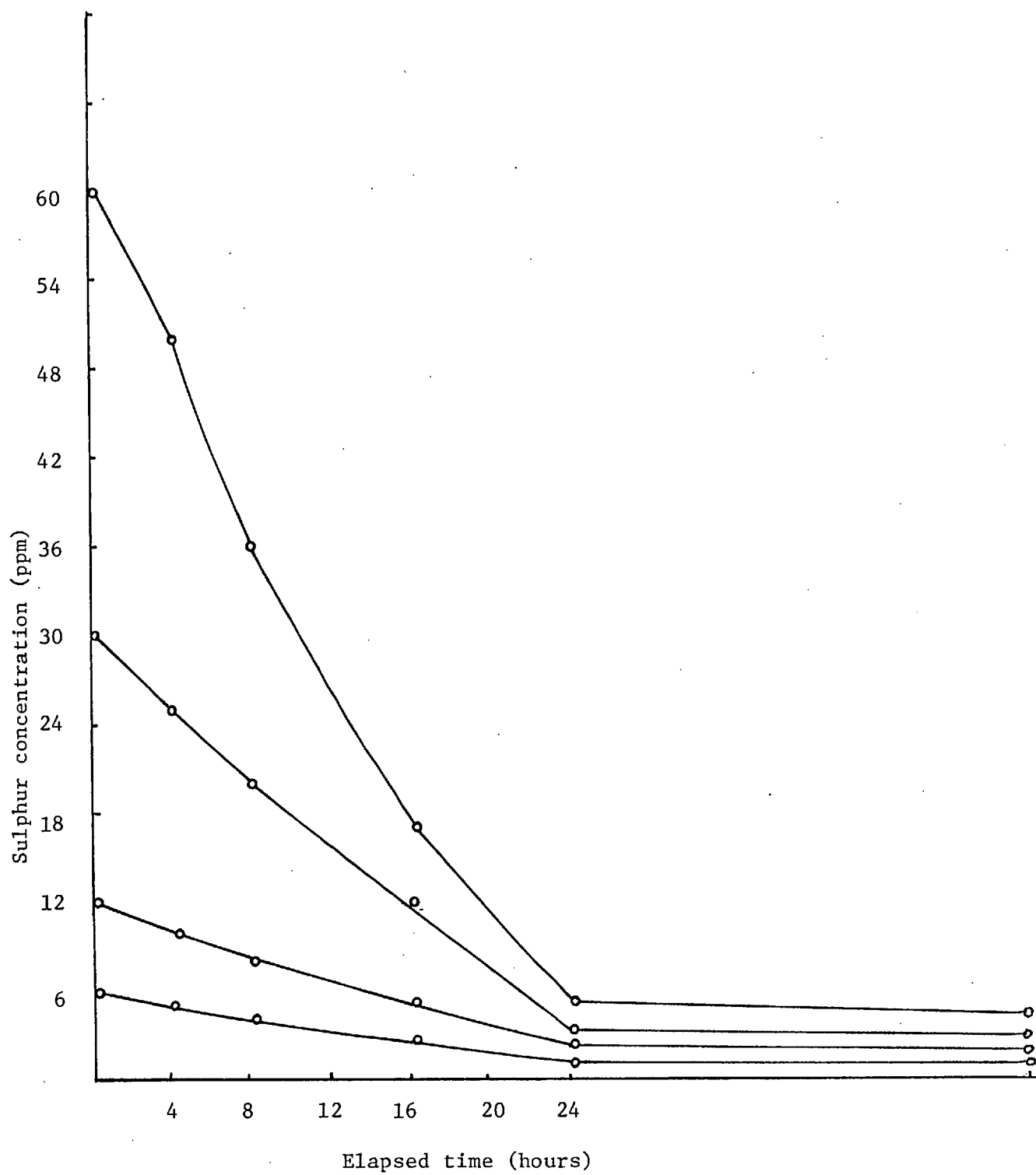


Figure (5.5)

Decay rate of unstabilised aqueous sodium sulphite solution

pH values lower than about 5, the stability of sulphite was reduced and at pH value higher than about 7.3 the mercuric hydroxide precipitated.

Feigl (208), say when sulphite is added to a mercury(II) solution, the very stable disulphitomercurate(II) ion, $\text{Hg}(\text{SO}_3)_2^{2-}$, is formed. West and Gaeke (209) made a detailed investigation of the stability of this complex and found out that the complex is most stable in a solution of mercury chloride and sodium chloride of molar ratio 1:2. They further showed that even potassium permanganate oxidises this complex only at a very slow rate. In order to prevent the catalyst effects of heavy metals, EDTA, as a complexing agent was added (214).

A standard solution was prepared by making a solution of sodium sulphite heptahydrate in water at the M/100 level and standardising it iodimetrically (191).

A 5 ml aliquot of the standardised sulphite solution was then immediately diluted to 50 ml with 0.2 M STCM/0.002 M EDTA buffered at pH 5-7.3 with sodium hydroxide. The 0.2 M STCM/0.002 M EDTA was prepared by dissolving 2.34 g NaCl, 5.44 g HgCl_2 and 0.06 g EDTA in 100 ml water.

The pH value lower than about 5 in STCM/EDTA solution can be due to the incorrect ratio or concentration of mercuric chloride and potassium chloride or when the EDTA is not the disodium salt (214).

Stability tests were carried out on stabilised and unstabilised 30 ppm S (as sulphite solutions) in open, stoppered and air evacuated flasks over a 24 hour period using the analytical method

described later. Results are shown in Table (5.1). In stabilised solution cases, no noticeable change in the sulphite concentration could be detected, whereas the levels in unstabilised solutions were reduced dramatically. The effect of temperature on the stability of sulphur dioxide in STCM solutions was investigated and was found that the percentage decay of sulphur dioxide in STCM is 2.5 and 12 at 30 and 40°C respectively (210).

The stabilised solution thus prepared were found reasonably stable for up to a month if kept in a cool place (5°C).

Scaringelli, et al., (211) indicated that the sulphur dioxide oxidation reaction is first-order and that it follows the equation:

$$\text{LnC} = kt + \text{LnCo} \quad (5.2)$$

where

LnC = natural log of observed concentration

k = rate constant (decay rate at definite temperature)

t = elapsed time

LnCo = natural log of the concentration at the time zero.

It is, therefore, possible to improve our values of the C at the time of analysing. Simply substitute in the above equation, where k, is the decay rate at temperature which the standard solutions were kept.

In the procedure for the determination of sulphur in petroleum distillates it was found advantageous to add a pH buffer and glycerol as an antioxidant, this will be discussed later.

Table (5.1)

Stability Tests on stabilised and Unstabilised Sodium Sulphite
Solutions.

	Conditions of Samples	Sulphur found after 24 hours ppm*
Unstabilised samples		
	open flask	0.6
	stoppered flask	3.2
	air-evacuated flask	22
Stabilised samples		
	open flask	28
	stoppered flask	30
	air-evacuated flask	30
* added sulphur 30 ppm		

(5.3) Burner Design Development.

The chemiluminescent emission of radiation for the S_2 species is supposed to result from the combination of two ^{sulphur} ~~suplur~~ atoms and formation of the dimer in an excited state (134). It is important, then from the viewpoint of maximum emission intensity, that the free atom population be created initially, that the formation of S_2 should be favoured and that the S_2 excited states should not be quenched. The optimum temperature for S_2 formation is found to be 390°C (119). At temperatures higher than this the molecular sulphur S_2 is not stable. These criteria are best met in the centre part of a hydrogen argon diffusion flame (cool part) in which the atmospheric oxygen, which supports the flame combustion, diffuses only a little way toward the centre of the flame and it is well known that the presence of carbon and hydrocarbon species quenches the emission markedly (134).

When hydrogen sulphide was employed as the intermediate gas in the analytical determination, it was passed directly into the cool part of an inward burning diffusion flame without having passed through the hot combustion gases (Chapter 3). This seemed to be perfectly adequate for efficient formation of the S_2 species and the consequent emission of radiation. Sulphur dioxide, however, has a much higher free energy of formation than hydrogen sulphide ($\Delta H^{\circ}_f(\text{SO}_2) = -296.8 \text{ kJ/mol}$; $\Delta H^{\circ}_f(\text{H}_2\text{S}) = -20.63 \text{ kJ/mol}$ (212)) and so the initial break-down of sulphur dioxide to sulphur atoms requires that much more energy. In order, therefore, to improve this initial

atomisation step, the burner design was altered to permit passage of the sulphur dioxide through the hot combustion gases prior to their entering the cool region where chemiluminescence is optimum (about 390°C).

The burners employed are illustrated in Figure 5.2 and 5.3. In the three-tube burner (Figure 5.3) argon and hydrogen pass up the inner tube and argon purges the cell passes up the middle tube and air, as supporting gas, passes up the outer tube. This burner consisted of three silica tubes of 4, 8 and 12 mm internal diameter, inserted in each other. Supporting air was used to increase the entering rate of sulphur dioxide into the flame. This can be seen in Figure (5.6) which was obtained at optimum flow rates of argon and hydrogen. Argon, hydrogen and air flow rates were optimised by injecting one ml of sulphite solution into the cell containing one ml of 2 M hydrochloric acid. When one flow rate was being optimised the other flow rates were at their optimum setting.

The hottest portion of the diffusion flame is the outer thin envelope where atmospheric oxygen and the hydrogen fuel gas burn on mixing (Table 5.2). The flame centre and edge temperatures were measured by inserting a calibrated thermocouple probe into the centre and edges of the flame. The measurement was carried out with and without air as supporting gas. The results are shown in Table (5.2). At optimised flow rates of gases using this burner the signal intensity due to one ml of sulphite solution was found to be improved 100 times compared with the burner used for hydrogen sulphide studies (Chapter 3). Another configuration of gases

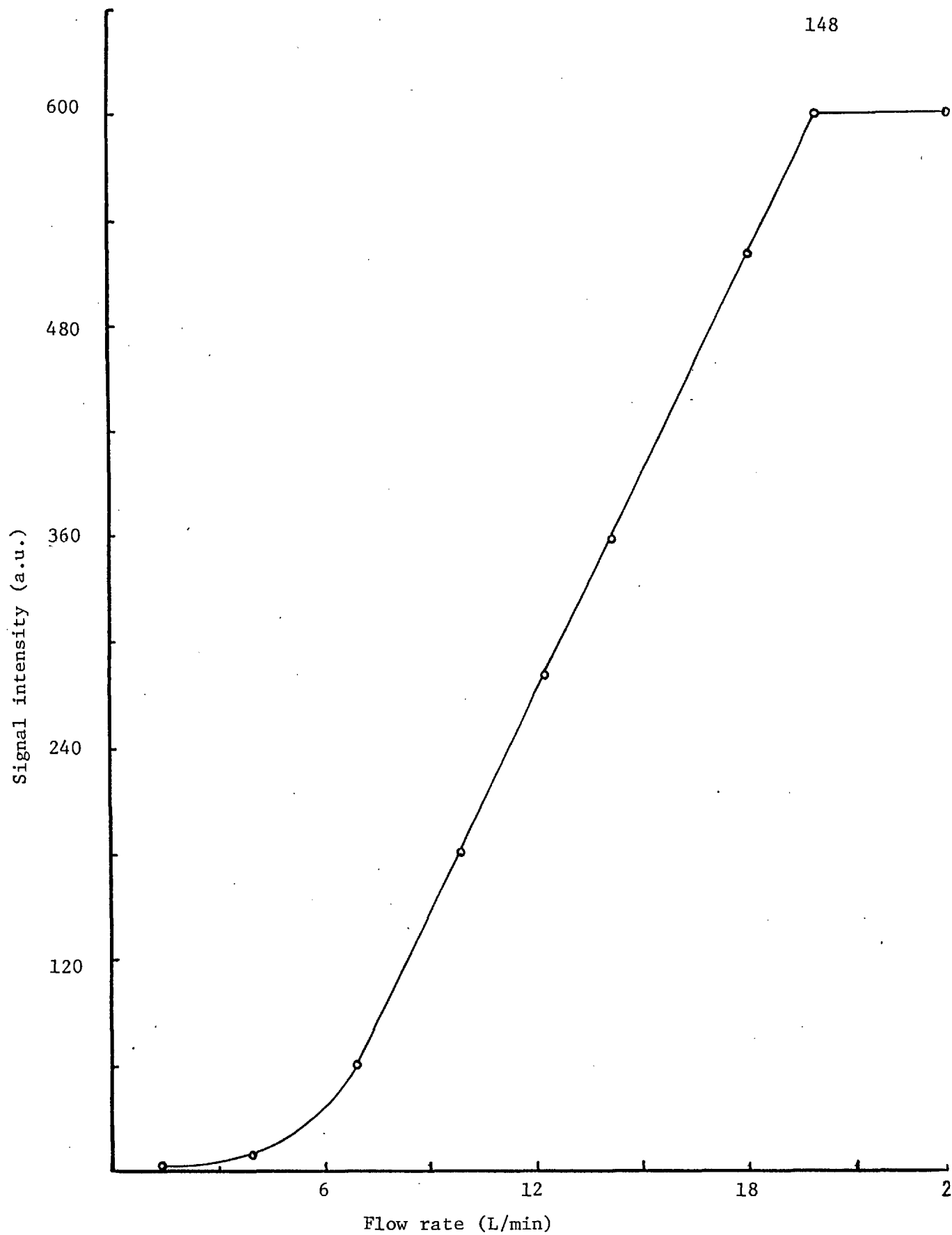


Figure (5.6)

Optimisation of supporting air flow rate.

Table (5.2)

Temperature of Flame Centre and Edge with and without air as
Supporting gas.

Distance above the burner head mm	Temperature °C			
	With supporting air		Without supporting air	
	Edge	Centre	Centre	Edge
5	780	400	180	700
10	790	540	350	750
20	800	800	550	790
35	850	850	700	800

(replacing the air with argon as supporting gas and purging the cell with air instead of argon) was used and found a decrease in signal intensity. This may be due to the diffusion of air towards the centre of the flame and consequent enhancement of the temperature of flame centre.

Using this three-tube burner and optimised analysing conditions, resulted in a minimum detectable concentration of 8 ppm S. This poor result compared with that attained (0.01 ppm S) when hydrogen sulphide was employed as the intermediate gas in the analytical determination (Chapter 3), can be due to the low efficiency of SO_2 -entering rate into the flame. In order to improve the minimum detectable concentration of sulphur another burner was designed and used (Figure 5.2). In this two-tube burner, argon and hydrogen passed up the inner tube and air, either a flow by passing the generation cell (to permit maintenance of the flame during cell cleaning) or one which purges the cell, passed up the outer tube. The burner, which consisted of two silica tubes of 4 and 8 mm internal diameter inserted in each other, was enclosed in a borosilicate glass tube with a restricting orifice at the open end. The burner tip was mounted in the sheath, by a cork, with the burner tip about 2 cm above the bottom of the sheath and closer to one side of the sheath (Figure 5.2). When the burner was located exactly in the centre of the sheath, there was some distortion in the peaks which could be due to the turbulence of the flame gases.

The actual mechanism of the influence of this sheath is not sure but its effect is most important. Under the same gas flow

conditions and with the same amount of sulphur dioxide going into the flame altering the dimensions of restrictor tube is given in Table (5.3). The length of the tube appears to make little difference whereas its diameter and the diameter of the restricting orifice seem to be rather crucial. This may suggest that the rate or efficiency of the flame gas mixing is the parameter being affected, although the slight increase in pressure due to the restrictor orifice can not be discounted as a possible influence, perhaps by preventing atmospheric air being drawn into the burner assembly and thus maintaining a cool flame.

The most intense signal was obtained using the sheath of 23 mm internal diameter. But in this case the blue glow emission of molecular S_2 was found not to be steady and had some movement inside the sheath and causes distortion in the peaks (Figure 5.7).

This movement was more clear when a continuous blue emission was created inside the sheath by a continuous introduction of sulphur dioxide into the flame generated continuously by decomposition of a crystal of sodium sulphite heptahydrate in dilute hydrochloric acid.

Air cooling the restrictor tube did not noticeably affect the signal intensity, neither did substitution of a silica tube for the borosilicate glass. The argon acts as a flame gas diluent thus maintaining a cool flame and it seems likely that its effect is through this mechanism. Stopping the argon flow at zero with air sweeping the cell, decreases the signal intensity by a factor of about 4 (Figure 5.8). Purging the generation flask with argon and

Table (5.3)The Effect of Restrictor Tube Dimensions on Peak Emission Intensity.

width (i.d.) (mm)	length (mm)	orifice diameter (mm)	Normalised peak height intensity (60 ng S)
12	145	5	100
12	75	5	97
18	145	5	225
18	75	5	220
23	145	5	340
23	75	23	0.00
23	75	10	160
23	75	5	340
23	75	2.5	flame extinguished

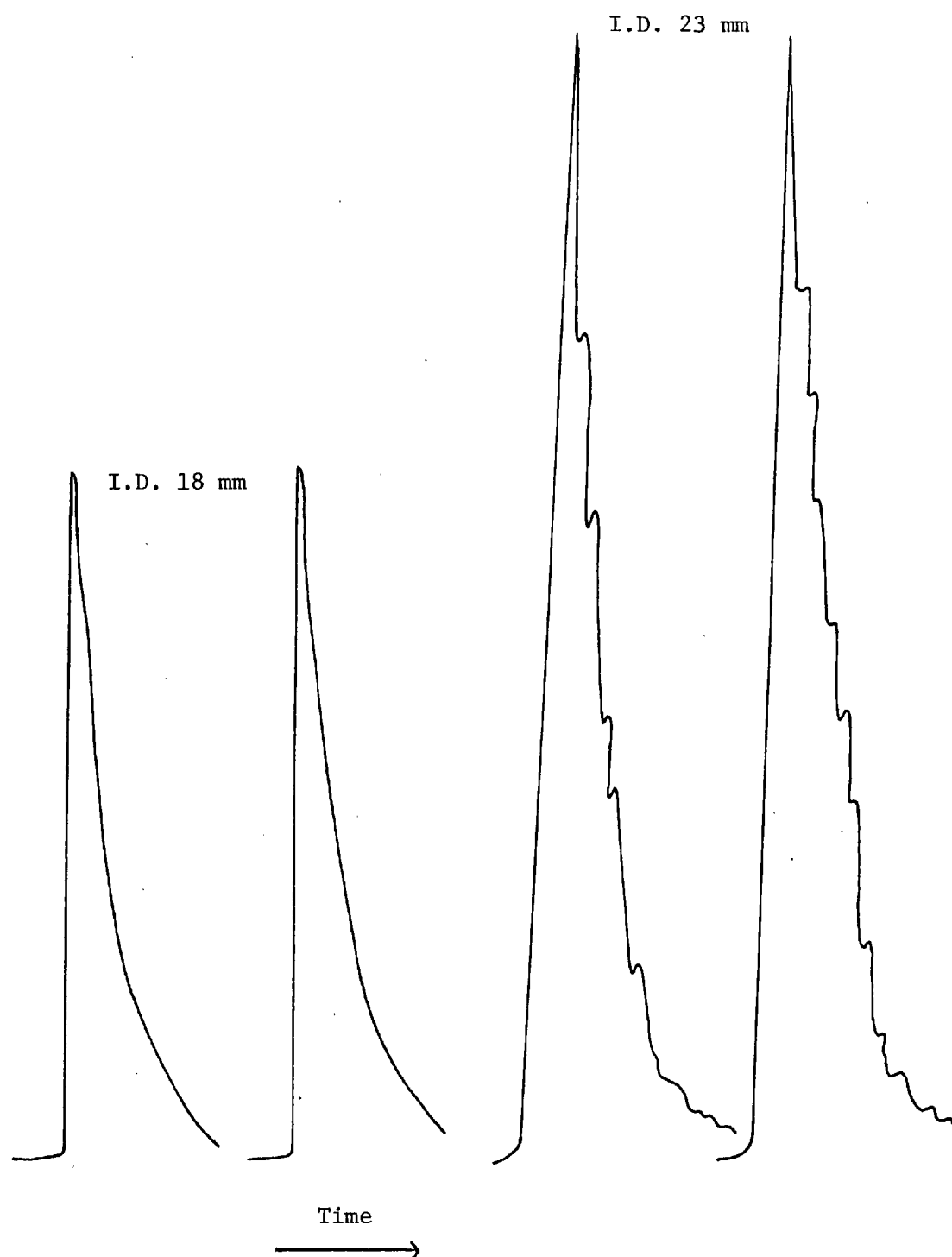


Figure (5.7)

Effect of the restrictor tube diameter on the shape of the peaks.

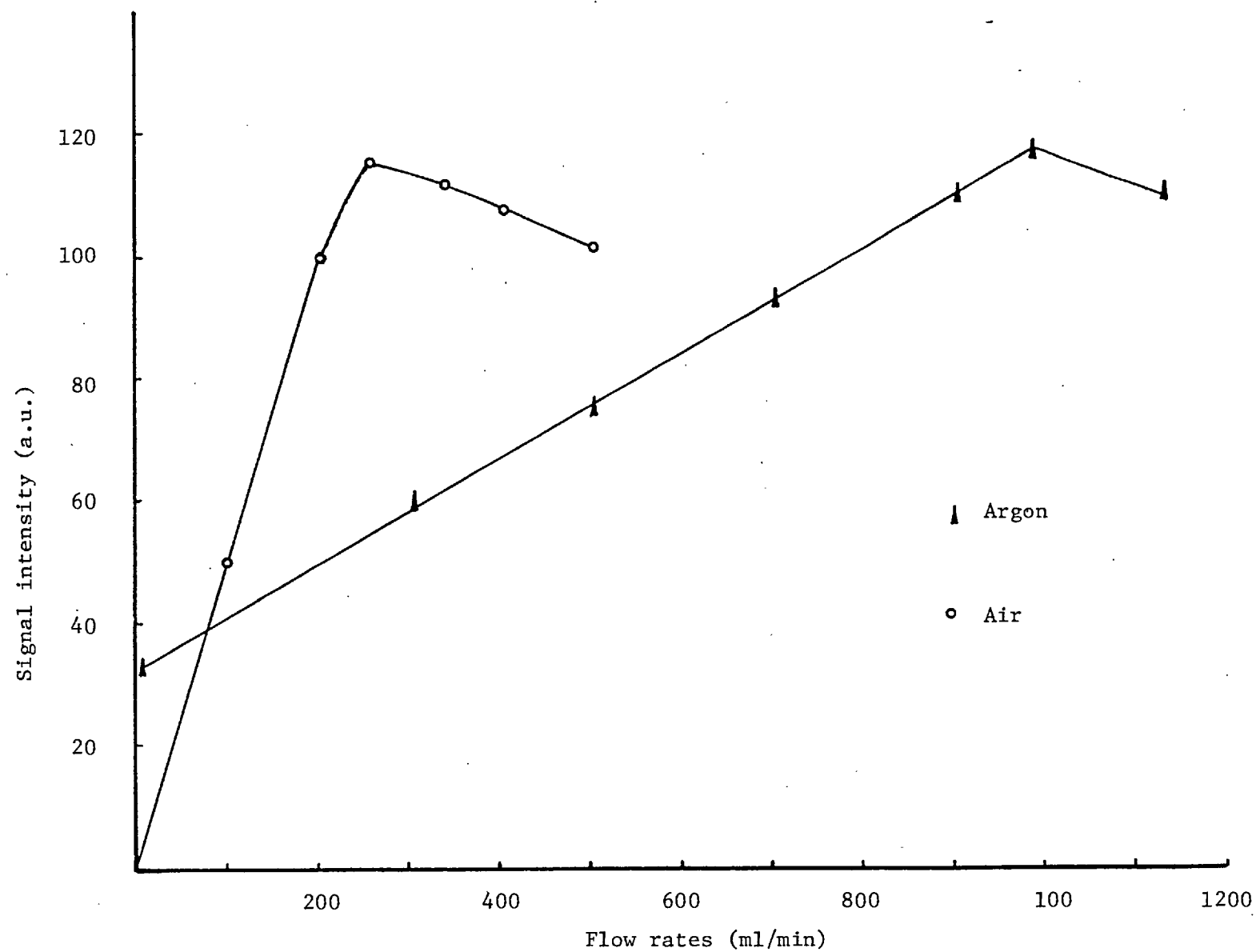


Figure (5.8)

Air and Argon flow rates optimisation

passing the $\text{SO}_2/\text{Ar}/\text{H}_2$ up the centre tube and air up the outside tube, resulted in a five-fold decrease in maximum signal intensity, thus illustrating the effect of the sulphur dioxide passing through the hot flame gases prior to formation of the S_2 species.

(5.4) Optimisation of Gas Flows.

The air flow through the cell and hydrogen and argon flows into the flame were optimised using a continuous steady stream of sulphur dioxide generated by the hydrolysis of a small crystal of sodium sulphite heptahydrate with dilute hydrochloric acid. The results are shown in Figure (5.8). It can be seen that the flow rates, specially air, are quite critical for maximum emission intensity from the flame. A total argon flow rate greater than 2.2 L/min caused the flame to be extinguished.

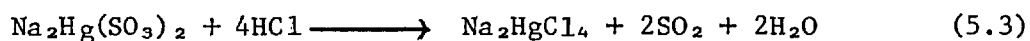
The air supply was sufficient to consume approximately 67% of the hydrogen supplied to the burner. Hence, flame was normally operated in a hydrogen-rich environment. In a hydrogen/air flame, the presence of large concentrations of H, O and OH flame radicals play an important role in both the sample decomposition chemistry and in the chemical reactions that result in light emission (149).

An important consideration in a diffusion flame is the fact that the hydrogen and air do not mix instantaneously. Consequently, such a flame contains spatial regions that are locally rich in H radicals and other spatial regions that are locally rich in O and OH radicals. Sample decomposition chemistry, the type of combustion products formed and the spatial distribution of light produced can

all have a strong dependence on whether the sample is introduced to the diffusion flame via the hydrogen gas stream or via the air gas stream (183). In the present work, sulphur dioxide from the generation cell enters the flame mixed with air. Consequently, sulphur dioxide initially is exposed to a flame region with an abundance of O and OH radicals and shortly thereafter they encounter a flame region with a large excess of H atoms. The environment of the flame can be described as consisting of a central core region rich in hydrogen atoms, surrounded by an outer periphery region with an abundance of O and OH radicals. Since the desired S₂ emission are well-known to occur in hydrogen-rich flame regions (183), the gas flow rates were chosen to maximise the spatial extent of the inner core of the flame.

(5.5) Generation of Sulphur Dioxide.

The sulphur dioxide can be created in a number of ways, depending upon the nature of the analytical sample. The most common way for light petroleum fractions would be by combustion in a lamp apparatus (204) and for heavier fractions by hot tube combustion. However, formed or occurring, the gas is first trapped in 0.02 M STCM/0.002 M EDTA solution, in which it is stable. The sulphur dioxide can then be released by acidification with hydrochloric acid:



The rate of evolution is affected by the acid concentration and by the speed of stirring of the solution in the generation vessel.

Normally, 1 ml acid was introduced into the empty generation cell and when purged, 1 ml sample was introduced by syringe through the rubber (subseal) septum.

The optimum acid concentration was established by changing the acid concentration from 0.1 to 6 M. Results are shown in Figure (5.9). It can be seen that the maximum peak intensity was obtained with acid strength above 2 M.

The rate of analyte solution and hydrochloric acid mixing is affected by the stirring. The speed of stirring was optimised while the purging air was only sweeping the cell and not bubbled through the solution. The results are shown in Figure (5.10). The fall off in emission intensity above the optimum stirring speed is due to the onset of splashing in the stirred solution. Although at optimised stirring speed the emission intensity was found to be maximum, the reproducibility was not satisfactory due to uncontrollable stirring. More reproducible and controllable conditions were achieved by using two small stirrer bars (1 cm long) rather than one. If the purging air was bubbled through the solution, rather than just sweeping the cell, improvements in peak height at the expense of peak width could be obtained. Bubbling the solution in the cell with the purging air (without using stirrer) enabled us to achieve signals as intense as those obtained using only stirrer without applying bubbling (Table 5.4). Adding the sample to the cell containing acid or reverse did not make any noticeable difference in the case of stirring alone. In the case of bubbling alone adding the sample to the acid improved the signal intensity by a factor of two compared to the reverse procedure (Table 5.4)

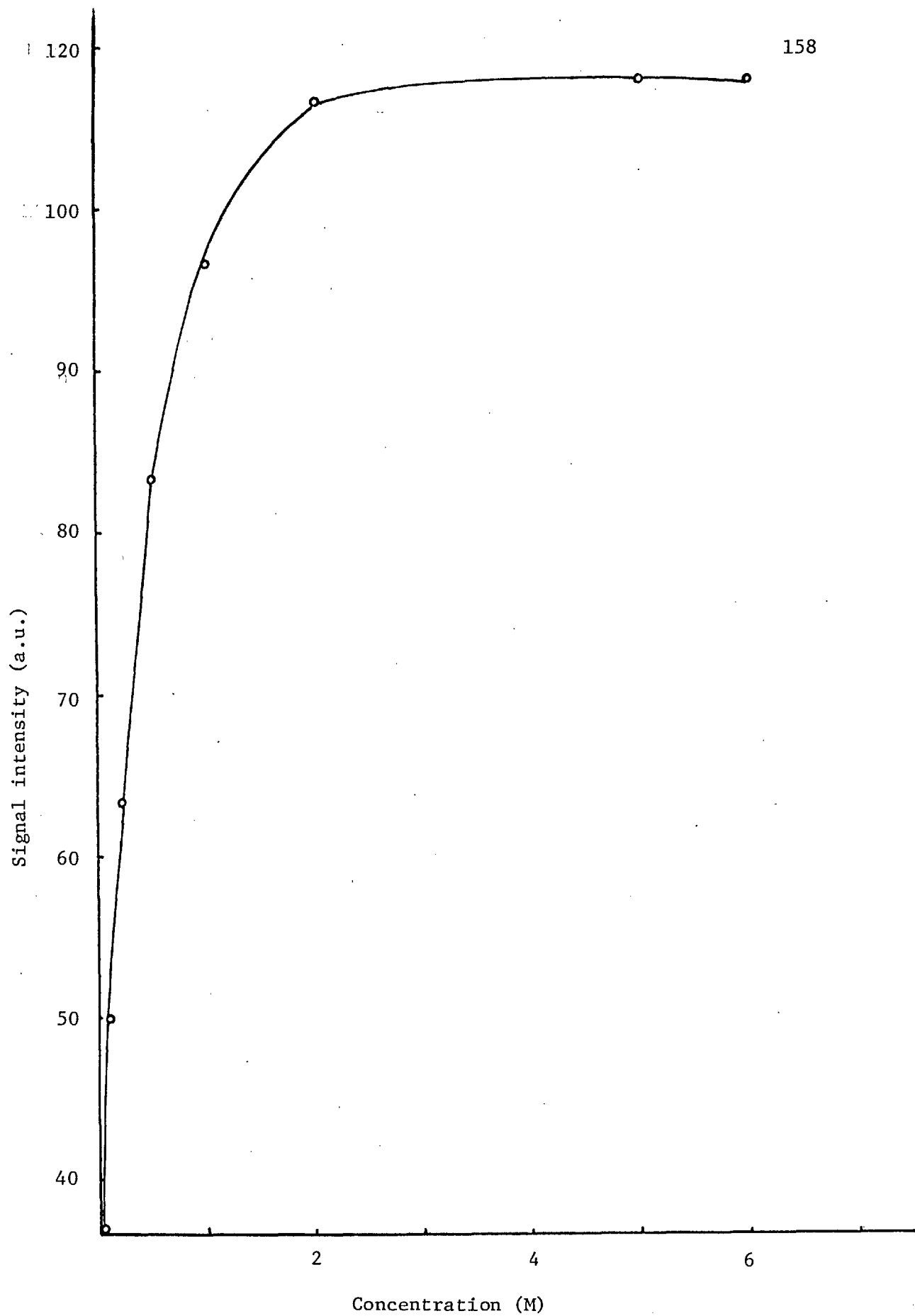


Figure (5.9)

Effect of hydrochloric acid concentration on signal intensity

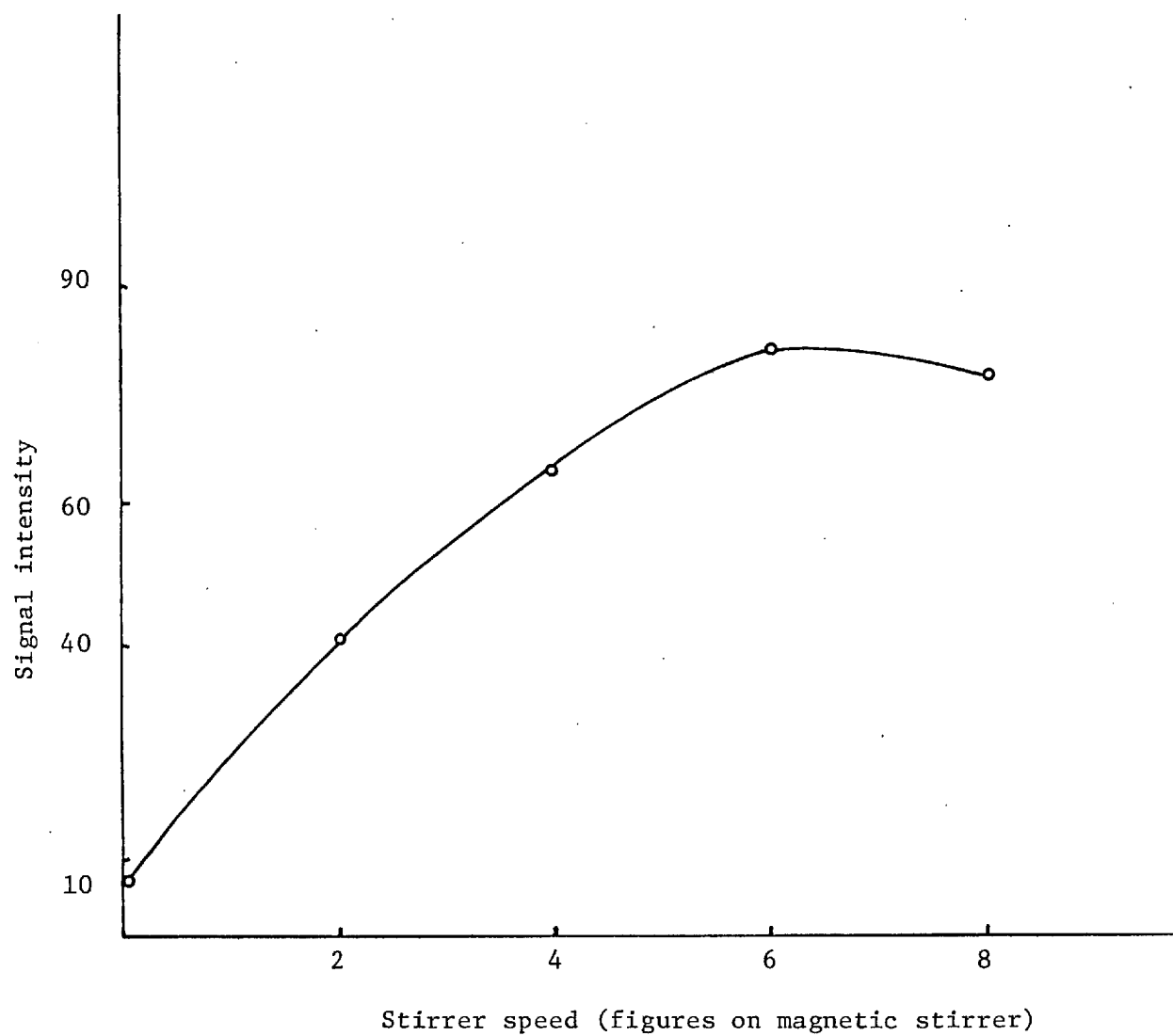


Figure (5.10)

Effect of stirring speed on signal intensity.

Table (5.4)Comparison of two used techniques of stirring and bubbling.

Method		Signal Intensity a.u.
Stirring alone	acid added to sample	35
	sample added to acid	35.2
Bubbling alone	acid added to sample	18
	sample added to acid	35.6

At the optimum conditions of acid concentration and stirring speed, the recorded signals were not reasonably sharp, 8 mm half-band width. It was thought that using an electronic integrator enables us to measure the signal with more accuracy. Using an electronic integrator (as shown in Figure 5.11) on the other hand caused the precision to change unfavourably. Using joint method of stirring and bubbling together, improvements in peak height at the expense of peak width could be obtained (Table 5.6). The reason for this could be the enhancement of the evolving rate of sulphur dioxide with using this joint method.

The solubility of sulphur dioxide is highly dependent upon temperature (Table 5.5). As we can see the solutbility of sulphur dioxide in water is four times lower at 40°C compared with that at

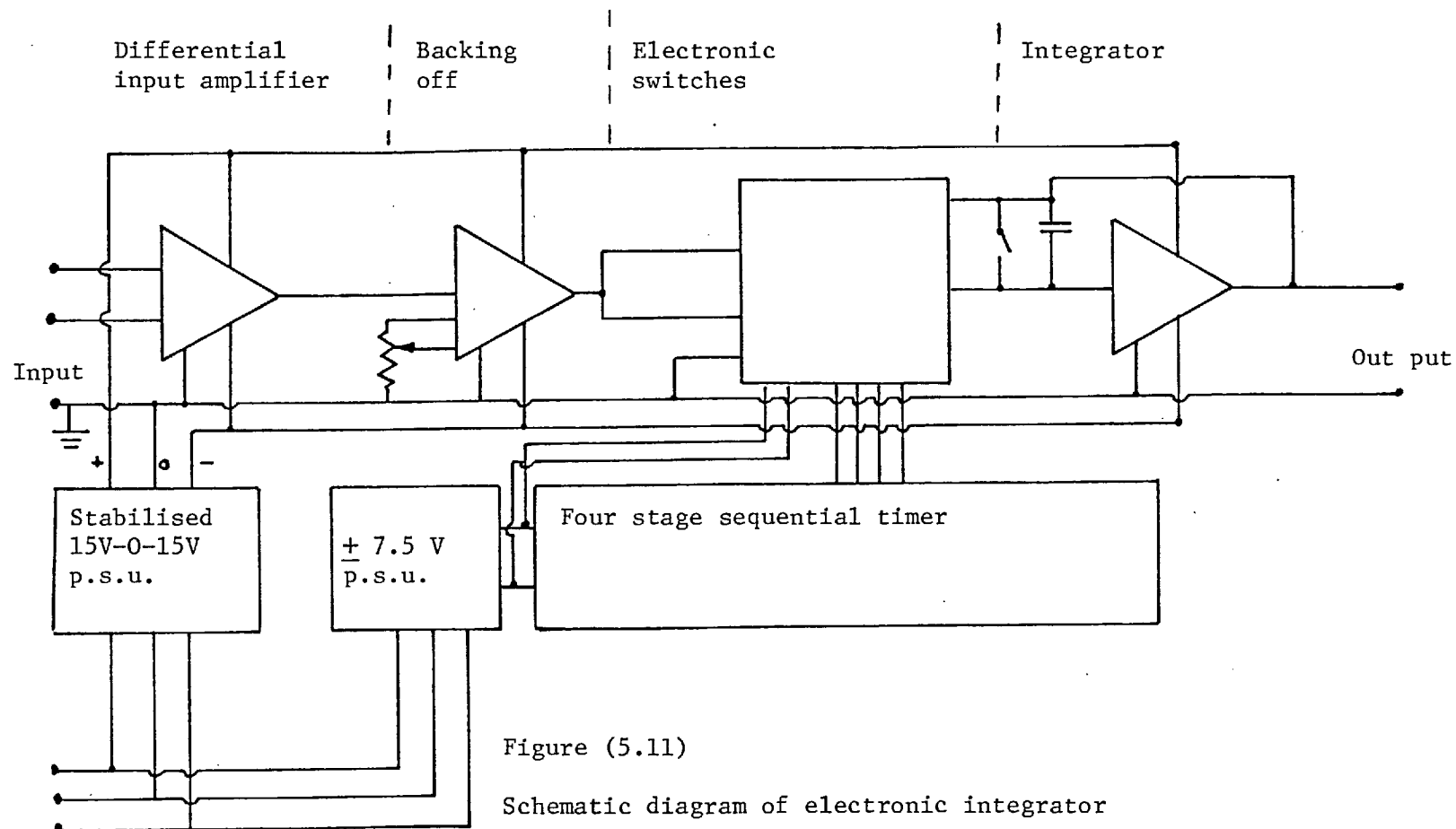


Figure (5.11)

Schematic diagram of electronic integrator

0°C. Heating the generation cell and hydrochloric acid to 50°C, using an electric heating tape, prior to introduction of the sample, in order to increase the rate of reaction (Table 5.3) and decrease the solubility of sulphur dioxide, resulted in further improvement (Table 5.6).

Table (5.5)

Solubility of Sulphur Dioxide in Water at Different Temperatures.

Solubility of sulphur dioxide in H ₂ O (Volumes) (71)	
0°C	68.6
10°C	51.4
20°C	36.2
30°C	26.8
40°C	17.0

Using optimum operating conditions (Table 5.7) the minimum detectable amount of sulphur was found to be 6 ng S present as sulphur dioxide in the 1 ml STCM sample aliquot. (Signal from 6 ng S = twice blank signal from distilled water/STCM).

Calibration curves, plotting I vs C and $\log I$ vs $\log C$, where I is the emission intensity and C the mass of sulphur present as sulphur dioxide, were constructed for aqueous sodium sulphite standard solutions (Figure 5.12 and 5.13).

Table (5.6)The Effect of Sample Mixing on Peak Emission Intensity.

Method	Normalised signal intensity from 80 ng S	
	peak height	peak area
2M HCl, bubbling alone cell temp. 22°C	100	100
2M HCl, bubbling alone cell temp. 50°C	200	101
2M HCl bubbling and stirring, cell temp. 22°C	163	102

The range of linearity of the $\log I$ vs. $\log C$ plot was 0.08 to 1.8 $\mu\text{g S}$ in 1 ml sample aliquot. The slope of calibration ($\log I$ vs. $\log C$) was 2. This leads support to the concept that the equation (3.12) again can be considered as an equation between I and C .

(5.6) Analysis of light distillates.

In order to check the applicability of the method, sulphur in some light distillates, previously analysed by B.P. Research Ltd., using X-ray fluorescence (XRF), was determined. The samples were burned in a lamp apparatus following the ASTM procedure D 1266 (101). Air was drawn through the system at 250 ml/min and the sulphur dioxide collected. Passing the air through the absorber solution containing

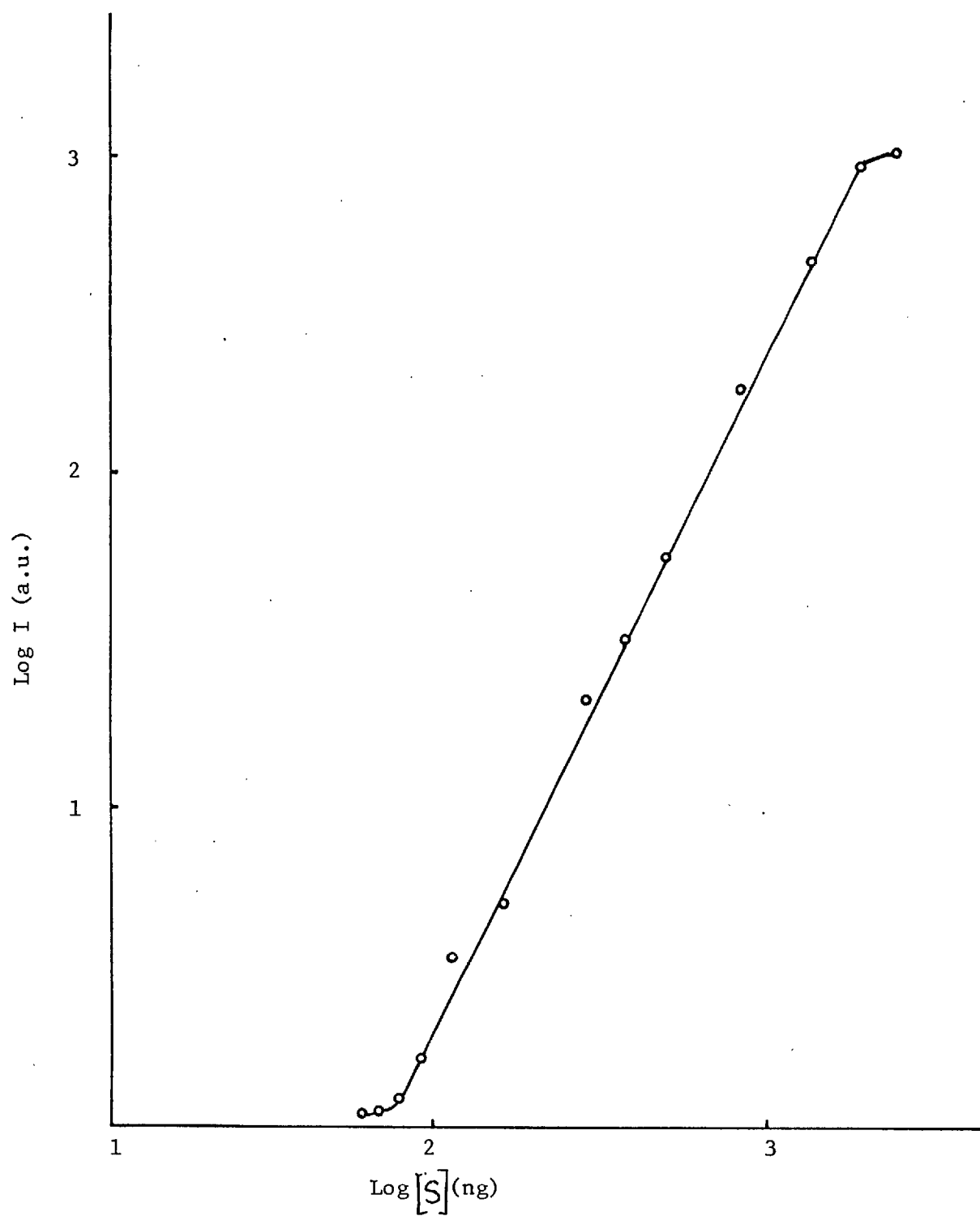


Figure (5.12)

Calibration curve for aqueous solution.

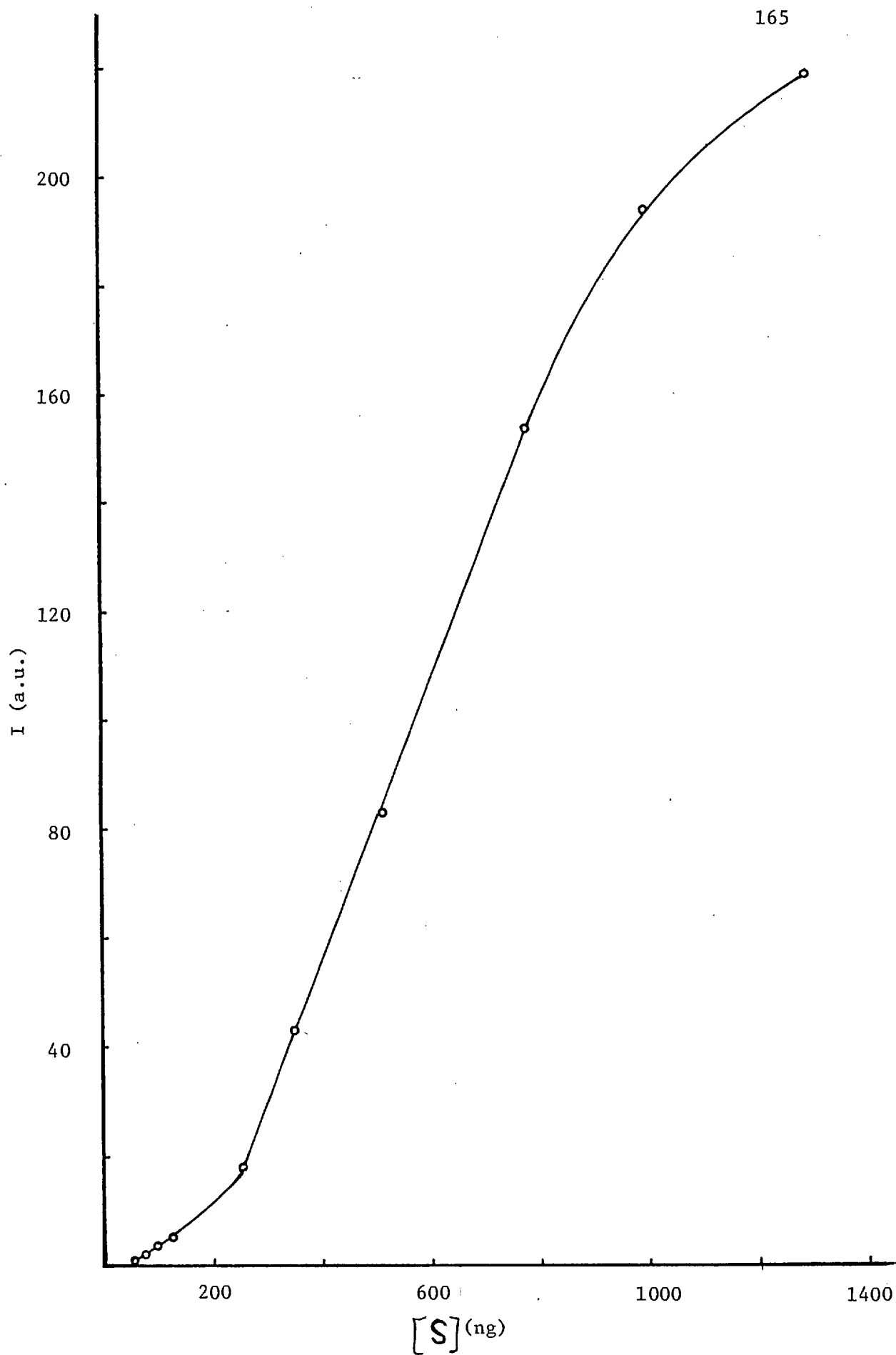


Figure (5.13)

Calibration curve for aqueous solution

Table (5.7).Experimental Parameters.

Hydrochloric acid conc.	2M
Emission wavelength	384 nm
Hydrogen flow rate	0.150 L/min
Argon flow rate	0.980 L/min
Air flow rate	0.250 L/min
Restrictor Tube Dimensions (mm)	
Width	18
Length	145
Orifice diameter	5

sulphur dioxide is likely to oxidise it. Haller (213) has shown that the addition of glycerol inhibits the chain reaction mechanism by which free sulphur dioxide is oxidised and its addition to the STCM/EDTA solution showed a noticeable increase in recovery (Table 5.8). In these recovery tests 0.1 and 1 ppm S as sulphite were fixed in the STCM solution and the gases from a 40 min combustion of pure 60°C - 80°C boiling range petroleum ether (60-80 pet. ether) in the lamp apparatus drawn through the solution. The absorbing solution was then analysed. Just as important is the correct buffering of the absorbing solution; the addition of a sodium dihydrogen orthophosphate/disodium hydrogen orthophosphate buffer increased the recovery of sulphur dioxide markedly. Increasing the STCM concentration from 0.02-0.2 M had some effect on the recovery (Table 5.8) and the absorbing solution adopted for this work was 0.2 M STCM/0.002 M EDTA/0.02 M NaH_2PO_4 /0.025 M Na_2HPO_4 /2% V/V glycerol; having a pH of 6.8-6.9.

Five ml samples of the light distillates diluted with 60-80 pet. ether, to bring them in the correct concentration range, were burned in the lamp apparatus and the combustion gases scrubbed in 50 ml of the absorbing solution which was then analysed. The sulphur content was calculated from peak emission intensity calibration curves (Figure 5.14) prepared from solutions of tert-butyl disulphide in 60-80 pet. ether treated in the same manner. The results obtained are shown in Table (5.9) and are in good agreement with those obtained by XRF. Replicated analyses revealed a $\pm$ 5% r.s.d. on the method.

Table (5.8).

The Efficiency of Various Absorbing Solutions.

Absorbing Solution	pH of Solution		Recovery (%)	
	Before combustion	After combustion	0.1 ppm S added	1 ppm S added
0.1 M STCM	5.2	2.6	70	75
0.1 M STCM/ 0.002 M EDTA	4.6	2.6	80	80
0.1 M STCM/ 0.002 M EDTA/ 2% v/v glycerol	4.6	2.5	85	87
0.1 M STCM/ 0.002 M EDTA/ 2% v/v glycerol phosphate buffer	6.8	6.8	99	100
0.2 M STCM/ 0.002 M EDTA/ 2% v/v glycerol phosphate buffer	6.75	6.85	99	100
0.1 M STCM/ 0.002 M EDTA/ 3% glycerol phosphate buffer	6.80	6.35	98	98
0.02 M STCM/ 0.002 M EDTA/ 2% v/v glycerol phosphate buffer	6.8	6.8	94	96

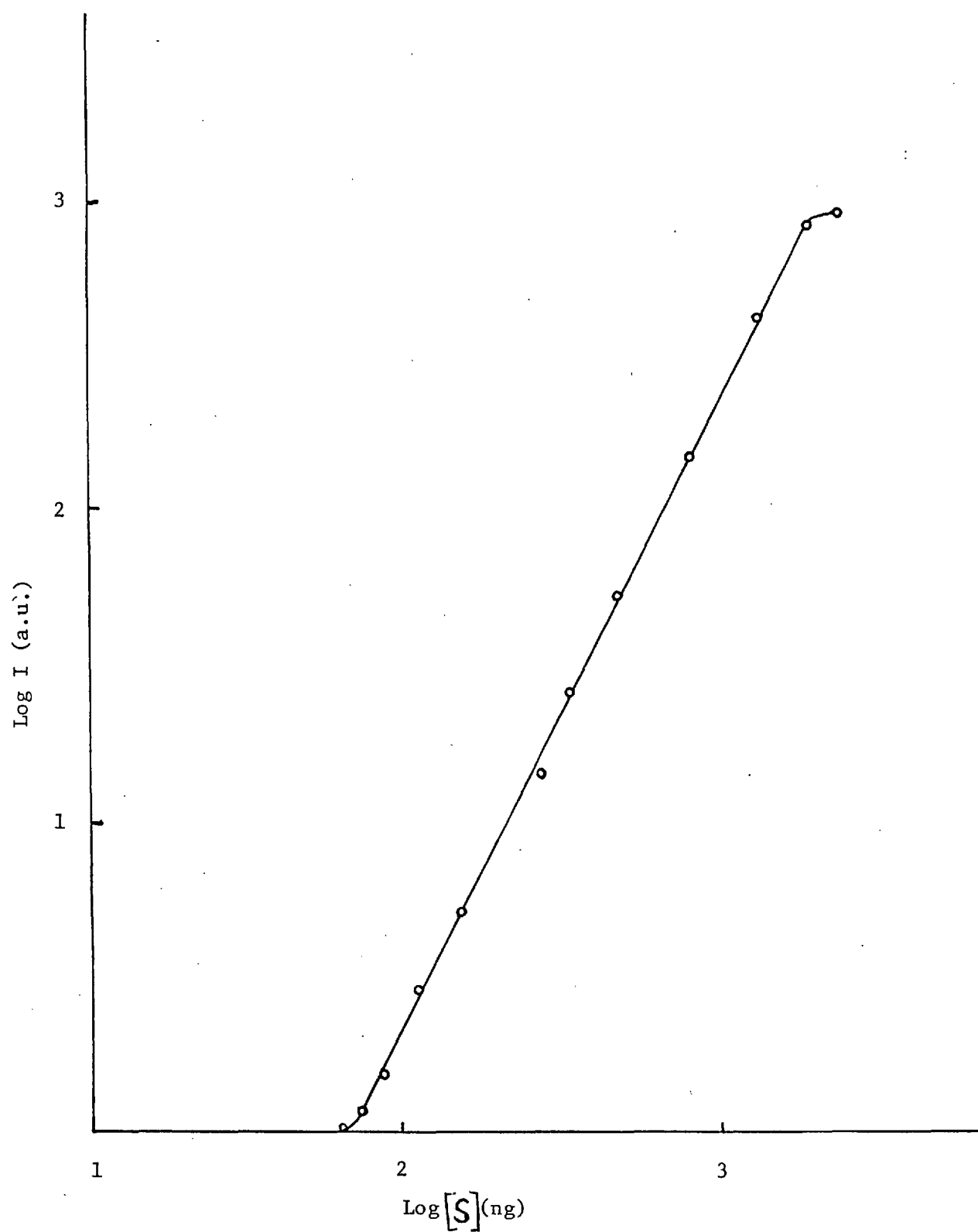


Figure (5.14)

Calibration curve for organic solution.

Table (5.9)Real Sample Analyses.

Sample	% S given*	% S found
7845	0.17	0.14
7846	0.08	0.06
7913	0.22	0.19
7914	0.21	0.19
7935	0.24	0.22
7950	0.12	0.15
7957	0.11	0.12
7968	0.03	0.023
8053	0.95	1.05
8110	0.26	0.23
* Data supplied by B.P. Research		

(5.7) Comparison between H₂S and SO₂ technique.

The method used in this Chapter, SO₂-technique, has some advantages over the method used in Chapter 3, H₂S-technique, as follows:

1. The minimum detectable amount of sulphur was found to be 0.006 ppm S present as sulphur dioxide and 0.01 ppm S present as hydrogen sulphide in SO₂- and H₂S-technique respectively.
2. 10 replicate analyses of aqueous samples revealed $\pm 3\%$ and $\pm 4\%$ r.s.d. on the SO₂- and H₂S-technique respectively.
3. Sulphur dioxide is introduced into the flame via the outer tube of the burner (The flame is not connected to the generation cell directly and the flame is less affected by the changing the conditions inside the cell) which enables us to employ the bubbling technique together with the stirrer. Employing the joint stirrer and bubbling (in SO₂-technique) increases the efficiency of stirring and makes the conditions of stirrer to be less critical in the SO₂-technique (compare Figures 5.10 and 3.7) than that in H₂S-technique.

In the H₂S-technique, applying bubbling causes multiplicity in peaks. Changing the sample size causes no significant problem in the SO₂-technique but introduces pressure changing problem in the H₂S-technique.

4. Stability of stock solutions do last for one week and one month respectively in H₂S- and SO₂-technique.

(5.8) Conclusion:

The SO₂-technique provides another means of determining sulphur

down to very low levels in organic matrices. Those compounds which, by nature of their reactive groups, are not amenable to determination by metal reduction methods can be analysed by this method.

The determination of sulphur in petroleum products by combustion, concentration of the sulphur dioxide in sodium tetrachloromercurate solutions and cool flame molecular emission is described. Improvements in burner design and optimisation of analysis conditions result in a minimum detectable amount of 6 ng sulphur. Perhaps of more interest, however, is the application of the technique to atmospheric determinations which will be discussed in the next Chapter.

CHAPTER 6

Atmospheric Sulphur Dioxide Determination.

(6.1) Introduction.

Among the different oxides of sulphur only sulphur dioxide and sulphur trioxide are of any importance as gaseous air pollutants (220). Sulphur trioxide is generally emitted with sulphur dioxide at about 1-5% of the sulphur dioxide concentration (221). Sulphur dioxide is oxidized readily by atmospheric oxygen in aqueous aerosols. Heavy metal ions in solution catalyse the reaction which stops when aerosols become acidic (222). Kellogg, et al., have estimated the world wide emission of sulphur dioxide to be about 100 megatons at present (223) and about 275 megatons for the year 2000. Much of this arises from the combustion of fossil fuels, industrial processes such as smelting, sulphuric acid manufacture and petroleum refining. Sulphur is present in significant quantities in coal (up to about 6%) and oil (up to about 4.5%). Except possibly for coal burned on grates at least 90% of the sulphur in fuel is emitted as sulphur oxides in the flue gas (220).

Sulphur dioxide has a relatively low toxicity and possesses the inherent safety factor of a pungent odour. Danger of acute

intoxication is slight, since one will not voluntarily tolerate an immediately toxic concentration.

Sulphur dioxide generally accelerate metal corrosion by forming sulphuric acid either in the atmosphere or on the metal surface. Temperature and relative humidity influences corrosion rates significantly. At relative humidity more than 70% the corrosion rate is greatly increased (224). Sulphurous or sulphuric acids are capable of attacking a wide variety of building materials, including limestone, marble, roofing slate and mortar. Textiles made of nylon, especially nylon hose, are also susceptible to pollutants in the atmosphere. Weakening is apparently caused by sulphur dioxide or by sulphuric acid aerosol (225).

The sulphur dioxide causes damage to nucleic acids in several ways. High sulphur dioxide concentration in the atmosphere lead to the major air pollution disasters that occurred earlier in big cities such as the London smog (1911) causing many deaths (226).

Analytical methods such as, volumetry, conductimetry, amperometry, spectrophotometry, MECA, iodimetry and flame photometry have been used for the determination of atmospheric sulphur dioxide.

In the volumetric method the atmospheric sulphur dioxide is absorbed and oxidized to sulphate by aspirating an air sample through a hydrogen peroxide solution; the sulphate formed is titrated with 0.005 M barium perchlorate either in aqueous

solution using chlorophosphonazo(III) as indicator (227) or in 80% isopropanol solution employing thorin indicator (228) (0.1-11 ppm). Budesinsky (227) has claimed that the standard deviation of the chlorophosphonazo method is four times smaller than that of the thorin method.

The conductimetric method (229) depends upon the increase in the conductivity of a dilute acidified hydrogen peroxide solution in deionized water created by dissolved sulphur dioxide. Carbon dioxide and any gas or particulate which finds its way into the cell and increases the conductivity will cause a positive error. Similar criticism could be directed towards the amperometric method in which the current required to regenerate the oxidant (iodine or bromine) reacting with sulphur dioxide is measured (230). Again, certain substances such as fine particulate matter, ozone, nitrogen oxides, organics such as unsaturated hydrocarbons and aldehydes, hydrogen sulphide and organic sulphur compounds are potential interferents (230).

In the iodimetric method the sulphur dioxide is collected in an impinger containing a standard solution of sodium hydroxide. After the sample has been collected the absorbing solution is acidified and the liberated sulphurous acid is titrated with standard iodine solution (231). This method is not specific for sulphur dioxide since the method responds to the total reducing gases present in the sample, including hydrogen sulphide and methyl mercaptan (231).

One of the atmospheric sulphur dioxide determination method is the West and Gaeke method (209). In this method, atmospheric sulphur dioxide is removed and concentrated by scrubbing through 0.1 M sodium tetrachloromercurate; the stable and non-volatile disulphitomercurate is formed. The subsequent determination of the isolated sulphur dioxide is based on the red violet colour produced when pararosaniline hydrochloride-hydrochloric acid mixture and formaldehyde are added to the sampling solution. Interfering heavy metals such as Fe(III), Cr(III) and Mn(II), can be complexed by adding EDTA to the sample solution (232). Concentrations of nitrogen dioxide in amounts exceeding 2 ppm induce a fading of test colours and, therefore, can not be tolerated. The ability of sulphamic acid to decompose nitrites has been utilized to remove interference by these species (233).

Scaringelli, et al., (232) introduced improvements in the West and Gaeke method. Especially pure pararosaniline was employed and phosphoric acid was used in the final colour development to control pH and to complex heavy metals. They reported that these improvements yield greater sensitivity, greater reproducibility and a larger working range; up to 43 µg sulphur dioxide compared with only 16 µg in the original method.

Stephens and Lindstrom (234) recommended an alternative spectrophotometric method for the determination of sulphur dioxide based on the reduction of Fe(III) by sulphur dioxide in the presence of 1,10-phenanthroline and subsequent formation of tris-1,10-phenanthroline Fe(III).

Attari, et al., (215) claimed that although the pararosaniline method is quite sensitive and specific, it requires very close controls to achieve satisfactory precision. They modified the Stephens-Lindstrom method (234) by introducing acetate ion for the formation of a labile Fe(III) acetate phenanthroline species. The amount of sulphur dioxide in the atmosphere was determined by passing 50 or 25 l of air at the rate of 2.2 L/min through a 25 ml aliquot of the reagent solution and measuring the absorbance at 510 nm. As little as 2 µg of sulphur dioxide per 25 ml have been determined. Hydrogen sulphide interferes seriously and must be removed, chloride interferes if present in excess of 100 ppm.

Kouimtzis (216) used MECA in a new method for the determination of sulphur dioxide in air. The method is based on the absorption of sulphur dioxide in 0.5 l of air by a 20-40 mg of silica gel which is then deposited into a cavity. The cavity is introduced into a hydrogen/nitrogen/air flame and the S₂ emission is monitored. The calibration curve covers the range 5-120 ng sulphur dioxide. The detection limit, corresponding to a signal/noise of 2 to 1 was found to be 3 µg sulphur dioxide. The standard deviation for the determination of 58 ng sulphur dioxide was ± 2.5 ng. The interfering compounds, such as sulphuric acid mist, mercaptan vapours, and vapours of various organic solvents can be removed by passing the air sample through glass tubes packed with glass fibre filter paper, copper sulphate and paraffin wax plus magnesium perchlorate respectively. Hydrogen sulphide can be

removed by purging the absorbtion tube with 0.5-1 l of purified air.

Crider (165) described the use of a flame photometric detector for the monitoring of atmospheric sulphur dioxide for the first time. Crider's apparatus required large volumes of hydrogen and air to achieve sub-ppm detection levels, and the system response to sulphur dioxide was approximately linear between 0.3 and 1.2 ppm. Every other sulphur compound present in the air sample interfered.

Stevens, et al., (159) for areas where hydrogen sulphide may co-exist with sulphur dioxide, offered a scrubber as an accessory, usually silver - heated to 135°C, to remove hydrogen sulphide without removing sulphur dioxide.

Minute amounts of pollutants like hydrogen sulphide, methyl thiol, dimethyl sulphide, dimethyl disulphide and sulphur dioxide present in the atmosphere have been determined using an exponential dilution flask to collect all the sulphur compounds except sulphur dioxide. These compounds are then oxidised in an electric furnace to sulphur dioxide which is then passed into a cool-flame detector (199). The sulphur dioxide was removed by passing the air through a Teflon tube, containing sodium bicarbonate before the furnace oxidation stage. A calibration curve was obtained for the concentration ranges of 0.3 to 5 ppb sulphur dioxide.

Stevens, et al., (144) have extended the specificity of flame photometric detector by coupling a special gas chromatograph column to the detector. The column is capable of separating

atmospheric concentrations of individual sulphur compounds, including sulphur dioxide, hydrogen sulphide, simple mercaptans, and organic sulphides. The column packing in this method introduces some problems: packing (144); the need for special treatment (217) or careful coating procedures (179). All of these disadvantages can be largely avoided by the use of a column packed with 2,6-diphenyl-p-phenylene oxides (218).

Sulphur dioxide has been detected at a concentration of 0.25 ppm using this column without resort to the larger sample volumes (10 ml) that would be necessary for lower concentration.

Considering the nearly 100% absorbtion efficiency of sodium tetrachloromercurate solution toward sulphur dioxide (209) and the rapid regeneration rate of sulphur dioxide by hydrochloric acid, the use of this absorber coupled with cool flame photometry, was applied to atmospheric sulphur dioxide determination.

(6.2) Experimental:

Sodium tetrachloromercurate (TCM) as sulphur dioxide collecting solution and sodium sulphite as standard solution were prepared following the procedure described in Chapter 5.

The arrangement of burner, sheath and all other parameters used were the same as those described in the previous Chapter except the SO₂-generation vessel which was bigger, was wrapped in a heating tape and connected to a condenser as illustrated in Figure (6.1).

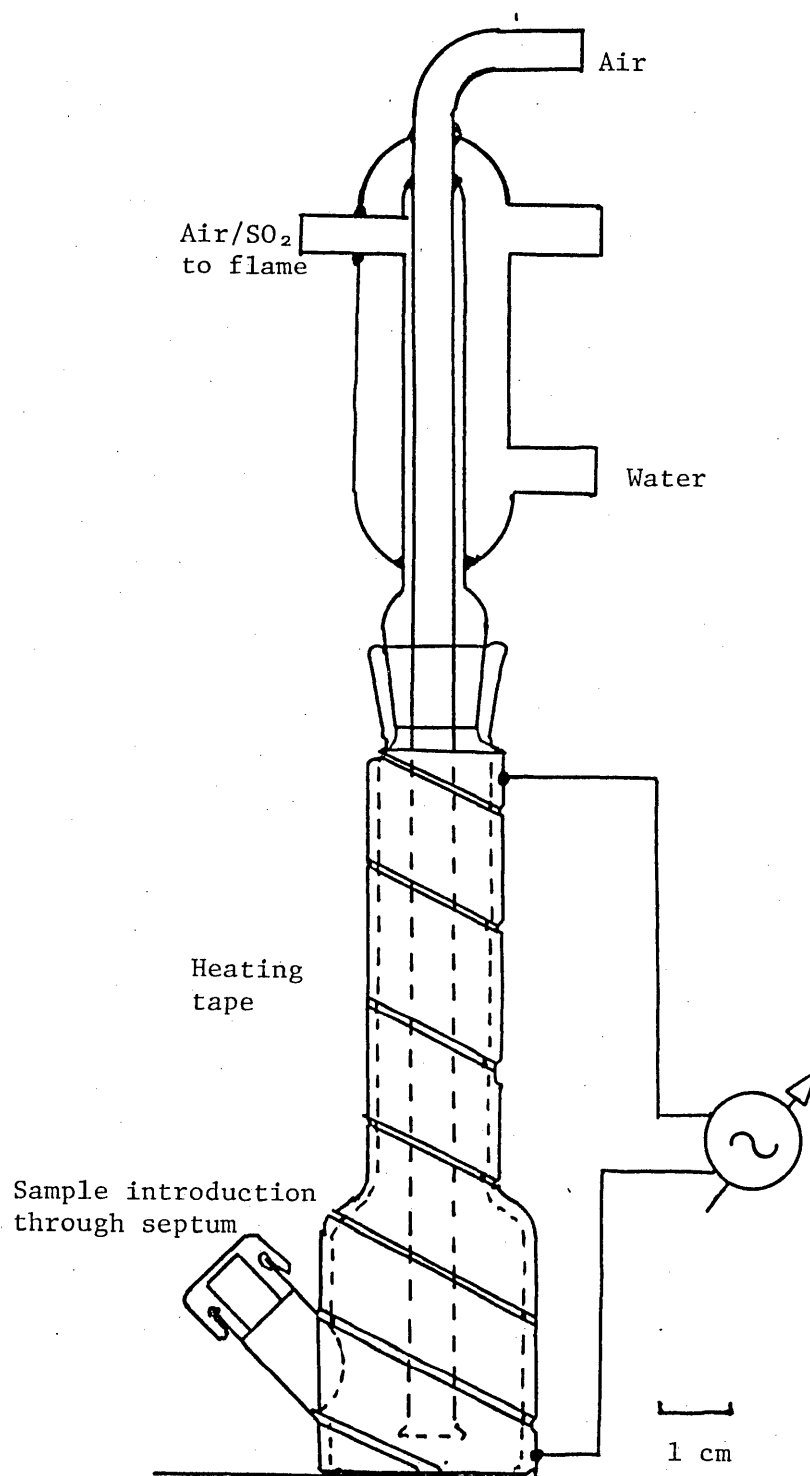


Figure (6.1)

Generation vessel

(6.3) Procedure.

Sampling: A sample of 30I was collected at the rate of 1 L/min through a small fritted bubbler containing 10 ml 0.02 M TCM and 4 mg EDTA (disodium salt).

When sampling was completed 1 ml 0.6% sulphamic acid was added and shaken for 10 minutes to destroy any nitrite originating from dissolved oxides of nitrogen.

Analysis: A 5 ml of sample aliquot was introduced via the septum into the SO₂-generation vessel, which contains 1 ml concentrated hydrochloric acid. The regenerated sulphur dioxide was swept out of the vessel into the hydrogen/argon flame with air and the S₂ radiation emitted from the flame measured, as described previously.

(6.4) Results and Discussion:

As was described in the previous Chapter, heating the SO₂-generation vessel with heating tape increases the rate of the sulphur dioxide regeneration and consequently makes the emission intensity peaks sharper.

The steam produced, however, must lower the flame temperature and finally decrease the sensitivity, since the flame temperature is at least twice that of the steam entering it.

In order to prevent the steam reaching the flame a condenser, as illustrated in Figure (6.1), was employed.

The heating was found to be more effective in present work in which a sample size of 5 ml was used than in the previous experiments when only 1 ml aliquots were employed.

Applied temperatures were optimised by changing the temperature from 20^o to 100^oC. The results are shown in Figure (6.2). Applying temperature more than 80^oC produces too much steam which will be beyond the capacity of small used condenser to condense it into water and prevent it to reach the flame.

In order to make the heating process reproducible the duration of each sample analyses was kept constant, 3 minutes, and samples were analysed immediately after each other.

(6.4.1) Optimisation of Sampling Parameters.

In all of the following experiments sulphur dioxide was washed from the air by passing it through the TCM solution prior to the absorbtion solution.

Sample solutions of different concentration of TCM (0 to 0.1 M) conatining varying amounts of sulphur dioxide, as sodium sulphite, were prepared. A 10 ml aliquot of each sample was transfered to a frit bubbler and aerated at a rate of 1 L/min for 30 mins. After adding 1 ml 0.6% sulphamic acid (as recommended by West and Ordovza (233)) 5 ml of the sampel was analysed following the procedure described previously (Section 6.3).

The results are shown in Table (6.1). No significant losses were detected in samples containing as little as 0.01 M TCM, whereas the samples without TCM lost as high as 60% of the added sulphur dioxide. This experiment was then repeated with samples containing as little as 0.001 M TCM and no appreciable loss of sulphur dioxide was detected. However, increasing ionization of

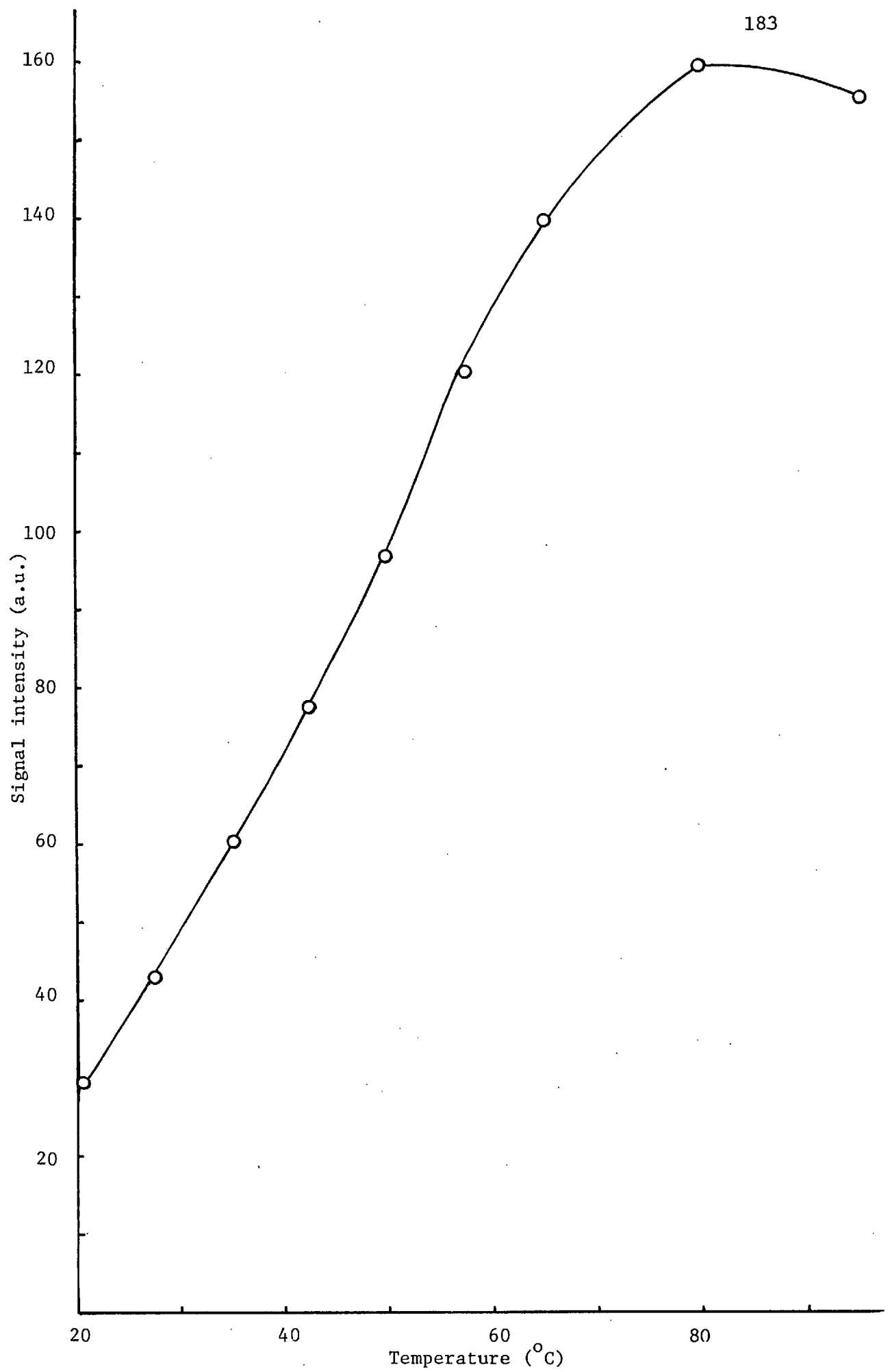


Figure (6.2)

Effect of heating on signal intensity.

Table (6.1)

The Effect of TCM Concentration on Stability of Sulphur Dioxide
in Aqueous Solution.

Concentration of TCM	Sulphur Dioxide content, $\mu\text{g}/10\text{ ml}$	Sulphur Dioxide recovery, %
0.00	10	48
	20	42
	50	40
0.01 M	10	97
	30	98
	50	95
0.02 M	10	98
	50	99
	100	98
0.1 M	20	99
	50	98
	100	99

the TCM in dilute solution reduces the pH and hence, reduces the collection efficiency (232).

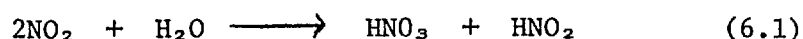
In order to optimise the flow rates and aeration time of air sampling a set of samples containing 10 µg sulphur dioxide as sodium sulphite in 10 ml 0.02 M TCM were aerated with varying combination of flow rates and aeration times. The results in Table (6.2) indicate that there is a direct relationship between the volume of air sampled and the amount of sulphur dioxide which is recovered.

(6.4.2) Interferences:

Nitrite: In order to illustrate the effect of nitrogen oxides on sulphur dioxide analyses two sets of samples containing sulphur dioxide as sodium sulphite and varying amounts of nitrite as sodium nitrite in 0.02 M TCM were prepared and to each sample of one set 1 ml of 0.6% sulphamic acid was added, then samples of both sets were analysed following the analysing procedure. The results are shown in Figure (6.3).

Nitrogen dioxide interferes in the colorimetric determination of atmospheric sulphur dioxide, inducing a fading of test colours.

In the present work the mechanism of interference is different. Wilkinson and Cotton (219) stated that nitrogen dioxide reacts with water,



and the nitrous acid produced is not stable, particularly on warming and produces nitric oxide

Table (6.2).The Effect of Aeration Volume and Time on Dichlorosulphitomercurate.

<u>Air Flow rate L/min</u>	<u>Aeration Time (min)</u>	<u>Air Volume (L)</u>	<u>Sulphur Dioxide recovery, %</u>
0.2	30	6	100
	60	12	98
	90	18	99
0.6	15	9	98
	30	18	100
	60	36	98
	90	54	91
1.00	30	30	99
	45	45	94
	60	60	90
	90	90	89
1.5	30	45	92
	60	90	87
	90	135	80

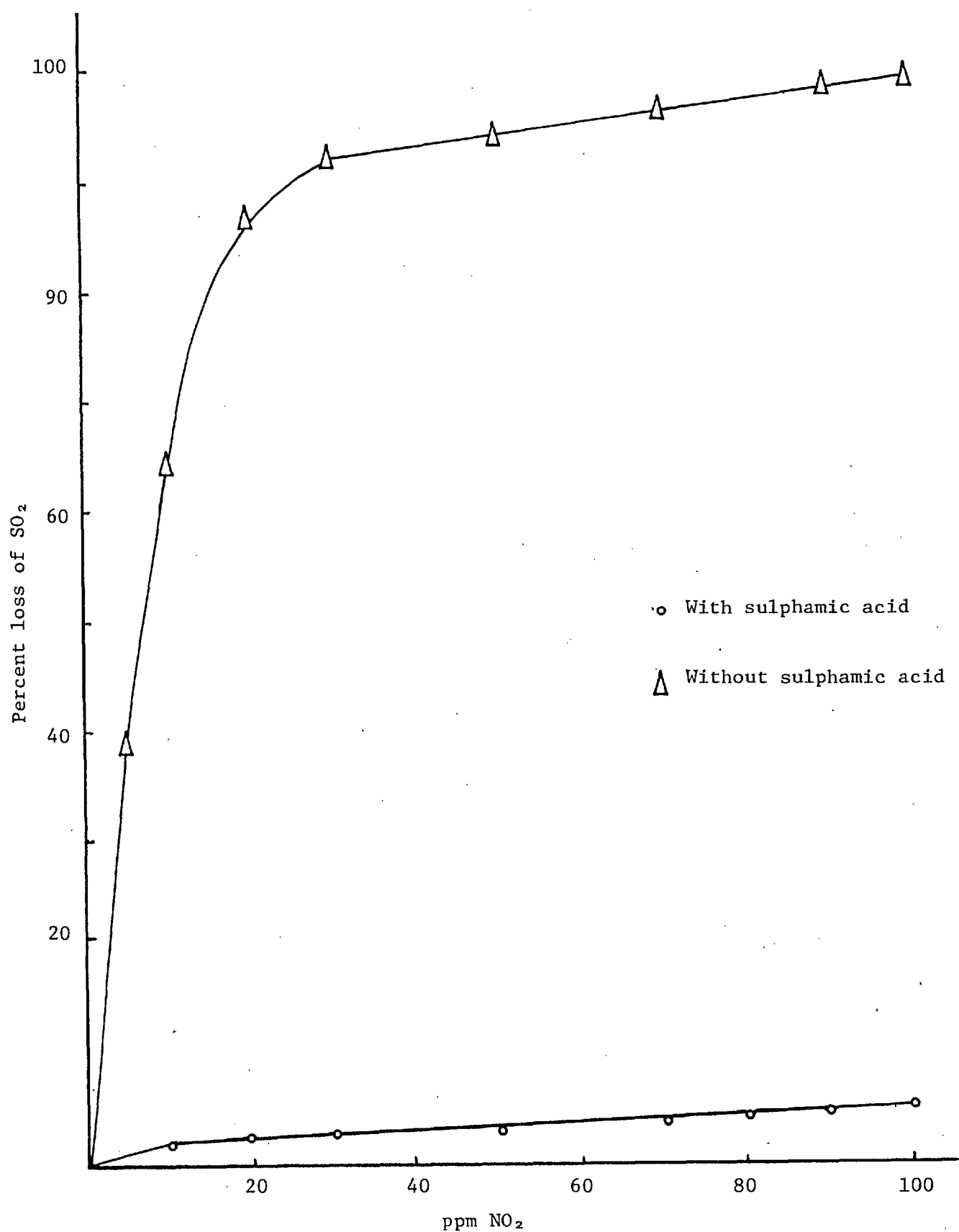
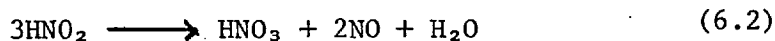


Figure (6.3)

Effect of nitrogen dioxide on the recovery of 1 ppm sulphur dioxide in presence and absence of sulphamic acid.



This nitric oxide is swept out of the SO₂-generation vessel, by the air, into the flame and quenches the S₂ emission.

The oxidising properties of nitrous acid are not observed since sulphamic acid was added just before analysing the sample and a long time after adding sodium nitrite.

Decomposition of nitrite by sulphamic acid takes place quantitatively and rapidly, releasing nitrogen (233)

Heavy Metals: The presence of heavy metals is not only effective during the aeration but they also interfere during the regeneration of sulphur dioxide in the vessel.

Salts of heavy metals [Fe(II), Fe(III), Cr(III), Mn(II), and Cu(II)] were added in increasing quantities to solutions of sodium sulphite in 0.02 M TCM, both with and without the presence of EDTA. A 10 ml portion of each solution containing 10 µg sulphur dioxide as sodium sulphite, was aerated in a sintered bubbler for 30 mins at the rate of 1 L/min with purified air.

All of the samples were analysed following the described analysing procedure after adding 1 ml 0.6% sulphamic acid to each solution and shaking for 10 minutes. The results are shown in Table (6.3).

No significant interferences were found (signal depression less than 6%) with 200 µg Fe(II), Mn(II) and Cu(II). Significant interferences were found with even 10 µg Fe(III) which may be

Table (6.3)

Heavy Metals Interference Effects.

Metal Compounds added	Metal Concentration $\mu\text{g}/10\text{ ml}$	EDTA Concentration $\text{mg}/10\text{ ml}$	Signal Supression %
FeCl_3	10		92
	20		98
	50		100
	10	2	4
	50	2	6
	200	2	23
	200	4	0.00
$\text{FeSO}_4, 7\text{H}_2\text{O}$	20		2
	200		3
	20	1	2
	200	2	2
$\text{CrCl}_3, 6\text{H}_2\text{O}$	10		15
	20		32
	50		50
	200		70
	20	1	3
	200	2	2
$\text{CrK}(\text{SO}_4)_2, 12\text{H}_2\text{O}$	20		2
	200		2
	20		0.00
	200		2
$\text{MnCl}_2, 4\text{H}_2\text{O}$	20		2
	200		5
	20	2	0.00
	200	2	2
CuSO_4	20		2
	200		8
	20	1	2
	200	2	0.00

due to the oxidation effect of Fe(III) on sulphur dioxide.

The interference effects produced by chromic chloride were found to be significant which is probably due to the fact that chromic chloride is a powerful oxidizing agent. Chromic chloride does not dissolve at a high rate in pure water, but in the presence of Cr(II) or other reducing agents which can generate some Cr(II) from the chromic chloride it dissolves readily (219).

(6.5) Conclusion.

The maximum reported values in the atmosphere for Fe, Mn, Cu and Cr were 22, 9.98, 10 and $0.24 \mu\text{g}/\text{m}^3$, respectively (232). These metal concentrations should not produce significant interference with the method as outlined, however, addition of EDTA is recommended when low levels of sulphur dioxide are to be measured or when contamination by heavy metals is unusually high. As much as $3 \text{ mg}/\text{m}^3$ nitrogen dioxide in air does not interfere in the presence of sulphamic acid.

The method is quite sensitive and the minimum detectable signal was found to be that due to 5 ml 0.002 ppm S which means that as low as about $1.2 \mu\text{g}/\text{m}^3$ sulphur dioxide in air can be detected.

CHAPTER 7

(7.1) Conclusions and Suggestions for Further Studies.

(7.1.1) Conclusions.

The recent emphasis upon low sulphur and sulphur-free products to minimise corrosion and pollutions, as well as the need for low sulphur feeds to refining processes using sensitive catalysts, has spurred the investigation of total sulphur measurements at ppm levels. Methods such as colorimetric, turbidimetric, X-ray spectrometry and coulometric are more often used for the measurement. The X-ray technique gives rapid and useful analysis, but the technique is sample matrix dependent, coulometric suffers from high cost and the analysis time increases to about two hours in colorimetric and turbidimetric methods.

The work presented in this thesis shows that the cool-flame molecular emission is a simple and sensitive technique for total and individual sulphur compounds determination.

Although the individual sulphur compound's determination can be performed down to low detection limits, total sulphur determination is associated with problems which are mainly due to the fact that flame molecular emission intensity of different sulphur compounds are different. These problems have been overcome by conversion of all sulphur compounds in the sample to a single intermediate (hydrogen sulphide or sulphur dioxide) and removing this intermediate from interfering matrix.

Conditions for the determination of sulphur in petroleum products, by sodium reduction, sulphide generation and chemiluminescent emission determination, have been optimised. An improved method of reduction involving refluxing of the product with sodium is described which results in a 90-95% recovery of sulphur and exhibits good accuracy and precision. Using hydrogen sulphide as the intermediate has shown that there are certain attractive features; storage of the gas in sodium hydroxide permits pre-concentration, the low solubility of hydrogen sulphide in acid solution; formation of hydrogen sulphide by metal reduction can impart selectivity to the method permitting a degree of speciation. The SO_2 -technique provides another means of determining sulphur down to very low levels in organic matrices. The determination of sulphur in petroleum products by combustion of sample in a wick lamp, concentration of the sulphur dioxide in sodium tetrachloro mercurate solution and cool-flame molecular emission is described in Chapter 5. Improvements in burner design and optimisation of analysis conditions result in a minimum detectable amount of 6 ng sulphur.

The use of sulphur dioxide as an intermediate does offer certain advantages over hydrogen sulphide in general (better sensitivity and precision) and in particular applications (for determinations where the matrix is reactive, for example, fatty acids or long chain esters, the use of sodium or acid/zinc as reductant to liberate hydrogen sulphide is precluded due to the formation of a soap.

The combination of Devarda's Alloy reduction of sulphur compounds in petroleum products coupled with release of hydrogen sulphide into a cool flame and measurement of the S_2 emission provides a useful method for the separate determination of sulphur species. With selective separation of the species, mercaptans with acrylonitrile (201), hydrogen sulphide with silver nitrate and sulphur with mercury, these species can all be analysed separately.

Another feature of SO_2 -technique is its application in atmospheric sulphur dioxide determination. The method is quite sensitive and simple. The minimum detectable signal was found to be that due to 5 ml 0.002 ppm S which means that as low as about $1.2 \mu\text{g}/\text{m}^3$ sulphur dioxide in air can be detected.

(7.2) Suggestions for Further Studies:

Most analytical procedures can benefit by becoming, at least partly, automated. The precision of H_2S -technique could be improved by controlling the speed and the pressure of injection by using an automatic device.

The H_2S -intermediate, H_2S -method, can also be applied to other organic matrices containing sulphur and its sensitivity opens up a wide field of application for the technique.

Introduction of sample into the diffusion flame via the hottest portion of the flame (flame edge) towards the flame centre in the SO_2 -intermediate method causes conditions in which the dissociation efficiency is higher than that in the H_2S -technique in which the sulphur compound was passed directly into the cool part

of an inward diffusion flame without having passed through the hot combustion gases. These conditions may be helpful in the analysis of sulphur compounds other than sulphur dioxide introduced into the flame. Alternatively, developing the methods concerned with conversion of inorganic sulphur compounds other than sulphite to sulphur dioxide would enable the SO_2 -technique to be more widely applied.

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