

To my parents

To my brothers and sisters

To Michael

ABSTRACT

The aim of the work described in this thesis is to investigate the use of irradiation techniques to produce sulphuric acid aerosols from sulphur dioxide. Since the aerosols are in principle removable by electrostatic precipitation, this irradiation technique could result in substantial removal of sulphur dioxide from a gas stream.

This thesis describes the oxidation of sulphur dioxide mixtures by the Van de Graaff electron beam, under favourable conditions (with air and water vapour present). Strong removal was obtained by this source; formation of sulphuric acid were investigated by light scattering techniques; the modal diameter of particles were in the range 0.5 to 0.6 μm . Particle size distributions were measured as functions of sulphur dioxide concentration and residence time. Plug-flow reactors of 0.5 and 2.0 cm diameters were used for kinetic analysis.

The order of reaction was found to be one with respect to sulphur dioxide concentration, with a rate constant of 0.04 s^{-1} .

The reaction mechanism of sulphur dioxide oxidation has not been further elucidated experimentally, but observations were made consistent with conditions during irradiation.

Further more preliminary experiments were carried out with plasma irradiation using air, nitrogen and argon plasmas. No aerosol was observed with argon and nitrogen plasma, but good results were obtained by air plasma irradiation. The modal diameter of this aerosol varies

from 0.3 to 1.1 μm . We believed that in the near future, this source could be used instead of Van de Graaff accelerator and thus could be guaranteed the removal of noxious compounds on an industrial scale.

ACKNOWLEDGMENTS

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CHAPTER 1

INTRODUCTION

Atmospheric pollution by smoke and other noxious substances formed during the combustion of fuel, for domestic heating, industrial usages or motor vehicle exhausts, is a problem of continually increasing gravity especially in large towns and in the more industrialised countries.

The main atmospheric pollutants, generated by the combustion of fuel, oil and coal, are sulphur dioxide (SO_2) and the oxides of nitrogen (NO_x).

Sulphur dioxide prevention methods depend on the source of pollution. Domestic fuel burning is preferably limited to low-sulphur fuels, but in populations of low density with adequate ventilation all conventional fuels are acceptable. High-volume emission sources (es. power stations) are often given very high stacks, and thus unacceptably high ground level concentrations are avoided; nevertheless effects in the long term and/or at considerable distances are considered to be quite severe. An alternative policy is to limit emissions by treating flue-gases at large emission source.

A considerable number of practical methods exist for the removal of pollutants at the source of emission and are in use in various areas of the world such as Japan, the U.S.A. and Europe. Most of these methods have been described in the literature. Ref. (61, 63, 73, 93) under the following headings.

1) Physical (For particles only)

- a) Screening
- b) Centrifuging
- c) Filtration
- d) Sedimentation
- e) Evaporation etc.

2) Chemical (Gaseous emissions, eg. SO_2)

- a) Limestone
- b) Neutralization
- c) Oxidation etc.

3) Other methods

- a) Thermal precipitator
- b) Electrostatic Precipitator
- c) Electron beam accelerator

In recent years, electrostatic precipitators^{Ref14} have been used in chemical processing, power-generation and mass-transport applications involving high temperatures and pressures such as 2000°F and 800 psi. The precipitator is used to combat, in a single operation, both the pollution of the atmosphere and the fouling or eroding of process equipment. However, limitations imposed by space, economics and time, require technology capable of removing SO_2 and NO_x simultaneously. This might be achieved by treatment of exhaust gases by electrostatic precipitators Ref. (14). Applications include blast furnace gas cleaning where the gas is saturated with moisture after passing through wash towers.

Wet and dry precipitators have been used in controlling the emission of iron oxide fumes from processes in the iron and steel industry.

A few years ago workers in Japan and the U.S.A. began the irradiation of exhaust gases.

This process has been studied by Kawamura et al Ref (60), Okiro Tokunaga et al. Ref. (100), S. Machi et al Ref. (78) in an effort to elucidate the mechanism for the oxidation of SO_2 and NO_x , from heavy oil combustion gases, into aerosols.

Investigations by the above workers suggest that sulphur dioxide oxidation in moist air results in the formation of sulphuric acid aerosols. The experimental work of Wood et al Ref. (113) showed that irradiation of sulphur dioxide mixtures with beta rays resulted in the formation of aerosols (See Chapter 6); while Cox (1976) Ref. (25) and Takahashi et al. (1975) Ref. (98) studied photochemical aerosol formation in the atmosphere and investigated the role of sulphur dioxide in this process. Previous work, Gerhart and Johnstone (1955) Ref. (15) have postulated a "three-body" oxidation of sulphur dioxide by oxygen atoms.

$$\text{SO}_2 + \text{HO}_2 \rightarrow \text{SO}_3 + \text{OH}$$

The aim of the work described in this thesis is to investigate the use of irradiation techniques to produce sulphuric acid aerosols from sulphur dioxide. Since the aerosols are in principle removable by electrostatic precipitation, this irradiation technique could result in substantial removal of sulphur dioxide from a gas stream. Development of these techniques, which has been adapted to aerosol production requirements, are explained in Chapters 3 and 4. Chapter 2 contains a review of the possible oxidation reaction mechanisms of sulphur dioxide in the atmosphere.

Chapter 5 of this thesis deals with the results of reactions between:

- a) Sulphur dioxide and nitrogen
- b) Sulphur dioxide, nitrogen and dry air
- c) Sulphur dioxide, nitrogen and moist air

Light scattering techniques and the results of analysis for aerosol size distribution are discussed in Chapter 6. All the above reactions were promoted by use of the electron beam accelerator.

The possible use of plasma jet irradiation, in place of electron beams, in the reaction of sulphur dioxide and moist air to form aerosols is dealt with in Chapter 7. Previous work by Houshang F. Behbahani et al. Ref. (49) has reported on the use of plasma radiation in the removal of NO by nitrogen atoms.

Finally, in Chapter 8, conclusions are drawn on the use of irradiation techniques (electron beam and plasma jet) in sulphur dioxide moist air systems and also on the use of light scattering techniques to determine particle size distribution. Some remarks are made on future research using these techniques.

CHAPTER 2

ATMOSPHERIC CHEMISTRY OF SULPHUR COMPOUNDS

2.1 Formation of sulphur dioxide gas in the atmosphere

The principal forms of sulphur in the atmosphere are sulphur dioxide (SO_2); hydrogen sulphide (H_2S) in the gas phase and sulphate ion (SO_4^{2-}) in the condensed phase.

The man-made, or artificial, sources of atmospheric sulphur may be enumerated as follows:

SO_2 , Coal combustion; Petroleum combustion; Petroleum refining; smelting;
 H_2S , Assorted industries.

Some studies indicate that SO_4^{2-} plays an important role in the composition of stratospheric aerosols (Junge et al.(1961) Ref. (58)). It is likely that these aerosols are formed by the oxidation of H_2S which penetrates into the stratosphere.

Another process which is probably of great importance for the atmospheric sulphur cycle is the oxidation of H_2S . There are several possibilities in that H_2S can be oxidized after absorption on surfaces, e.g. on aerosol particles or photochemically in solution. The latter process would result in the fixation of the H_2S dissolved in cloud or rain droplets. Unfortunately, we have no quantitative knowledge of these various possibilities, because the chemistry of H_2S in the atmosphere has not been studied extensively. It is generally assumed that H_2S is oxidized to SO_2 .

Healy et al. Ref. (44) have pointed out that in the United Kingdom, enough ammonia is produced from the decomposition of animal urine to play a significant role in the oxidation of sulphur dioxide when the humidity is near 100%. They suggest that catalysis by transition metal ions might be important at lower relative humidities.

However, our knowledge of the sources of atmospheric SO_2 and H_2S is not good enough. Obviously, most natural sulphur enters the atmosphere as H_2S , produced in certain sea and land areas by the reduction of sulphate. This reduction occurs whenever water depletes the swamp or soil of free oxygen. Under such conditions, sulphate is a source of oxygen and the H_2S formed cannot be reoxidized before escaping into the air.

2.2 Oxidation of Sulphur dioxide

Sulphur dioxide in air is commonly considered to be oxidized to sulphate by two principal methods: photochemical and catalytic. If the reaction product is entirely in the gas phase the product is generally assumed to be sulphur dioxide, which can rapidly combine with any ambient water vapour to form sulphuric acid aerosols.

The photooxidation of sulphur dioxide to sulphur trioxide and sulphuric acid may be a significant source of condensation centres for the accumulation of photochemical reaction products and formation of particulates in the size range effective in reducing visibility.

The concentration of condensation centres or nuclei resulting from the photooxidation of sulphur dioxide in air is high, in the order of 10^5 to 10^6 nuclei per cc. Health implications of nuclei production in the ambient urban air deserve the attention of investigations concerned with the aspects

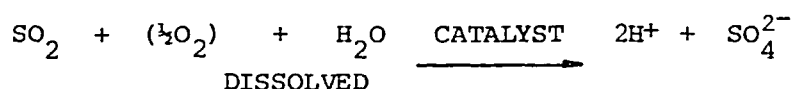
of air pollution.

The rate of nuclei production, its dependence on external conditions, and the nature of the nuclei are important in this research. Photochemical aspects of sulphur dioxide will be discussed further in this thesis.

However, the reaction systems which are probably of major importance for the removal of sulphur dioxide from the Earth's atmosphere are:

- (1) Photochemical oxidation occurring naturally in sunlight.
- (2) Catalysed oxidation of SO_2 absorbed in soot particles
- (3) Liquid phase oxidation of SO_2 catalysed by dissolved metal ions such as Mn^{2+} ; Cu^{2+} and Fe^{3+} or ammonia ions such as NH_4^+ .

Johnstone and Coughanour Ref. (52) have investigated the absorption and subsequent oxidation of sulphuric acid in air by aqueous drops containing dissolved catalysts. More recently Cains and Carabine Ref. (17) investigated the changes in size distribution of water droplets in an aerosol by measuring them when they were exposed to humid air dosed with sulphur dioxide. We can write these reactions as:



Sulphate (SO_4^{2-}) formation in solution does not continue indefinitely, but reaches a final value which depends upon the amount of catalysts present and which is proportional to the sulphur dioxide partial pressure in the air. The controlling factor is thought to be the pH value of the solution, which stops the oxidation after dropping below a certain value

Ref. (57).

Studies by Van den Heuvel and Hobbs Ref. (105); Scott and Hobbs Ref. (94) and Junge and Ryan Ref. (57) have suggested that ammonia is an important factor in increasing the rate of SO_2 oxidation in cloud and fog drops. Based on equilibrium considerations, there is sufficient ammonia in cloud droplets to neutralize the sulphuric acid as it is formed.

If a cloud droplet evaporates the pH value decreases rapidly, but may soon be raised again by the absorption of additional ammonia. In each condensation-evaporation cycle, additional sulphate SO_4^{2-} will thus accumulate. Estimates show that a sulphuric acid nucleus goes through an average of ten condensation cycles before it is removed by rain.

Returning to system (1) of the three alternatives listed above, sulphur dioxide can be oxidized photochemically by sunlight. Depending on atmospheric conditions other reactions occur with other gases and with aerosol particles containing either alkaline compounds (CaCO_3) or alkaline earth metals. It is felt that SO_2 oxidation in droplets is the more important process, especially in polluted atmospheres. In such circumstances, the fate of water soluble trace-gases in the atmosphere is complicated by their chemical reactivity.

2.3 Further details of SO_2 oxidation

The recent works by other workers H.S. Johnstone and K. Dev Jain Ref. (53); T.C. Hall Jr. Ref. (40); Y. Ogata, Isawa, and T. Tsuda Ref. (86); have confirmed the existence of reactions of electronically excited sulphur dioxide molecules under a variety of conditions.

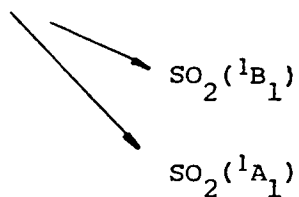
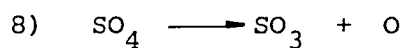
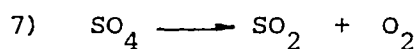
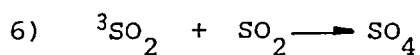
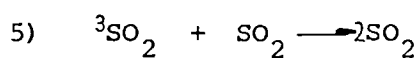
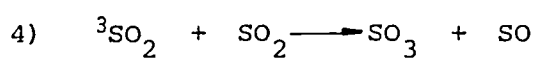
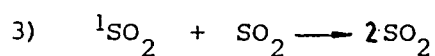
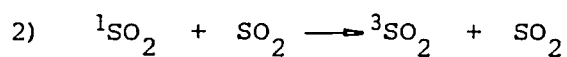
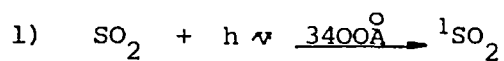
Under atmospheric conditions, the high S-O bond dissociation energy of sulphur dioxide precludes its direct photochemical decomposition, but

there is a certain probability that sulphur dioxide may enter into reactions in electronically excited states and more probably that it may undergo attack by free radicals.

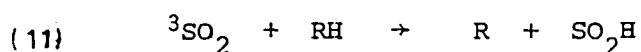
The first investigation of electronically excited molecules appears to be the studies of previous workers, T.C. Hall Jr. Ref. (40) in irradiation of mixtures of sulphur dioxide and hydrocarbons ($\text{SO}_2 + \text{RH}$). Subsequent investigations have confirmed the existence of reactions of electronically excited sulphur dioxide molecules. H. Güsten and R.D. Penzhorn Ref. (39).

Appreciable absorption by sulphur dioxide commences around $3300\text{\AA}$ with an absorption band extending to $2300\text{\AA}$. It appears that this band corresponds to singlet electronic states ($^1\text{B}_1 \leftarrow ^1\text{A}_1$) transition Ref. (42). The lifetime of the singlet electronic state ($^1\text{B}_1$) with respect to fluorescence is unusually long with values of 4×10^{-5} seconds and 2×10^{-4} seconds. Rao et al. Ref. (91) made a detailed investigation of SO_2 photochemistry in this absorption band. Among the significant results they report is the efficient quenching of the singlet electronic state of sulphur dioxide ($^1\text{SO}_2$) by sulphur dioxide with 92% of the collisions resulting in relaxation of the singlet state of sulphur dioxide to the ground state and chemical change, not involving excited molecules of sulphur dioxide. The remaining 8% of the collisions produced spin inversion to the triplet electronic state ($^3\text{SO}_2$). The collisional quenching of the singlet electronic state to ground state sulphur dioxide was found to be within the order of magnitude of the collision frequency. They also report that collisional quenching by oxygen molecules is only one - third as efficient as that by sulphur dioxide. On the other hand, collisional deactivation of triplet electronic state ($^3\text{SO}_2$) by sulphur dioxide (SO_2), carbon dioxide (CO_2) and oxygen (O_2) are all much slower

processes, occurring more slowly than deactivation of singlet electronic state ($^1\text{SO}_2$) by a factor of approximately a thousand and thus of the order of 10^{-4} of the collisional frequency, as shown in the following reactions:



Although the photoreaction of sulphur dioxide with hydrocarbons (RH) has been recently investigated by R.D. Penzhorn et al. Ref. (88) they suggested that a marked influence of sulphur dioxide on aerosol formation in photochemical smog simulation experiments may be due, at least in part, to the reaction of triplet excited state with hydrocarbons

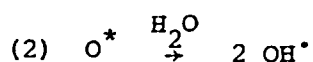
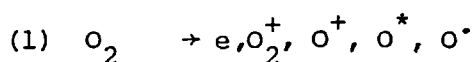


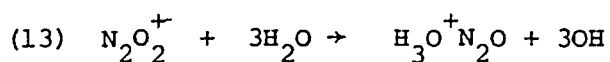
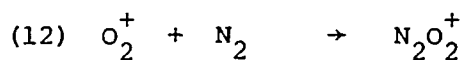
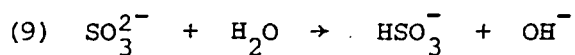
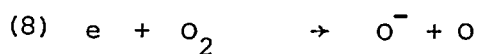
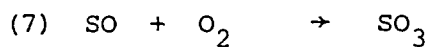
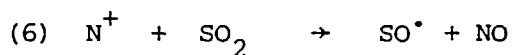
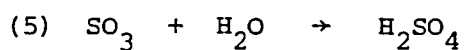
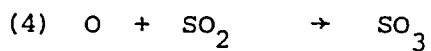
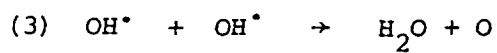
The formation of aerosols has been shown to occur upon sunlight irradiation of n-butane and sulphur dioxide in air. Ref. (15)

Most of these investigations are an attempt to clarify SO_2 systems for kinetic studies. R.D. Penzhorn et al. Ref. (88) have reported some preliminary results concerning the identification of the products of the photoreaction of sulphur dioxide with n-propene, n-butene Ref. (41); other general comments on a possible reaction mechanism will be seen later in this thesis.

2.4 Possible oxidation steps under irradiation, e.g. by Van de Graaff electron beam.

Many reactions have been proposed to account for oxidation in the electron beam Ref. (59, 60, 61) in the presence of air.

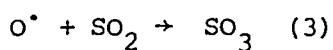
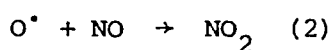
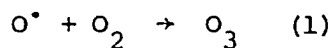




The oxidising species are either oxygen atoms ($\text{O}^\bullet$) or ($\text{OH}^\bullet$) radicals or oxygen ions (O^-) but it is not possible at present to distinguish the individual contribution to the oxidation of SO_2 .

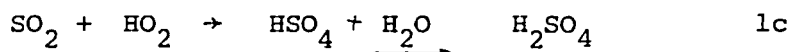
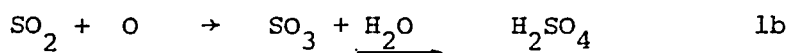
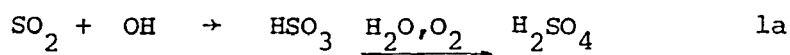
As previously mentioned above, oxygen atoms are also involved in the photochemical oxidation of SO_2 in UV irradiated air.

e.g.



here the oxygen atoms are produced in photolysis of oxygen in air. The SO_3 which is formed in the above reaction, will subsequently react with H_2O to give sulphuric acid. Johnson et al. Ref. (55).

The effect of moisture on the oxidation of sulphur dioxide to sulphur trioxide and sulphuric acid has been attributed to the following reactions:



The radiolytic formation of H_2SO_4 from the moist mixture of SO_2 , O_2 and N_2 was recently confirmed by Juerguen W. Leonhardt et al. (1980) Ref. (70). They have concluded that SO_2 oxidation may occur by the presence of OH radicals and oxygen atoms. But the HO_2 radicals can also oxidize SO_2 through reactions (1c).

CHAPTER 3

IRRADIATION TECHNIQUES

3.1 Introduction

The emphasis in this chapter will be on the characteristics of sources which are important for inducing effects on gases, with particular reference to sulphur dioxide undergoing chemical oxidation.

The study of radiation effects on gases is of fundamental as well as practical interest. Much of the sulphur trioxide in the combustion products of sulphur-containing fuels is derived from reactions between sulphur-dioxide and oxygen atoms in the gaseous phase Ref. (10). Oxygen atoms can be transiently present in "above-equilibrium" concentration during combustion and the rate of formation of sulphur trioxide has been correlated with the magnitude of this concentration Ref. (66,110)..

Previous direct investigation of the reaction between SO_2 and atomic oxygen has not been extensive as will be seen further on in this thesis, Chapter 7. The apparatus and methods were quite similar to those used by S. Machi et al. Ref. (76).

TABLE 3.1PRINCIPAL SOURCES OF IONIZING RADIATION

TYPE OF SOURCES	RADIATION EMITTED
Natural Radionuclides Ra, Th, Po	Gamma, Beta, Alpha
Reactor core	Neutron, Fast and Thermal, Gamma, Fission Fragment Recoil
Fission Products Spent fuel elements	Gamma
Gross Mixed such as Z Nb	Gamma and Beta Gamma and Beta
Separated such as: Cs, S, Pm, K	Gamma and/or Beta
Activated radionuclides Portable such as Co - 60	Gamma and/or Beta
Activated radionuclides-stationery such as: Na and I _N reactor loops	Gamma
Particle accelerators Van de Graaff, Linear accelerator	Electron, Beta, Proton
Resonant transformer, capacitron, Targets of accelerators	Deuteron, Alpha, Positive ions
including X-ray tubes	X-rays, neutrons
Electric discharge Spark, glow, silent-corona, high frequency	Electrons
Ultraviolet light Electron excited	Low energy photons
Plasma irradiation Plasma jet	Electron

3.2 Radiation source

To provide a context for the discussion of the Van de Graaff source used in this work, principal sources of ionizing radiation are listed in Table 3.1.

The model AS-2000 Van de Graaff accelerator, which has been used in this research, produces a precise, controllable beam of monoenergetic electrons, and is suitable for research in various fields of surface chemistry and solid state physics. This type of machine operates as follows: Negative electrical charge is sprayed on a moving insulating belt and is taken by the belt to a discharge point which transfers it to the outside of a metal hemisphere. The metal hemisphere is insulated from the outer tank by a high pressure of gas. The high potential difference between the hemisphere and the lower end of the accelerator is used to accelerate electrons through the evacuated accelerating tube. The beam of electrons can be scanned magnetically so as to emerge through the window as a broad beam suitable for the irradiation of large objects. Production of an accelerated beam, an evacuated accelerating path, and an electron source, in a vacuum system, resulted in an adequate control system. In the model AS-2000 these requirements are met as described in the next paragraphs. Ref. (84). See fig. 1.

3.3 The accelerating voltage

A Van de Graaff belt type, electrostatic generator is used to develop accelerating voltages up to 2MeV. A constant potential is characteristic of the Van De Graaff high voltage generator.

3.4 The acceleration path

The acceleration path for the electron beam is provided internally by a highly evacuated accelerator tube, and externally, by a similarly evacuated tube extension assembly. A uniform voltage gradient is developed along the accelerator tube, and accelerates the electrons to energies of up to 2MeV. This gradient is developed by the column current flowing through a series string of resistors.

3.5 The electron source

The electron source is a directly heated tantalum cathode; the emission level of which is controlled automatically. Electrons, emitted by the heated cathode, are attracted into the accelerating path by the electrostatic field developed between the cathode region and the first electrode of the accelerator tube.

3.6 The associated vacuum system

The accelerator tube system must be operated with a high vacuum and low pressure to minimize collisions between the accelerated particles and gas molecules in the tube. The normal operating pressure of the accelerator tube system is in the order of 10^{-6} mmHg. The maximum permissible continuous operating pressure is $3 \cdot 10^{-5}$ mmHg, a relay operates to disconnect the belt drive motor and shut down the generator. The vacuum system consists of: a cold trap assembly, a mercury diffusion pump, a vane-type motor-driven backing pump, a Penning gauge, and various operating and protective circuits and devices.

3.7 Line width of beta-radiation

Beta particles do not have a definite range, in the same sense as alpha particles do. Nevertheless, it is possible to specify a more or less definite thickness of absorber. This absorber will reduce ionization produced by beta particles of given energy almost to zero, without effecting ionization due to bremsstrahlung.

The approximate ranges, in air, of beta particles at various maximum energies are given in Table 3.2. It may be noted that the average maximum energy of beta particles from fission products is about 1.2 MeV. The absolute maximum energy probably does not exceed 3 MeV and is appreciably less in most cases.

3.8 Dosimetry

In this work, the quantity of energy absorbed by the sulphur dioxide, irradiated by a voltage of 2 MeV electron beam, was estimated. The conversion rate of ethylene to H_2 (plus other products) is known to be 1.2 molecules per 100 eV energy absorbed; conveniently expressed as: $G(H_2) = 1.2$. Thus measuring the hydrogen content of the ethylene after irradiation, an estimate of the energy absorbed can be made. The energy absorbed by another gas irradiated in the same way as the ethylene is then given by $E_E = E_G Z_a/Z_e$; where E_E is the energy absorbed by the ethylene; E_G is the energy absorbed by the gas; Z_a ; Z_e the number of electrons per molecule of the gas and ethylene respectively. Thus the case of sulphur dioxide is $E_{SO_2} = E_e \frac{32}{16}$.

This approximation is accurate enough for our present purposes. The concentration of H_2 was determined with a gas chromatograph equipped with a thermal conductivity detector (Model G.C.D. gas chromatograph, Pye (Unicam Ltd)). See Appendix 2.

It can be assumed with the dilute SO_2 mixtures used that absorption of energy is predominantly due to N_2 and O_2 , each having a values of $Z = 0.5$. In appendix 2 an estimate is made of $G(-SO_2)$, The energy (100 eV) per molecule of SO_2 dissociated. The low value compare with some previous work probably reflects the high conversions achieved.

TABLE 3.2

ELECTRON RANGES IN AIR (1 atm.)

ENERGY MeV	ELECTRON RANGES IN AIR (1atm) METERS
0.1	0.11
0.5	1.5
1.0	3.7
2.0	8.5
3.0	13.0

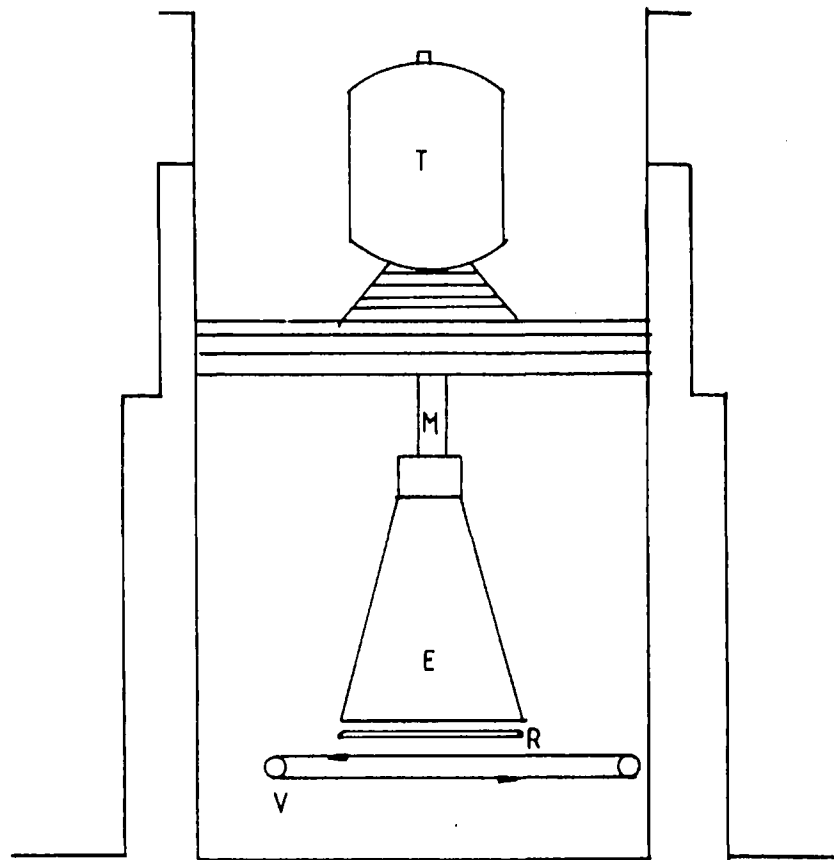


FIG.3.1 VAN DE GRAAFF ELECTRON BEAM ACCELERATOR

E- electron beam scanner
V- conveyor
T- high voltage shell
M- metal tube for high vacuum
R- reactor

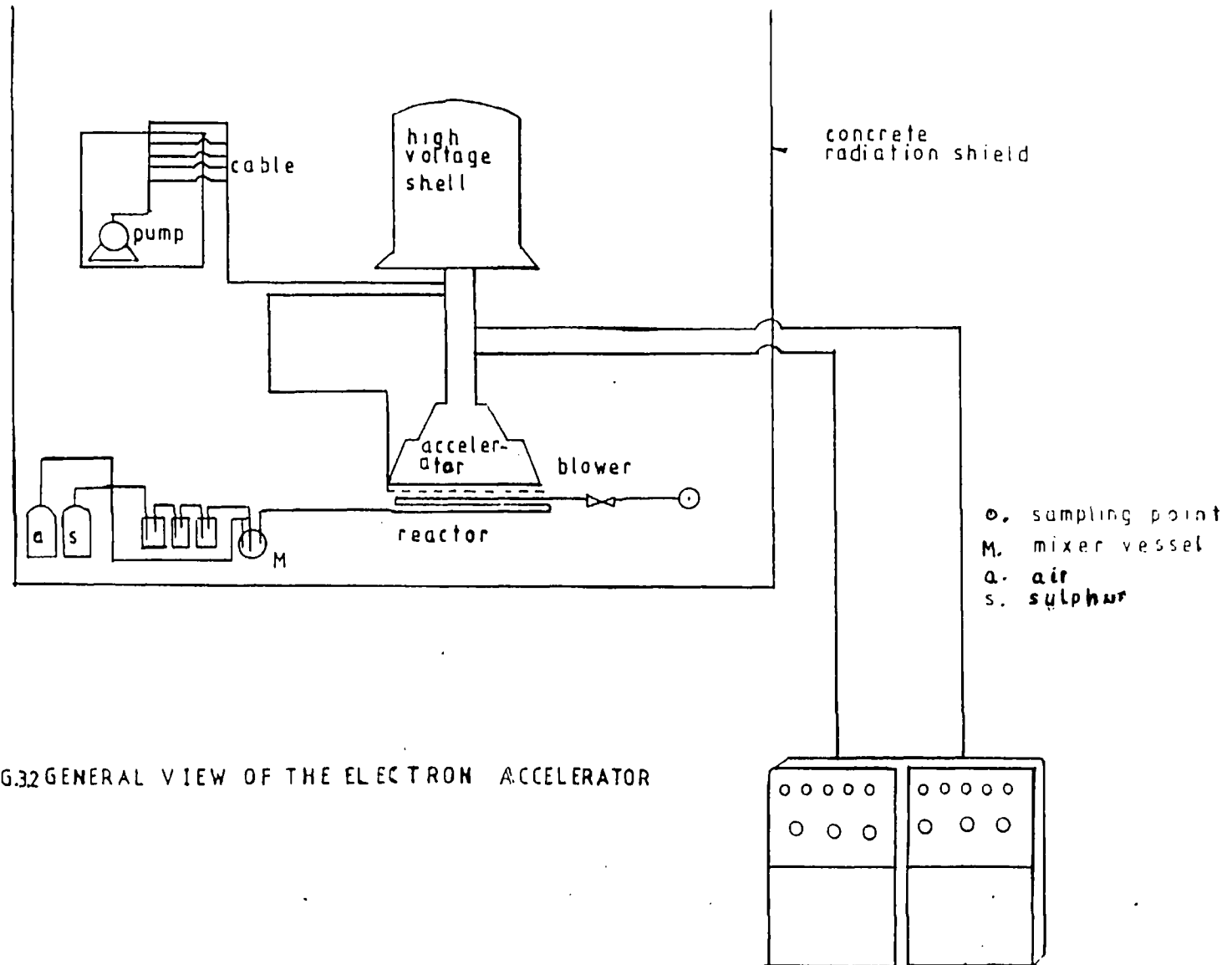


FIG.32 GENERAL VIEW OF THE ELECTRON ACCELERATOR

CHAPTER 4

DEVELOPMENT OF EXPERIMENTS USING THE VAN DE GRAAFF ACCELERATOR

4.1 Introduction

In this chapter will be described the planning and setting-up of irradiation experiments, designed to reduce the sulphur dioxide in a gas flow, using the Van de Graaff accelerator electron beam.

Experiments in a dynamic flow type of reactor seemed especially suitable because the irradiated volume under such an electron beam is relatively small. Hence batch reactions did not suggest themselves, having no obvious advantages, and the positive disadvantages of small working quantities of SO_2 if concentrations similar to those in combustion flue gases were to be used.

In common with previous workers, the intention was to simulate such concentrations, eg. in the 500 - 1000 ppm range, and test the potential for almost complete removal of the SO_2 . In addition, it was expected that aerosol would form if the gas stream were humidified and characterisation of the aerosol was a principal aim of the project. It was considered important to measure the size distributions produced as a guide to the practicability of ultimate removal by electrostatic or other means.

4.2 Apparatus

The electron beam accelerator has been fully described in Chapter 3, together with dosimetry assessments. The experiments described were all carried out at a fixed voltage of 2 MeV

Fig. 4.1 shows in schematic form the layout of the experiments with flow reactors. Experimental variables used were:

- (1) The composition of the gases
- (2) The residence time in the reactor
- (3) The dose rate of irradiation
- (4) Duration of flow experiments, and of delay time between collection and analysis of the aerosol samples.
- (5) The temperature of the reactor

The principal variations were made in the composition of the gas-stream. Sulphur dioxide was mixed in wide varieties of combinations with nitrogen and/or argon (representative of "inert" or "non-oxidising" carrier gases) or with air. The primary sources of SO₂ were prepared mixtures in cylinders in the 1% - 0.05% range in either nitrogen or argon.

The flow system is depicted in Fig. 4.1. Gas streams were controlled by needle valves and calibrated "rotameter" flow-meters (FM).

In order to humidify the air stream, it was passed via glass and P.V.C. tubes through three dreschel bottles (a,b,c,) which contained water.

The streams were introduced into a mixing vessel (M) and then into the irradiation reactor (R). The gas was irradiated during its residence

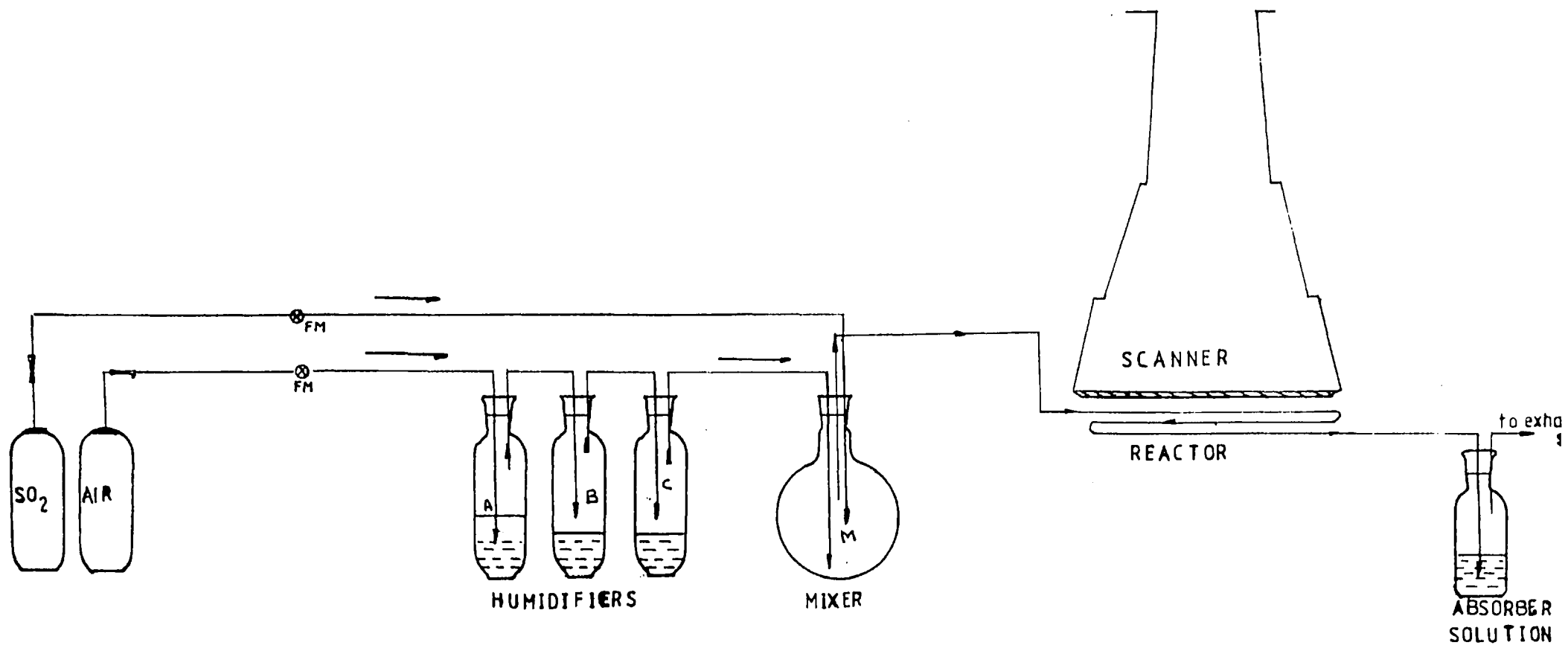


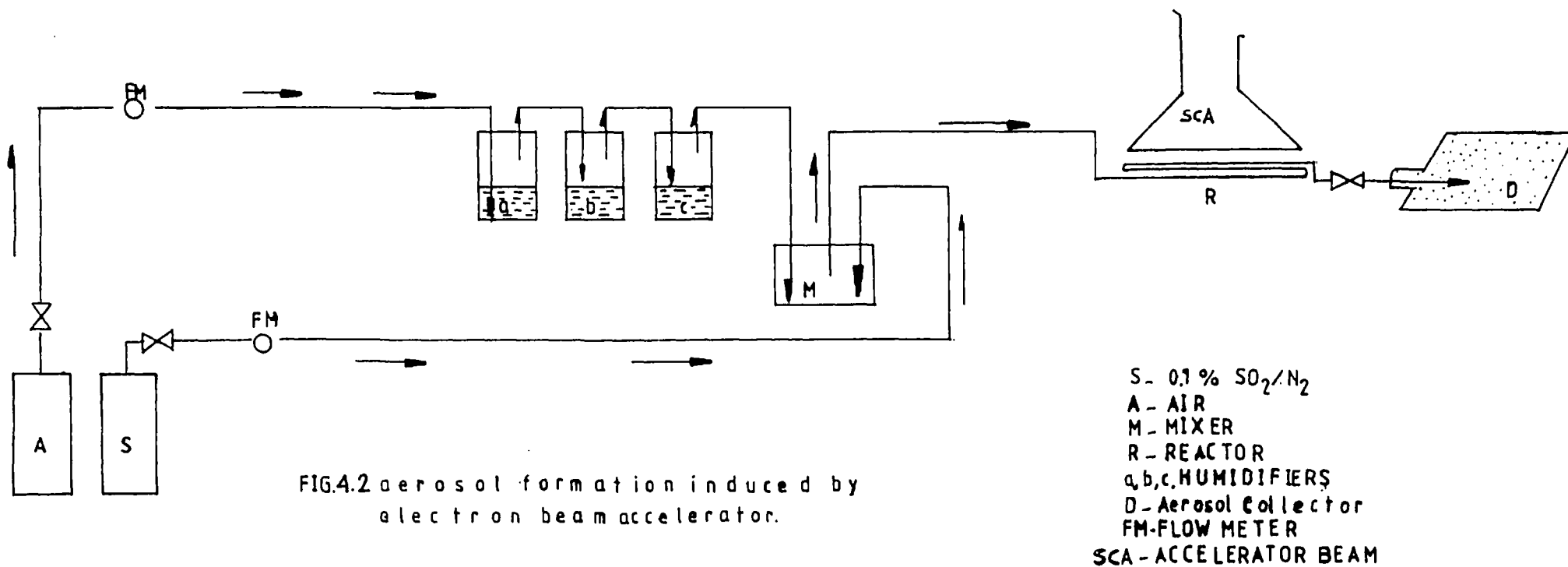
FIG.4.1. Apparatus for SO_2 reduction by electron beam

time in the reactor, and the irradiation time was varied by changing the gas flowrate and diameter of the reactor . This irradiated gas was then directed into 0.1M - NaOH absorbing solution for chemical analysis of the sulphur dioxide. The concentration of sulphur dioxide in the gas after irradiation was determined for various flow times. When measurements of the aerosol were required, the gas was collected in a plastic bag (D) Fig. 4.2, and the NaOH trapping system dispensed with.

4.3 Analytical methods

The chemical analysis of gas mixtures containing SO_2 , air and H_2O was determined using titrimetric methods.

The absorbing solution was acidified with Hydrochloric acid (0.6M) and the volumetric determination carried out using iodine solution (10^{-3}M). Before the end point of the titration was reached, starch solution was introduced as an internal indicator Ref. (56). All chemicals were supplied by B.D.H.



CHAPTER 5

EXPERIMENTAL RESULTS: CHEMICAL CONVERSION OF SULPHUR DIOXIDE

5.1 Summary of the procedure

The sources of sulphur dioxide in the experiments were mixtures in nitrogen or argon, at concentrations 10,000 ppm, 1000 ppm, 500 ppm. These were mixed with an air or inert gas stream, optionally humidified, and controlled and measured as detailed in Chapter 4.

The combined streams were then passed directly through a tubular reactor (variously fused silica and borosilicate (pyrex glass)), placed in the path of the electron beam. The dimensions of reactors used were about 160 cm length and diameter 0.5, 1.0 or 2.0 cm.

Initial concentrations of SO_2 in the stream, and final values after radiolysis were measured by timed collection in the alkaline absorption solution for runs both with and without the electron beam running. The solutions were then acidified and titrated with iodine (See Chapter 4).

5.2 Identification of the products

A series of experiments were done to confirm the existence of sulphuric acid aerosol in the product stream, subsequent to radiolysis with air containing water vapour. The sulphuric acid aerosols produced during the experiments were tested by litmus paper, and barium chloride solutions.

5.3 Radiolysis of sulphur dioxide in nitrogen

The sulphur dioxide concentrations before and after radiolysis are shown in Figs. 5.1,2 for various durations of experiment. The temperatures relating to the trapping solutions in the reaction were 23°C and 30°C, in a 0.5cm reactor.

The decreases of sulphur dioxide are in the range 60% - 75% (Fig. 5.2) and 26% - 85% (Fig. 5.1) The values at larger durations are less subject to error due to the unavoidable passage of sulphur dioxide for short times before and after irradiation. (See p. 61 for a discussion of this "lead time").

The greater constancy of percentage reduction in SO₂ apparent for the experiments of Fig. 5.2 suggest greater reliance on these values.

Repetition of these experiments to carefully determine the lead time, and the associated unavoidable contribution of full-strength SO₂ mixtures to the titre, yielded the results in Fig. 5.14.

The lead time was about 2.2 mins., and nearly constant (35%) conversions were determined at all run durations.

The temperature in these experiments was 23°C, and the reactor was of 0.5cm diameter. The residence times in the reactions were:

For Fig. 5.1 3 secs.

For Fig. 5.2 3 secs.

For Fig. 5.3 3 secs.

FIG. 5.1 Electron irradiation of SO_2/N_2 mixture, iodine titration vs. time of flow, conditions are 1000 ppm. SO_2/N_2 , 23°C ; beam current $100\mu\text{A}$. 1. unirradiated 2. irradiated

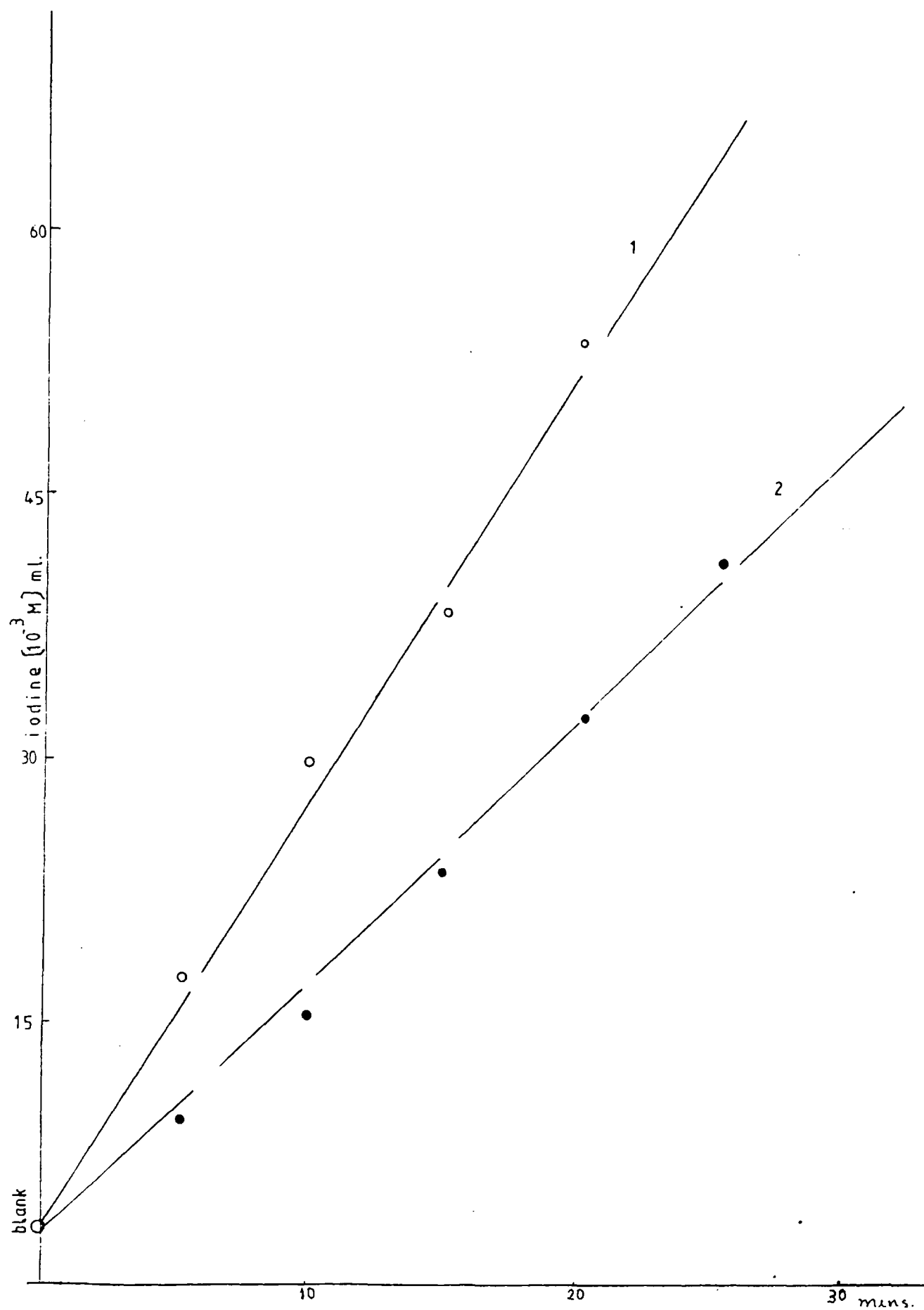
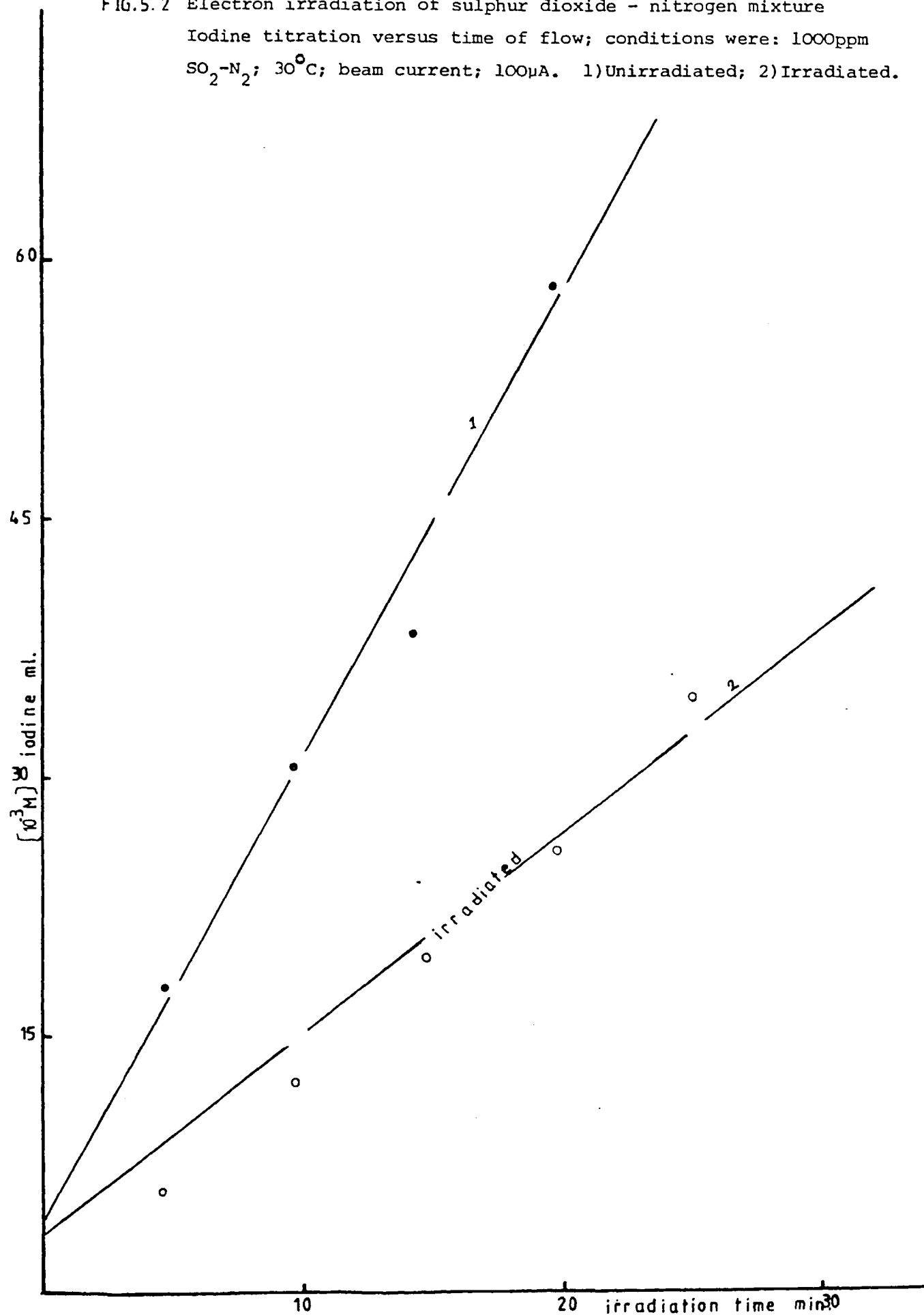


FIG.5.2 Electron irradiation of sulphur dioxide - nitrogen mixture

Iodine titration versus time of flow; conditions were: 1000ppm

$\text{SO}_2\text{-N}_2$; 30°C ; beam current; 100 μA . 1)Unirradiated; 2)Irradiated.



The above quoted experiments were done with 100 μ A beam current. The effects of varying this over quite a large range are demonstrated in Section 5.6, below.

5.4 Radiolysis of sulphur dioxide in argon

Experiments were done, before and after radiolysis as shown in Figures 5.4, 5.5 the temperatures relating to the two figures being 23°C.

The decreases of SO₂ are in the range 36 - 51% (Fig. 5.4) and 51 - 54% (Fig. 5.5). The values at larger durations are less subject to error due to the unavoidable passage of SO₂ for some time before and after irradiation.

These experimental runs were done at the same conditions mentioned before.

Other inert gas mixtures, ex.. with nitrogen and/or argon gave results shown in Figures 5.7, 5.8, 5.9, and 5.10.

5.5 Radiolysis of sulphur dioxide in nitrogen and air mixtures

Experiments were done, initially with substantial proportions of air added to the SO₂/N₂ mixtures. For example in Fig. 5.6 are shown the effects of irradiation when flows of 100 cm³ min⁻¹ of 1000 ppm SO₂/N₂ and 350 cm³ min⁻¹ humidified air were used.

The strong decrease of SO₂ (78 - 100%) shows the importance of the addition of moist air.

When the air used was not humidified (but not specially dried) results were obtained as shown in Fig. 5.3.

FIG.5.3. Electron irradiation of $\text{SO}_2\text{-N}_2$ and dry air. Conditions were: 1000ppm SO_2/N_2 , 100cc min^{-1} ; dry air; 500cc min^{-1} ; room temperature, Beam current 100 μA , 1)Unirradiated, 2)Irradiated

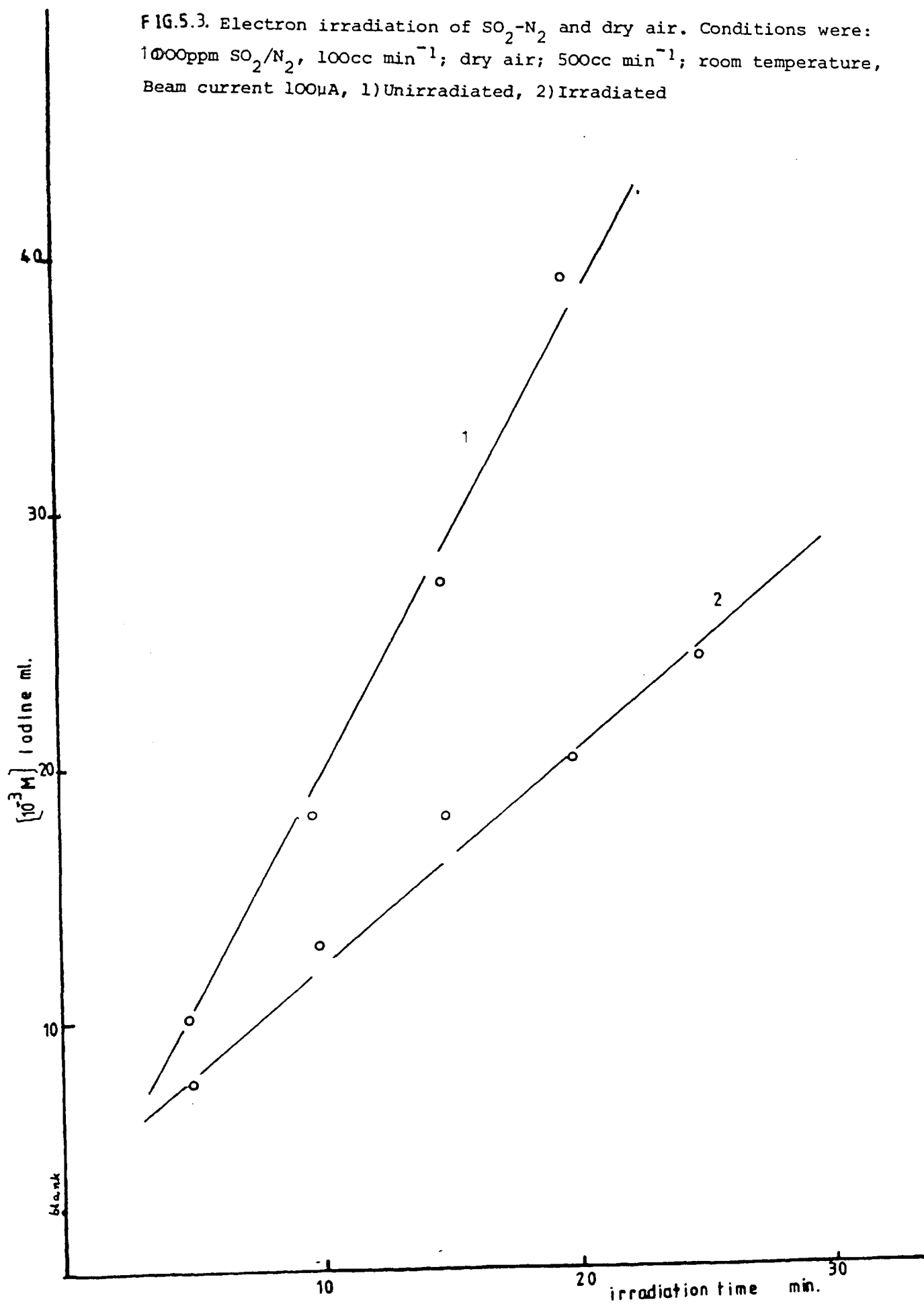


Fig.5.4 Electron irradiation of sulphur dioxide - argon; Iodine titration versus time of flow; conditions were 500 ppm SO_2/Ar , 100cc min^{-1} , Beam current, $65\mu\text{A}$, Reactor diameter 0.5cm 1) Unirradiated ;
2) Irradiated

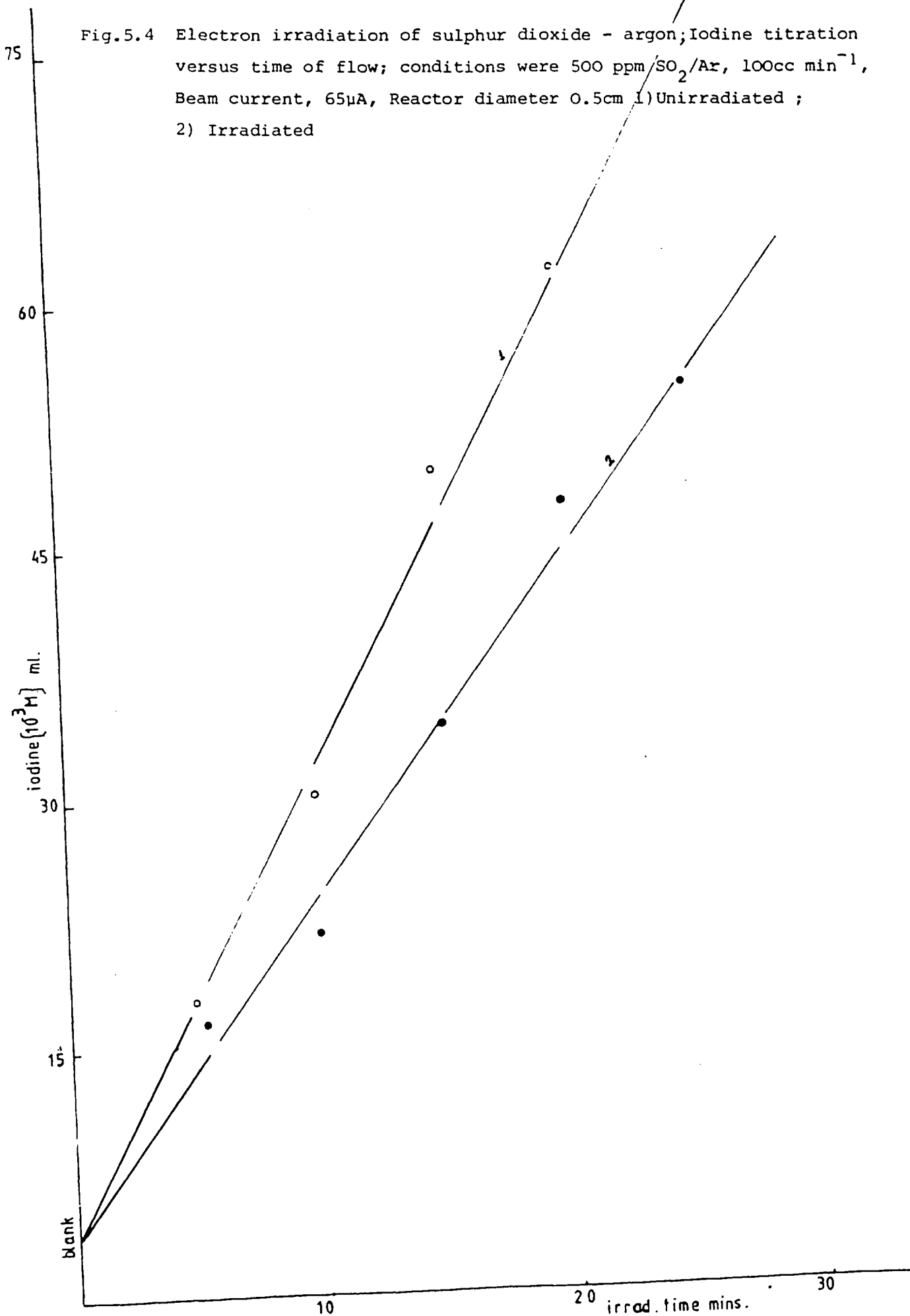


FIG.5 5 Electron irradiation of sulphur dioxide/argon - argon.

Iodine titration versus time of flow; conditions were 500 ppm SO_2/Ar , 100cc min^{-1} ; Argon 300cc min^{-1} ; Beam current $65\mu\text{A}$; Reactor diameter 0.5cm . 1)Unirradiated 2)Irradiated

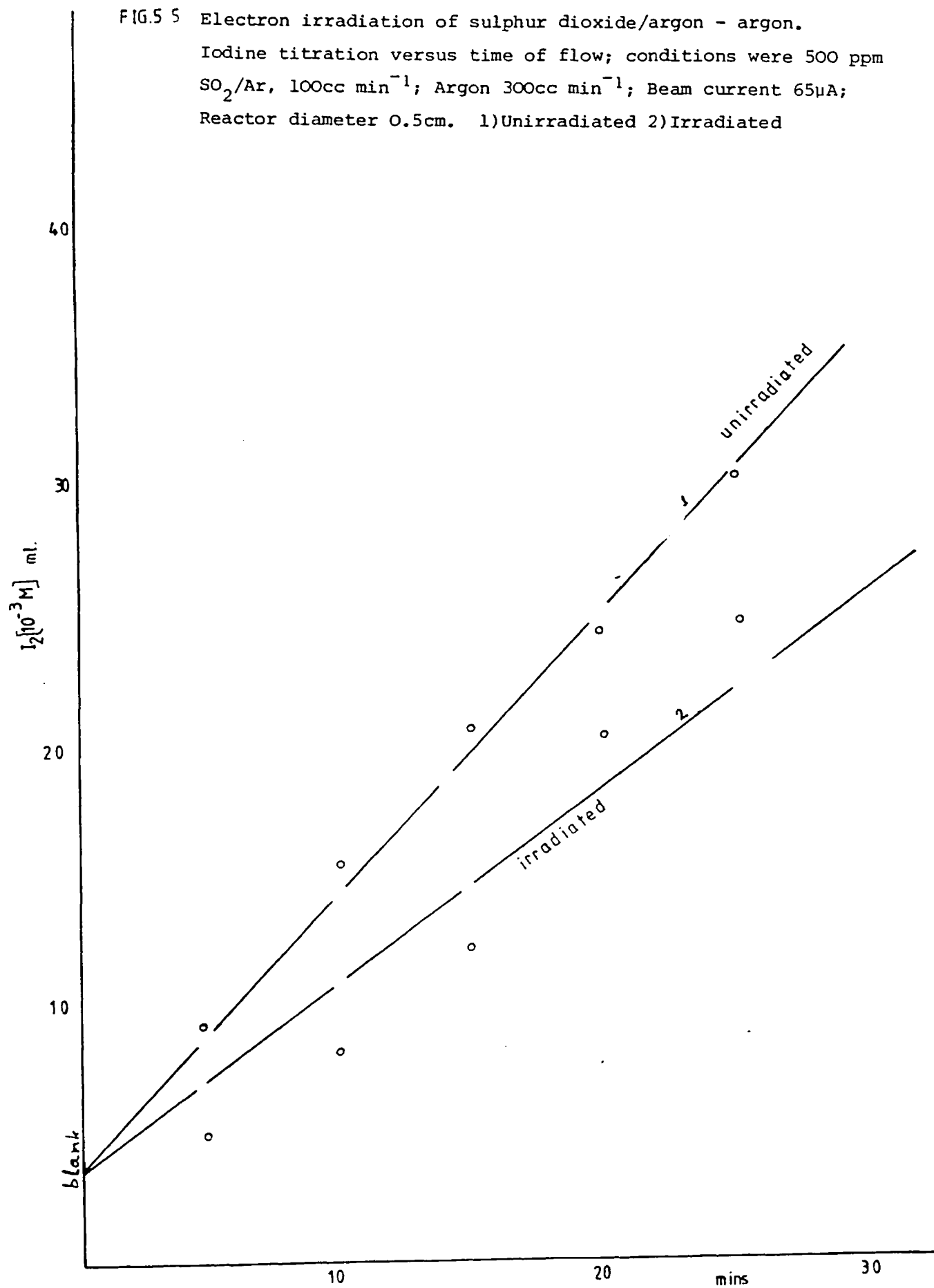


FIG5.6. Electron irradiation of sulphur dioxide-nitrogen and moist air mixtures
 Iodine titration versus time of flow; conditions were 1000pm SO_2/N_2 mixture flowing
 100cc min^{-1} ; moist air, 350cc min^{-1} ; beam current, $100\mu\text{A}$;
 1) Unirradiated 2) Irradiated

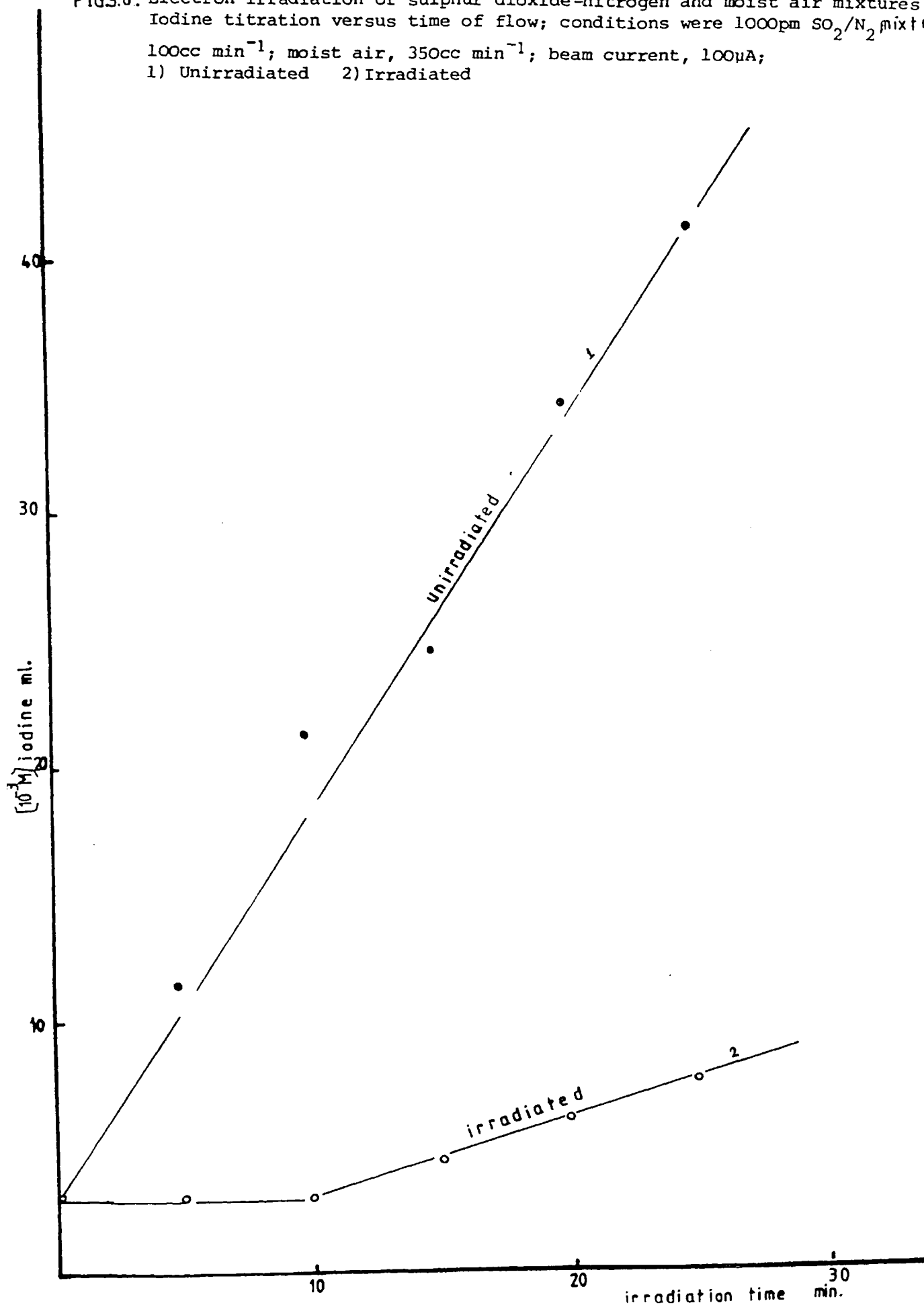


Fig. 5.7 Electron irradiation of sulphur dioxide-Argon mixtures, with nitrogen and argon. Conditions were 1000 ppm $\text{SO}_2/\text{Ar.}$, 90cc min^{-1} ; nitrogen, 400cc min^{-1} ; argon, 85 cc min^{-1} . Beam current 100 μA ; Room temperature, $\text{SO}_2 = 157\text{ppm}$.

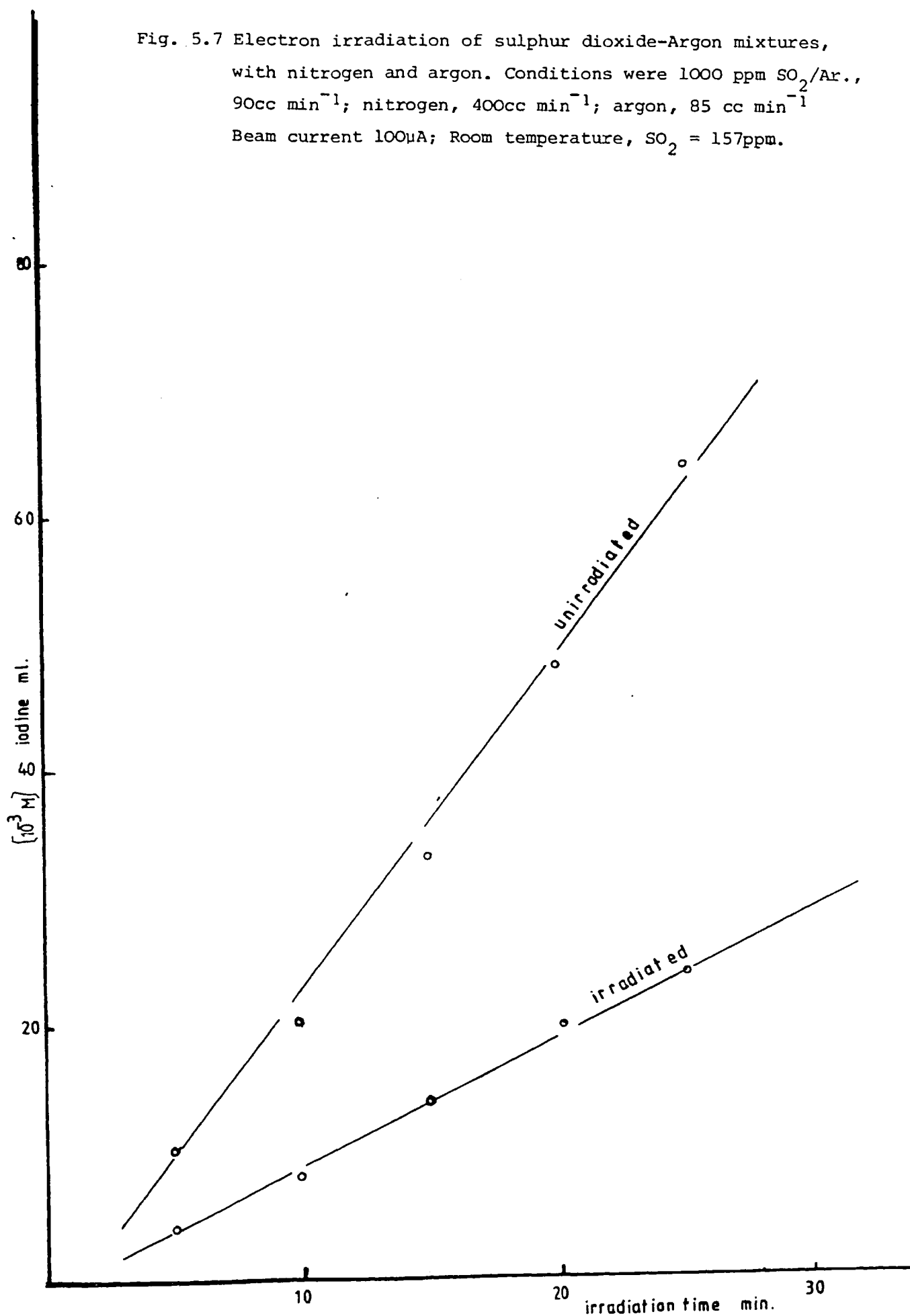


Fig. 5.8 Electron irradiation of sulphur dioxide-Argon; nitrogen and argon. Conditions are: 1000ppm SO_2/Ar , 104cc min^{-1} , nitrogen 75cc min^{-1} . Room temperature, Beam current, 100 μA , $\text{SO}_2 = 370\text{ppm}$.

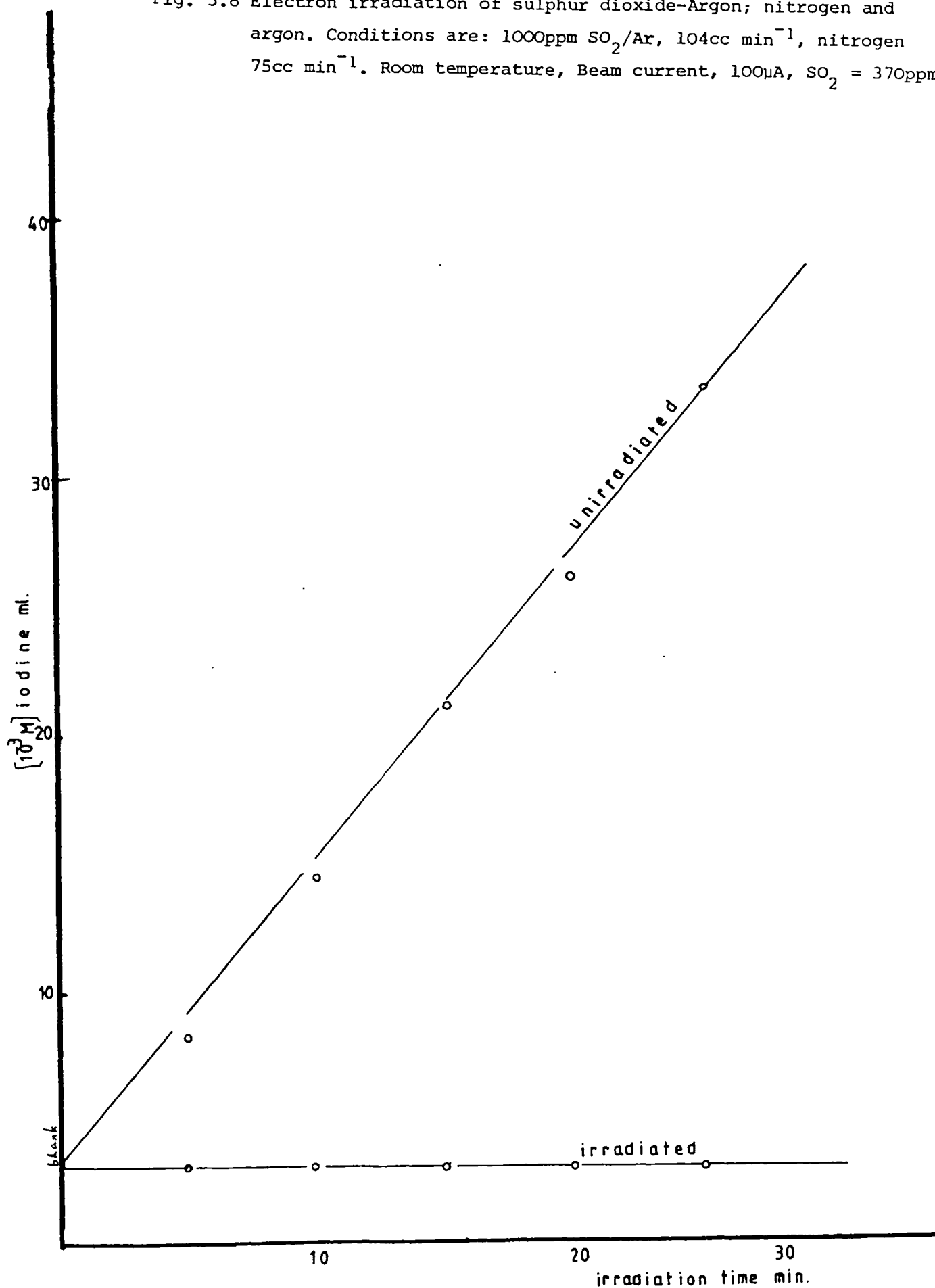
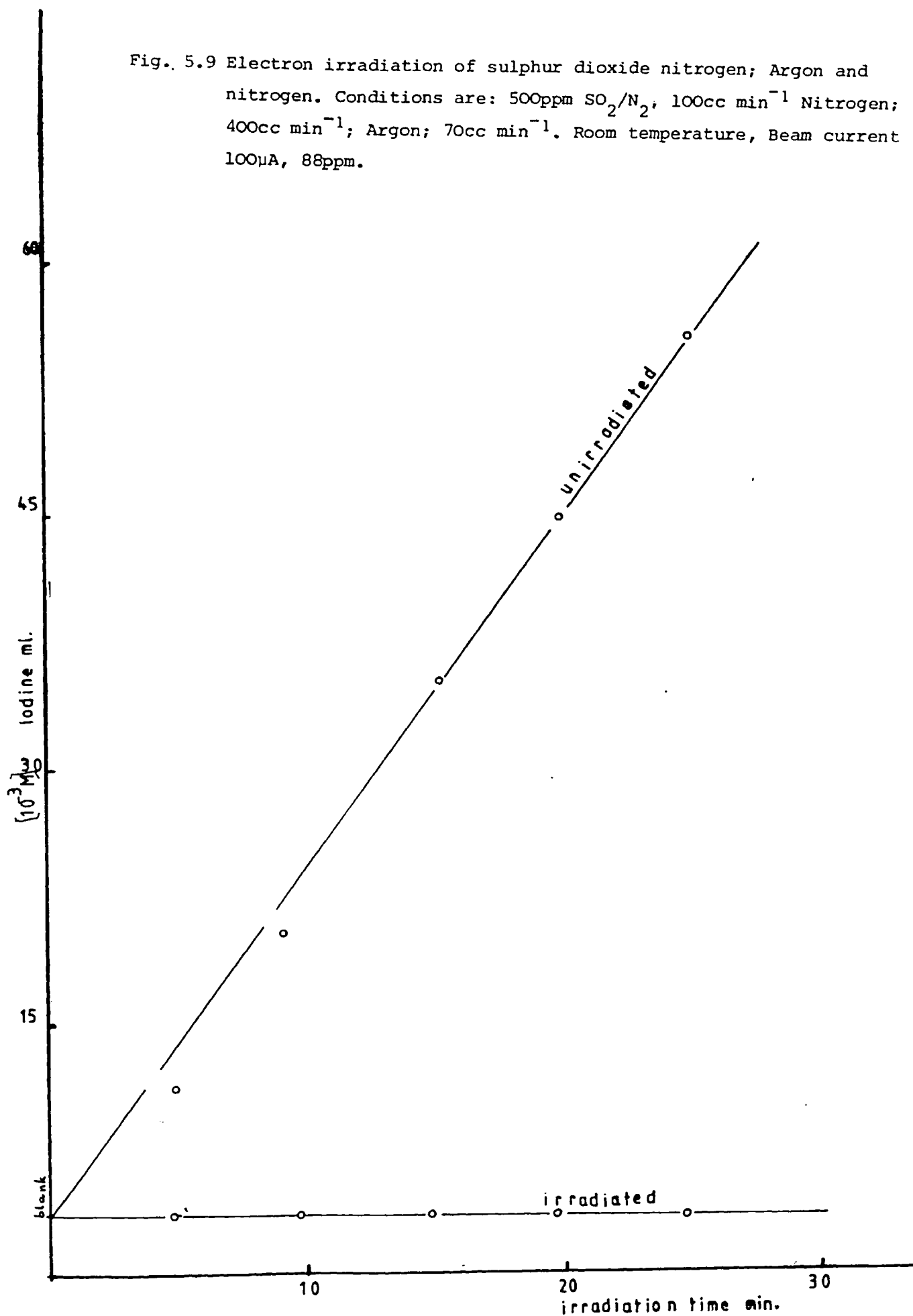


Fig. 5.9 Electron irradiation of sulphur dioxide nitrogen; Argon and nitrogen. Conditions are: 500ppm SO_2/N_2 , 100cc min^{-1} Nitrogen; 400cc min^{-1} ; Argon; 70cc min^{-1} . Room temperature, Beam current 100 μA , 88ppm.



FIGS 10. Electron irradiation of sulphur dioxide-Argon; Argon and nitrogen.
Conditions are: 500ppm SO_2Ar , 100cc min^{-1} ; Argon; 100cc min^{-1}
Nitrogen; 80cc min^{-1} . Room temperature, Beam current $100\mu\text{A}$, 179ppm.

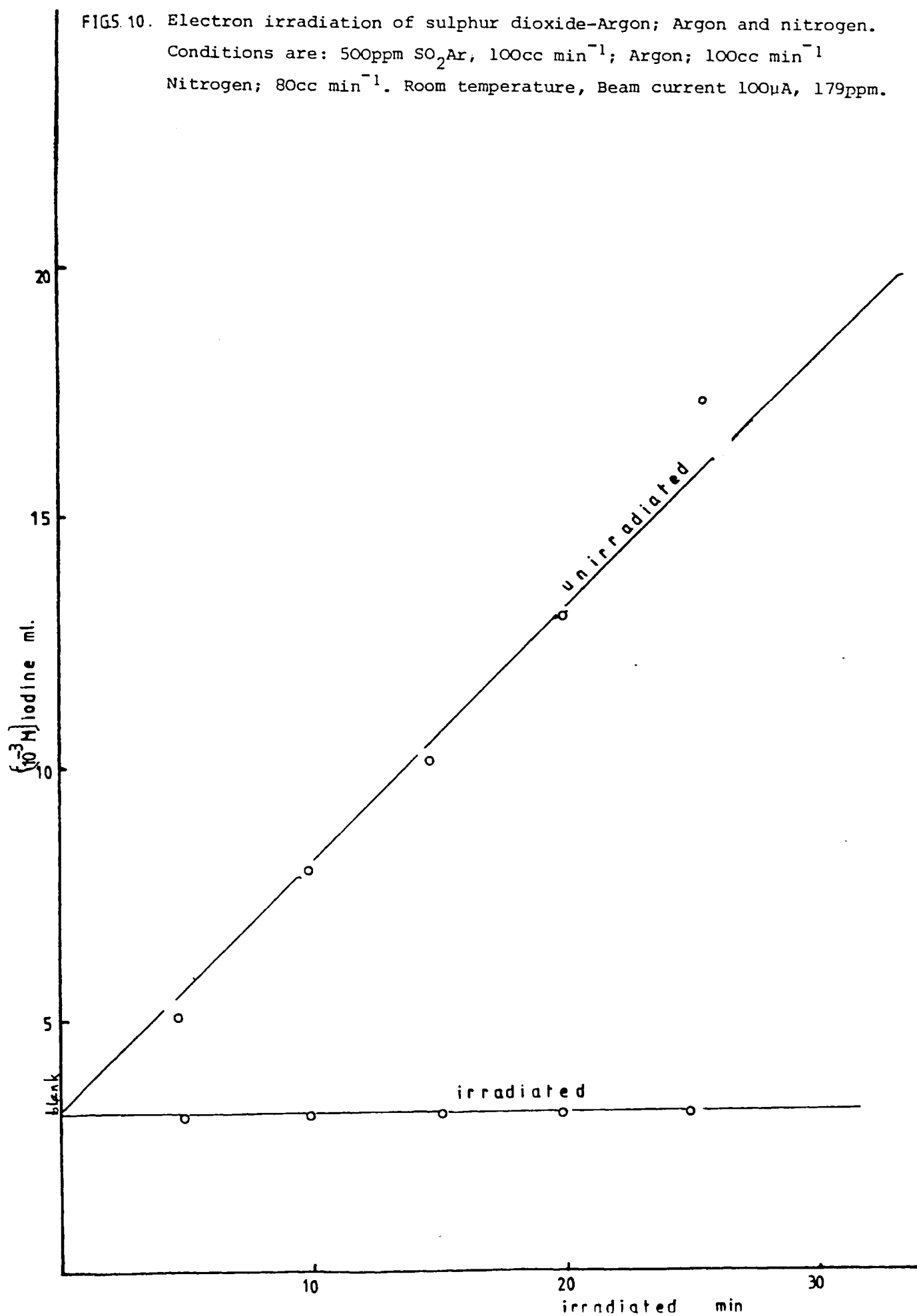
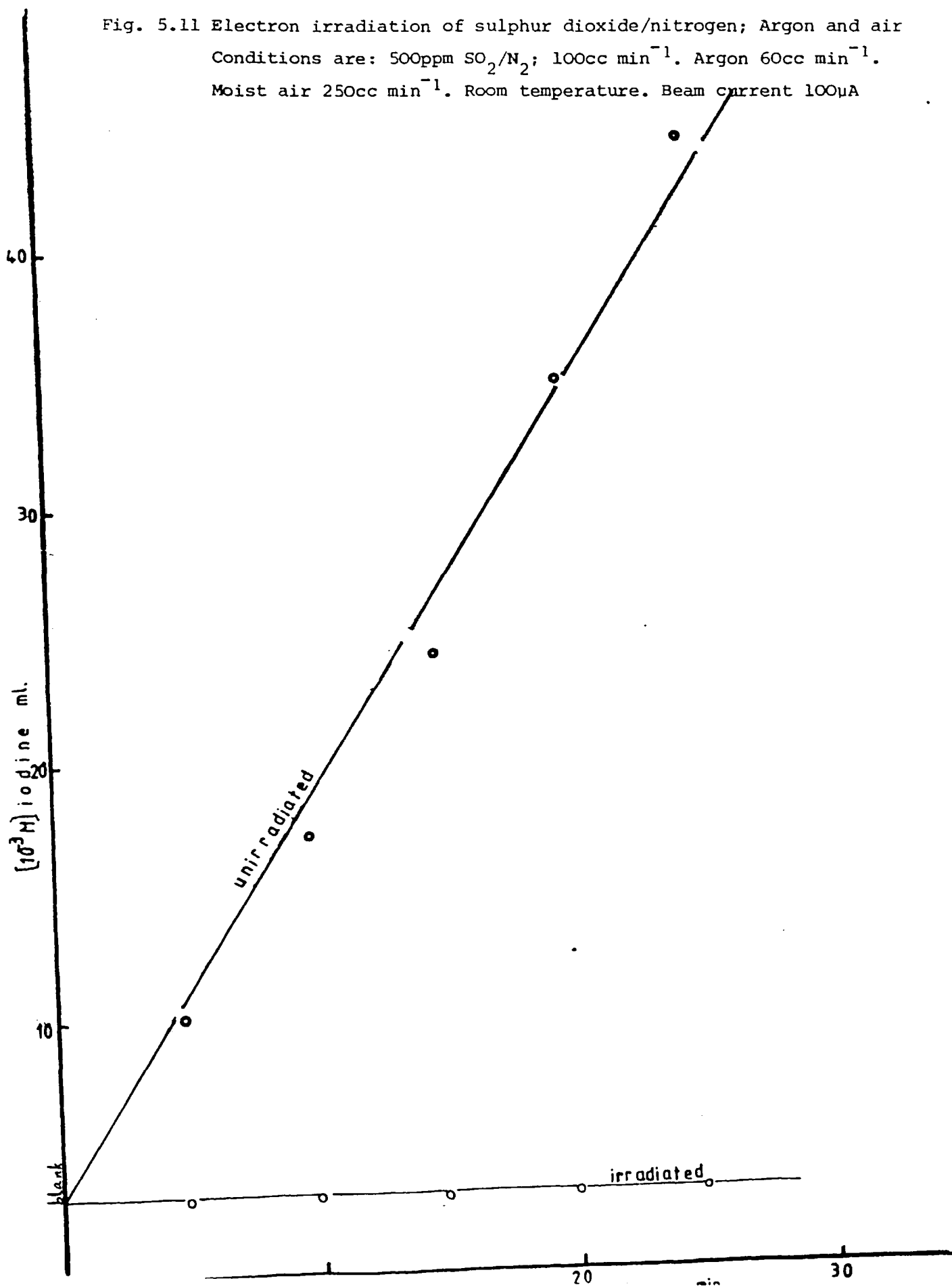


Fig. 5.11 Electron irradiation of sulphur dioxide/nitrogen; Argon and air
 Conditions are: 500ppm SO_2/N_2 ; 100cc min^{-1} . Argon 60cc min^{-1} .
 Moist air 250cc min^{-1} . Room temperature. Beam current 100 μA



The reduction in this case is about 58% and the "lead" time and titre are in good agreement with those determined in Fig. 5.13.

Comparing Figures 5.3 - 5.11 it is seen that air, and particularly moist air, strongly enhance the percentage removal of SO_2 . Invariably, sulphuric acid aerosol was observed in the product stream using moist air, but not with the dry mixtures.

5.6 Effects of varying electron beam currents

Sulphur dioxide moist air mixtures at a chosen set of concentrations were irradiated with the electron beam set at 2MeV with varying beam currents.

The results of measurements of SO_2 concentration (equivalent iodine titre) are shown before and after irradiation in Fig. 5.12.

After irradiation, there is a strong tendency of all results towards a "blank" titre, approximately $2\text{cm}^3 \text{I}_2$ solution. That is essentially all the sulphur dioxide was removed irrespective of the beam current varied from 10 to 115 μA . The results are shown in Table 5.2

FIG.5.12. Variation of conversions by electron irradiation of sulphur dioxide-nitrogen and moist air. Conditions were 1000ppm SO_2/N_2 ; 100cc min^{-1} ; and moist air 450cc min^{-1} ; currents are $115\mu\text{A}$; $75\mu\text{A}$; $30\mu\text{A}$; $25\mu\text{A}$; $10\mu\text{A}$, Room Temperature; 1) Unirradiated; 2) Irradiated

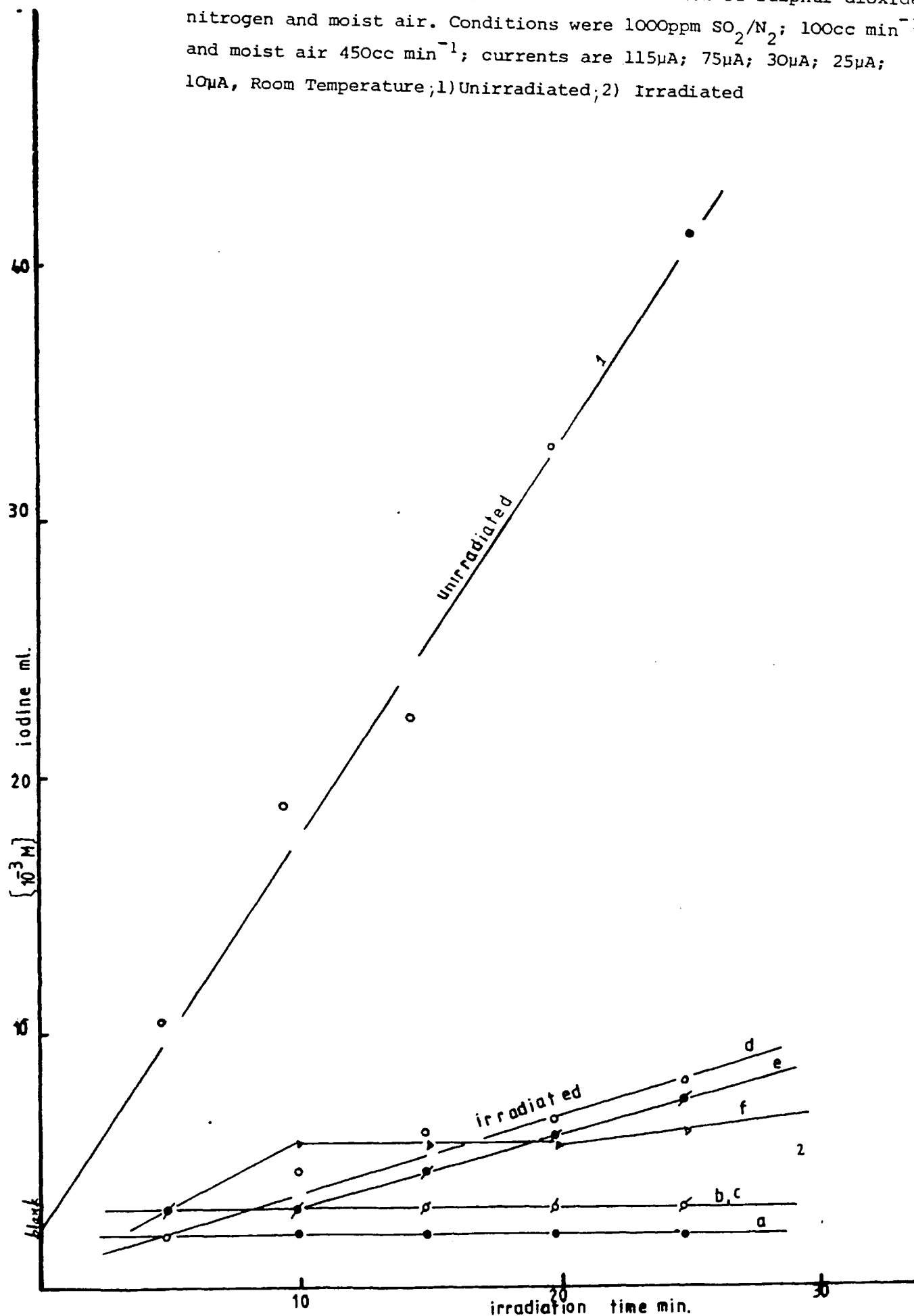


TABLE 5.1

Variation of conversions for the irradiation of sulphur dioxide in moist air and argon mixtures with electron beam currents							
Gas	Mixture	CONVERSION %					Beam current
		Irrad. Time(mins.)					
		25	20	15	10	5	μA
0.1%	SO ₂ /Ar	.31	.41	.51	.60	.58	235
0.05%	SO ₂ /N ₂ -Air-Ar.	.98	.54	.39	.46	.35	150
0.05%	SO ₂ /Ar	.25	.25	.28	.71	.90	65

TABLE 5.2

Variation of conversions for the irradiation of sulphur dioxide in moist air and nitrogen mixtures with varying electron beam currents.							
Gas 0.1%	Mixture	C O N V E R S I O N %					Current μA
		time (Minutes)					
		25	20	15	10	5	
SO ₂ /N ₂	Air	0.86	0.92	0.90	0.94	0.78	115
SO ₂ /N ₂	Air	0.95	0.93	0.90	0.89	0.78	95
SO ₂ /N ₂	Air	0.79	0.85	0.75	0.86	0.96	90
SO ₂ /N ₂	Air	0.94	0.98	0.985	0.98	0.96	30
SO ₂ /N ₂	Air	0.965	0.946	0.92	0.91	0.96	10

5.7. Irradiation and reaction vessel geometry

TABLE 5.3

Reactor Length (cm.)	Reactor Diameter (cm.)	Material
126	0.5	Quartz
80	1.0	Pyrex
42	2.0	Pyrex

This length of the reactors correspond to the irradiated surface by the electron beam.

5.8. Kinetic analysis

Kinetic studies of sulphur dioxide removal in moist air by electron beam accelerator were performed in one of the plug-flow reactors described above.

The experiments were carried out as follows. Initially the reactor was purged with air for about 30 mins. before each run. The purging time was more than sufficient to clear any residual aerosol. The tubular reactor (of 0.5cm diameter) was wrapped in aluminium foil to protect it from breaking in the discharge from the electron beam and also to prevent possible photochemical reaction. It was kept at 70 - 80°C by means of an air-blower, to prevent the formation of (NO)_x compounds.

The irradiation was carried out at 2MeV with electron beam through the aluminium window.

After the entire stream had passed through the reactor it was absorbed in NaOH solution (0.1M) and analysed using iodine solution (10⁻³M). Results are reported in section 5.10 below.

5.9 Calculation of rate constant for the decomposition of sulphur dioxide.

Suppose the reaction is first order with respect to the concentration of SO₂

$$\text{ie. } r = k [\text{SO}_2]$$

(The rate is actually thought also to depend on the concentrations of nitrogen and oxygen, but since these are present to such a large excess, their concentrations can be assumed to remain constant). It was decided to test the data in the familiar model for a first order reaction in a

plug flow reactor. Ref. (74)

$$r = - \frac{dn_A}{dv_r}$$

$$\text{But } [SO_2] = \frac{n_{SO_2}}{F}$$

$$\therefore V_r = \int_{n_{SO_2}^o}^{n_{SO_2}^e} \frac{dn_{SO_2}}{k \left(\frac{n_{SO_2}}{F} \right)}$$

$$\therefore V_r = \frac{F}{k} \ln \frac{n_{SO_2}^e}{n_{SO_2}^o}, \text{ if } F \text{ is assumed to be constant}$$

$$\text{And, if conversion } X = \frac{n_{(SO_2)^o} - n_{(SO_2)^e}}{n_{(SO_2)^o}}$$

Where:

r = rate of reaction

V_r = volume of reactor

n_A = number of moles of reacting species (A)

F = total volumetric flowrate

$(SO_2)^o$ = initial conditions

$(SO_2)^e$ = existing conditions

X = fractional conversion

τ = residence time

$$\therefore -V_r/F \cdot k = \ln(1-X)$$

$$\therefore \ln(1-X) = -k$$

Therefore, a graph of $\ln(1-X)$ versus τ will be a straight line having a slope of $(-k)$ if the reaction is first order.

5.10. Analysis of results of kinetic experiments

a) Method of calculation for lead time.

There is a lead time associated with the irradiated runs because of the time required to operate the safety systems, seal the laboratory, switch on the accelerator and bring it up to the require voltage and current.

Conversion is defined by

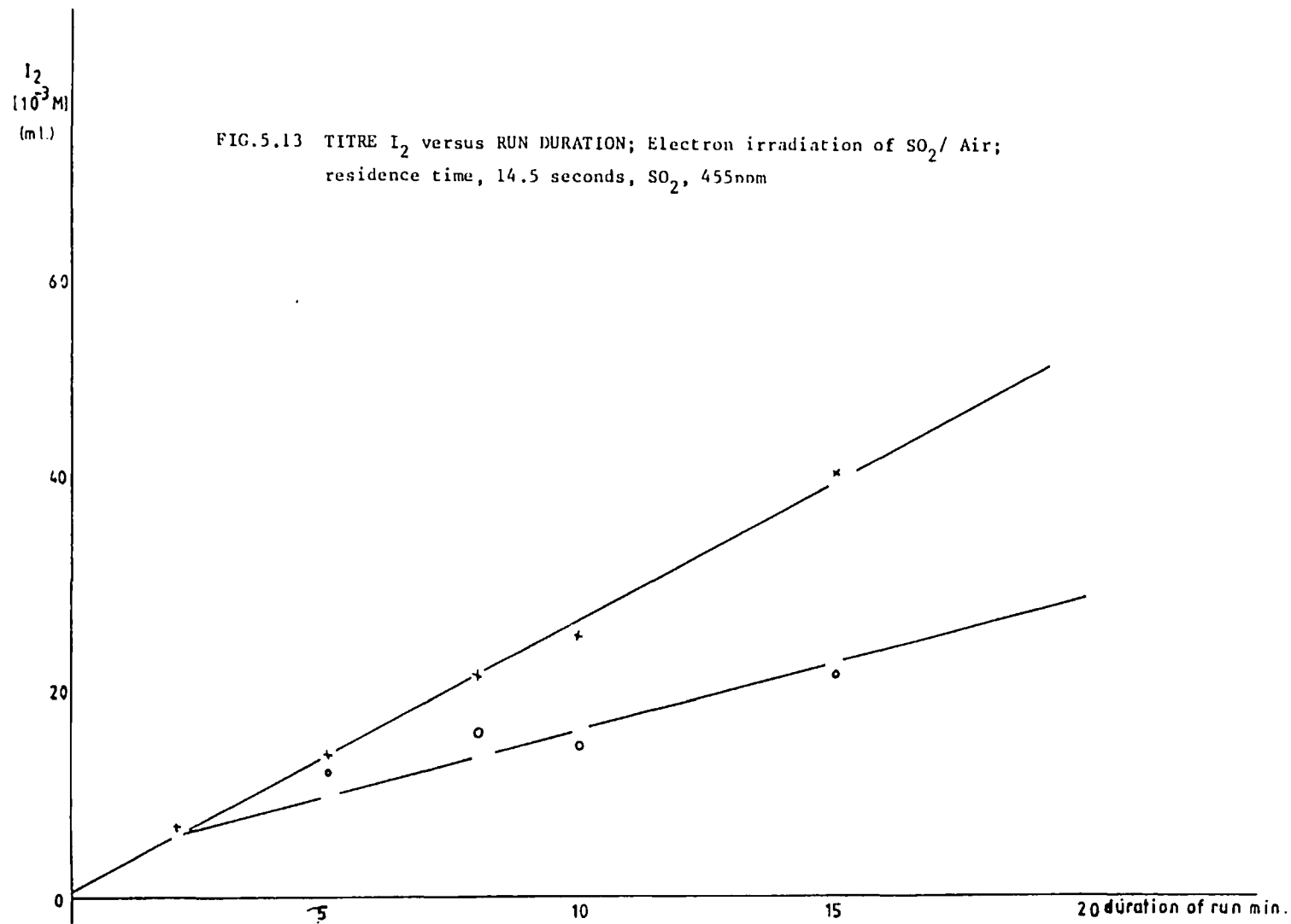
$$X = \frac{x' - y'}{y'}$$

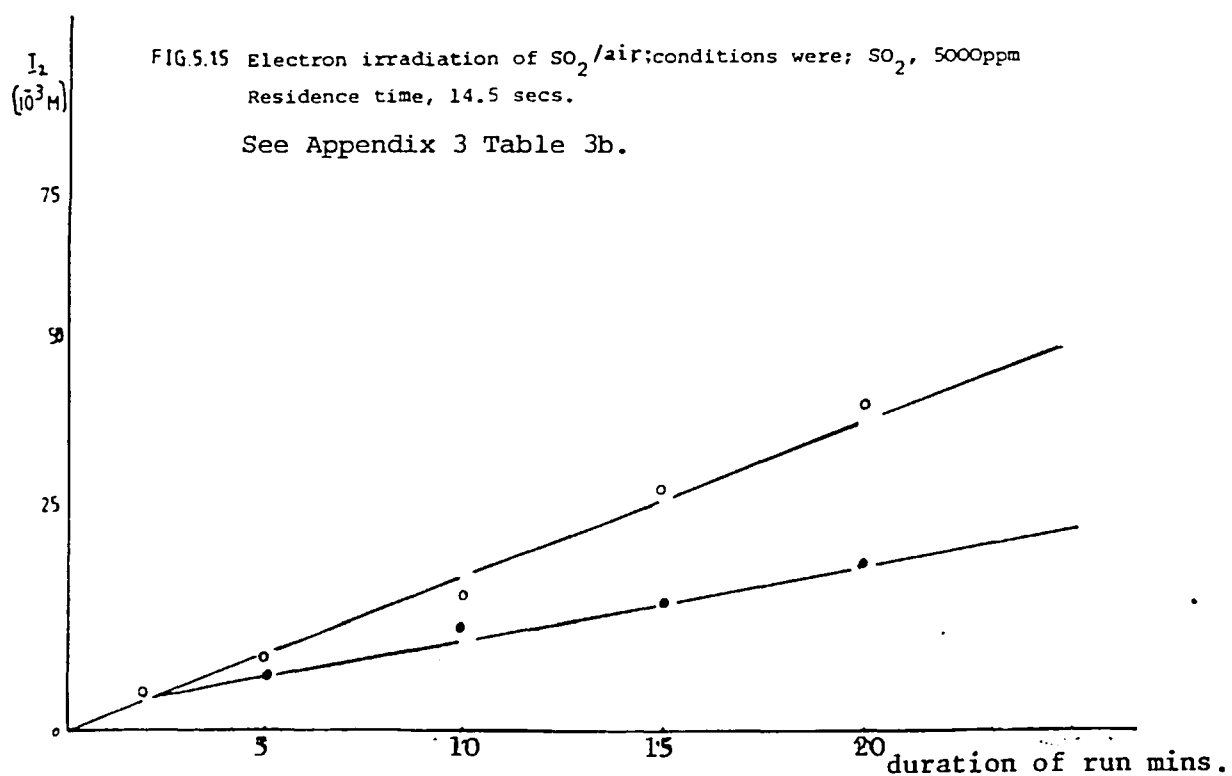
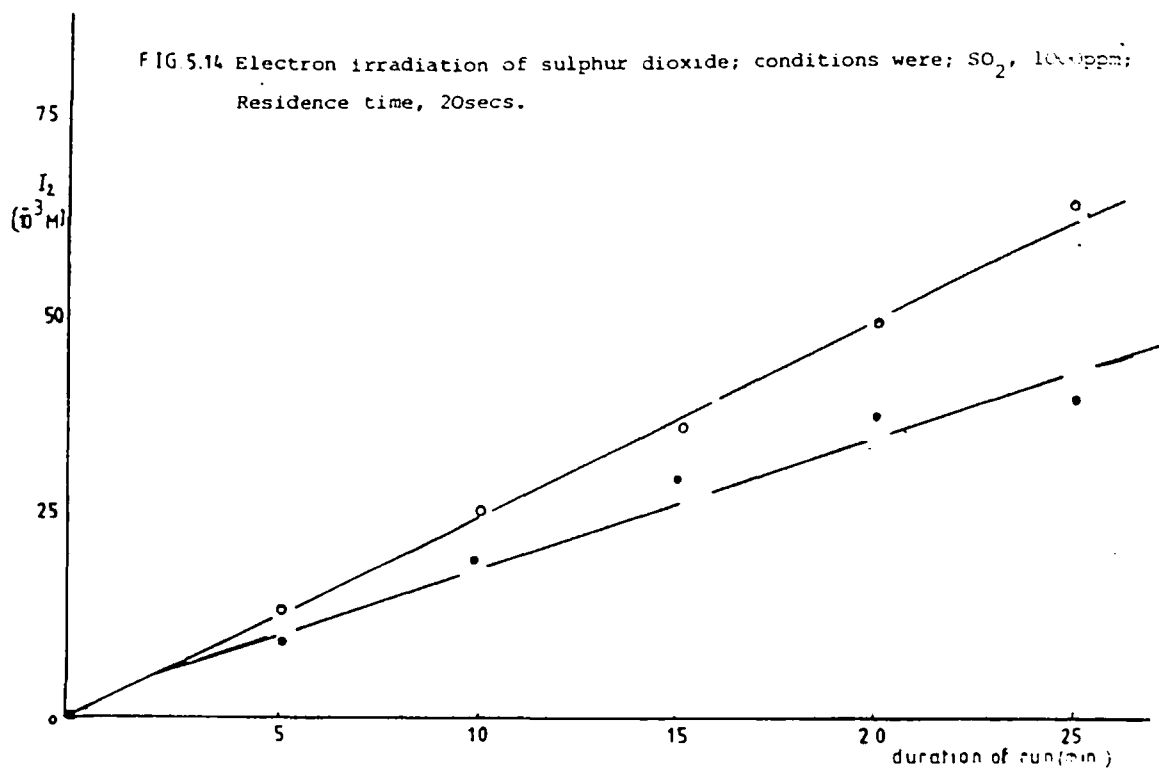
(x', y' defined below, p. 64).

Typical experiments were done to correct the titres, with and without irradiation, as shown in Figures 5.13, 5.14, 5.15.

To calculate, it is assumed that up to the value of the lead time no oxidation reaction took place, but from that time onwards the rate of reaction was constant, giving a linear increase titration of irradiated reactants against length of run. Figure 5.13 shows this characteristic. Thus the point where the line representing irradiated reactants intersects the line for non irradiated reactants represents the lead time.

For lead time t and total duration of run T , the corrected titre of iodine is calculated as:





$$x' = x(1-t/T)$$

$$y' = y - xt/T$$

Where:

x, y = titre readings on blank, radiated runs respectively.

x', y' = corrected titre readings

xt/T = quantity of iodine equivalent to the number of moles of sulphur dioxide which passed into the absorbing solution during the lead time.

V_r = volume of reactor

V_t = flowrate through the reactor; *variable never used and seems to be the same as F*

In subsequent experiments the corrected titres were first calculated and then plotted, with the best line possible fitted to these points. From the blank and irradiated graphs using the curves (rather than the actual points, in an attempt to reduce error) the conversions were then calculated.

The fractional conversion was then used to calculate the rate constant.

b) Results of chemical conversion

Cylinders containing three different concentrations of sulphur dioxide were used: 0.05% SO_2/Ar , 0.1% SO_2/N_2 , 1.0% SO_2/N_2 . The first set of experiments were to find the lead time, and a different SO_2 -Air ratio was used with each cylinder. The results obtained from graphs of titre vs run duration are summarised in Table 5.4 and Figs. 5.16, 5.17 and 5.18.

TABLE 5.4Measurement of lead-time for various mixtures

SO ₂ conc. in N ₂ mixture %	SO ₂ conc. (ppm) in reactor	ratio SO ₂ -Air	residence time (s)	lead time and titre	
				(mins)	I ₂ (10 ⁻³ M) ml
0.05%	455	10:1	14.5	2.1	6.25
0.1%	1000	no air	20	2.25	7.0
1.0%	5000	1:1	14.5	2.2	40

For each set of conditions, the same lead time of 2.2 mins. was obtained. From these graphs, conversions of 50%, 38%, and 47% respectively, were calculated.

The next set of experiments involved gauging the effect of the ratio of air to the mixture of sulphur dioxide in nitrogen as seen below, Table 5.5 and Appendix 3 Table 3a.

FIG.5.16 Electron irradiation of sulphur dioxide/ N_2 -Air

$SO_2 = 5000$ ppm; 1part SO_2/N_2 : 1 part air

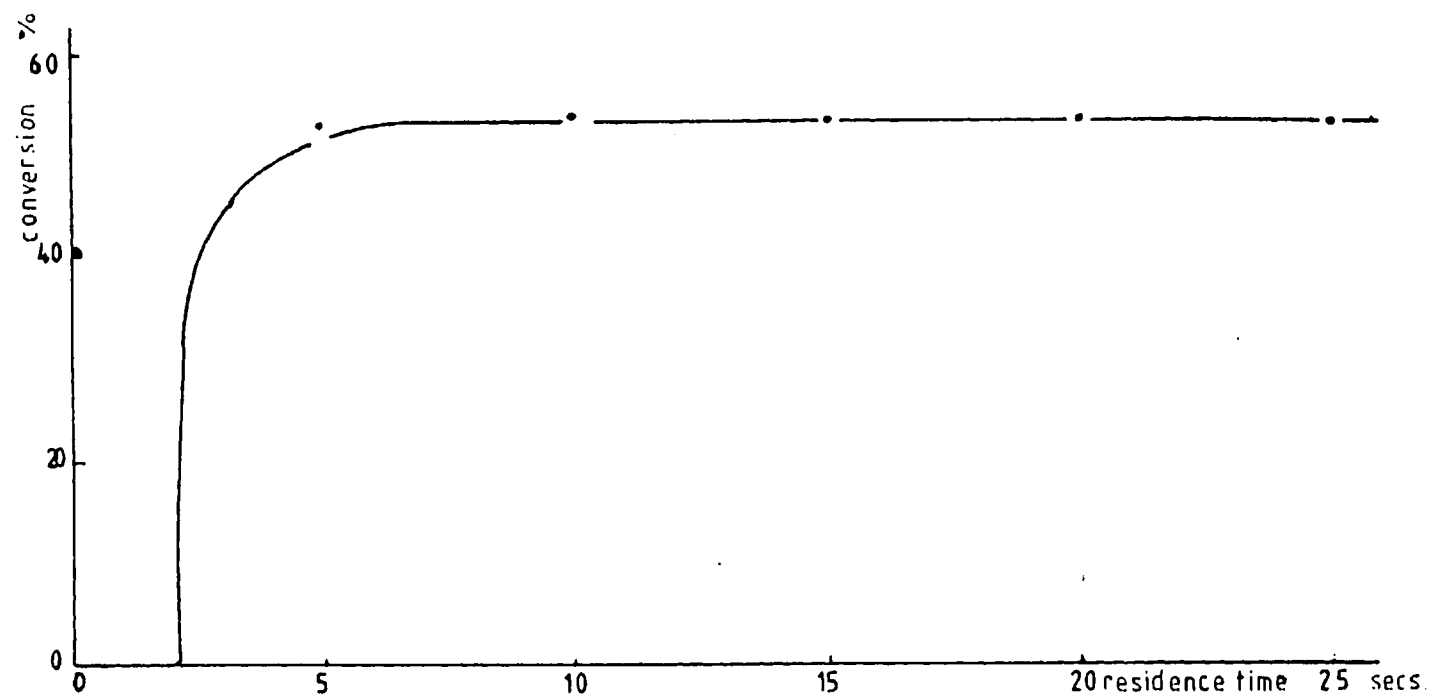


FIG.5.17. Electron irradiation of SO_2/N_2 without air
 SO_2 , 1000 vpm

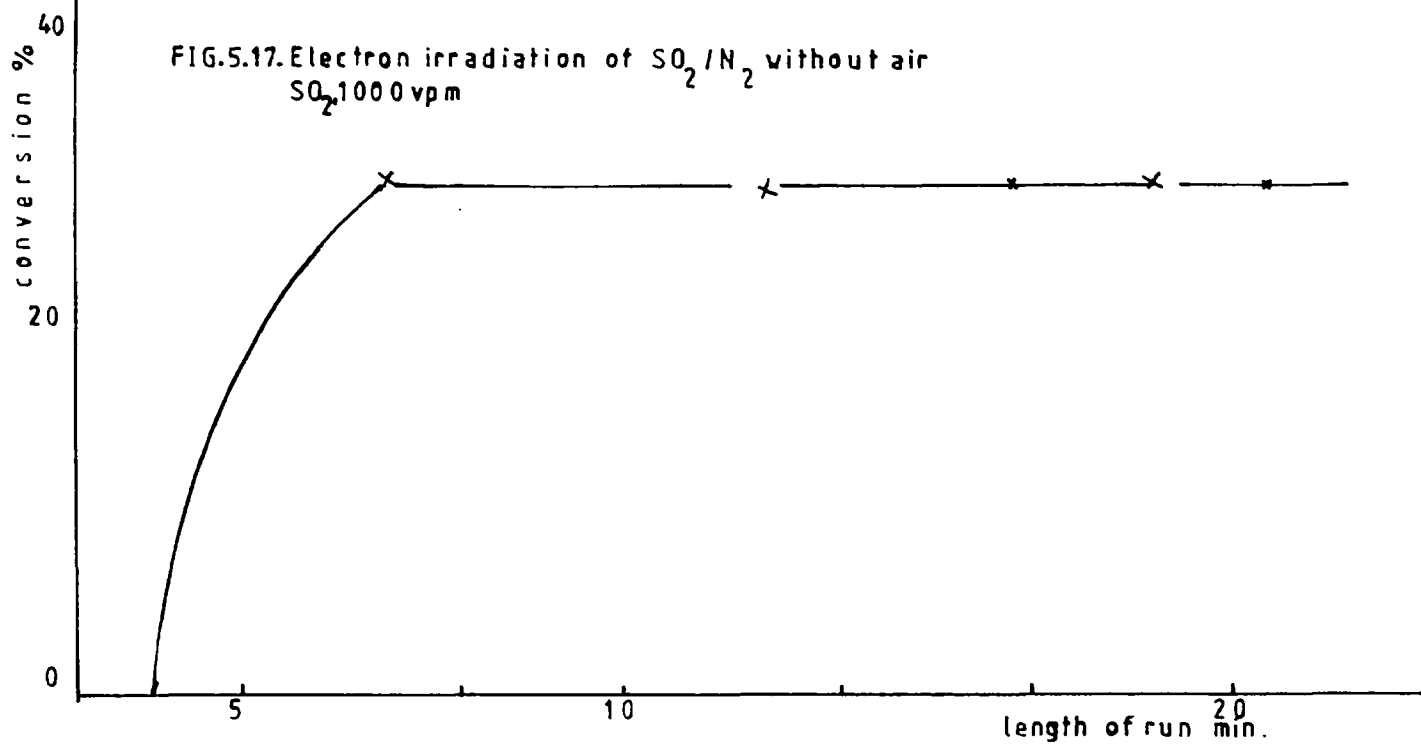
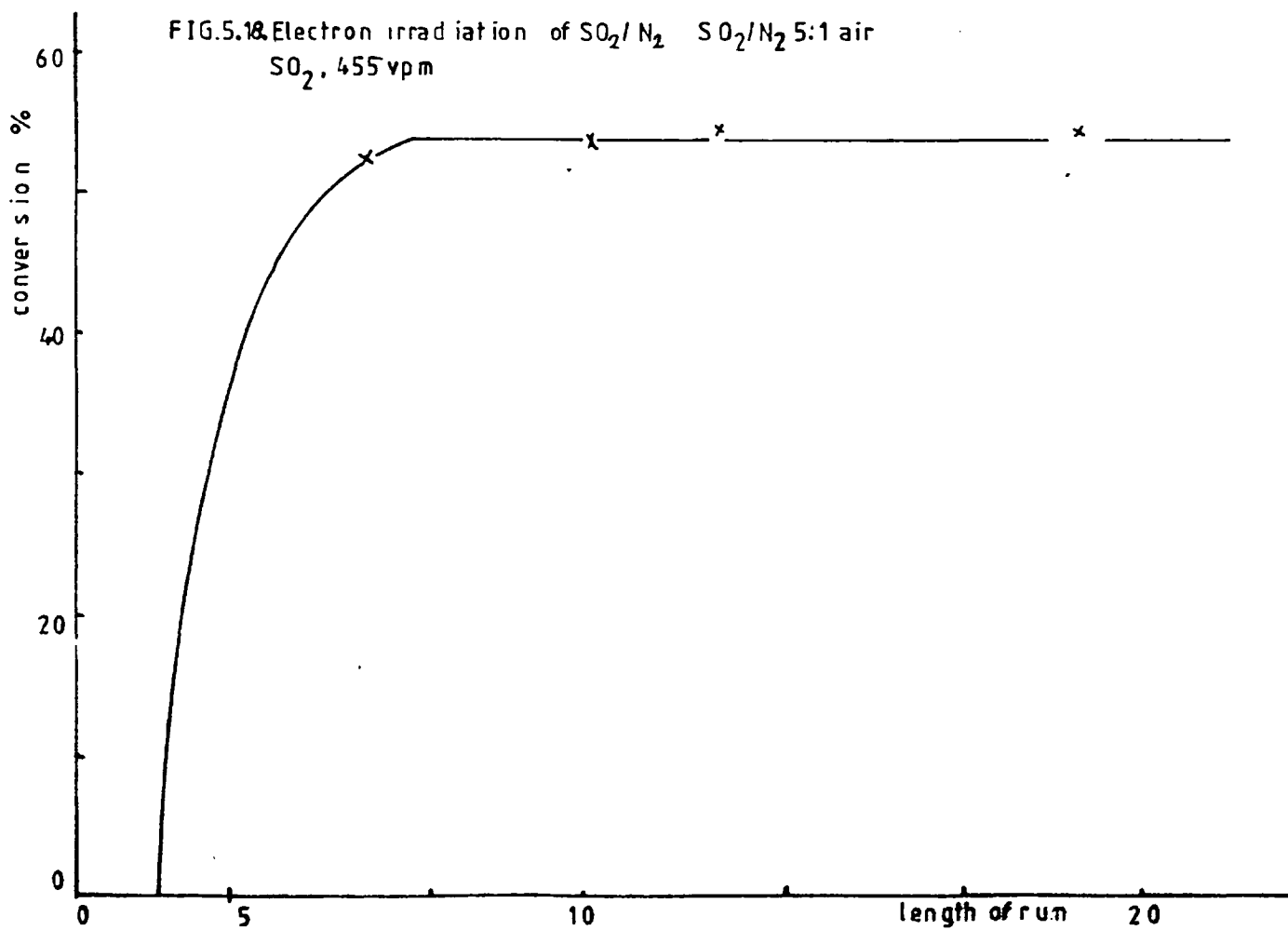


FIG.5.18. Electron irradiation of SO_2/N_2 SO_2/N_2 5:1 air
 SO_2 , 455 vpm



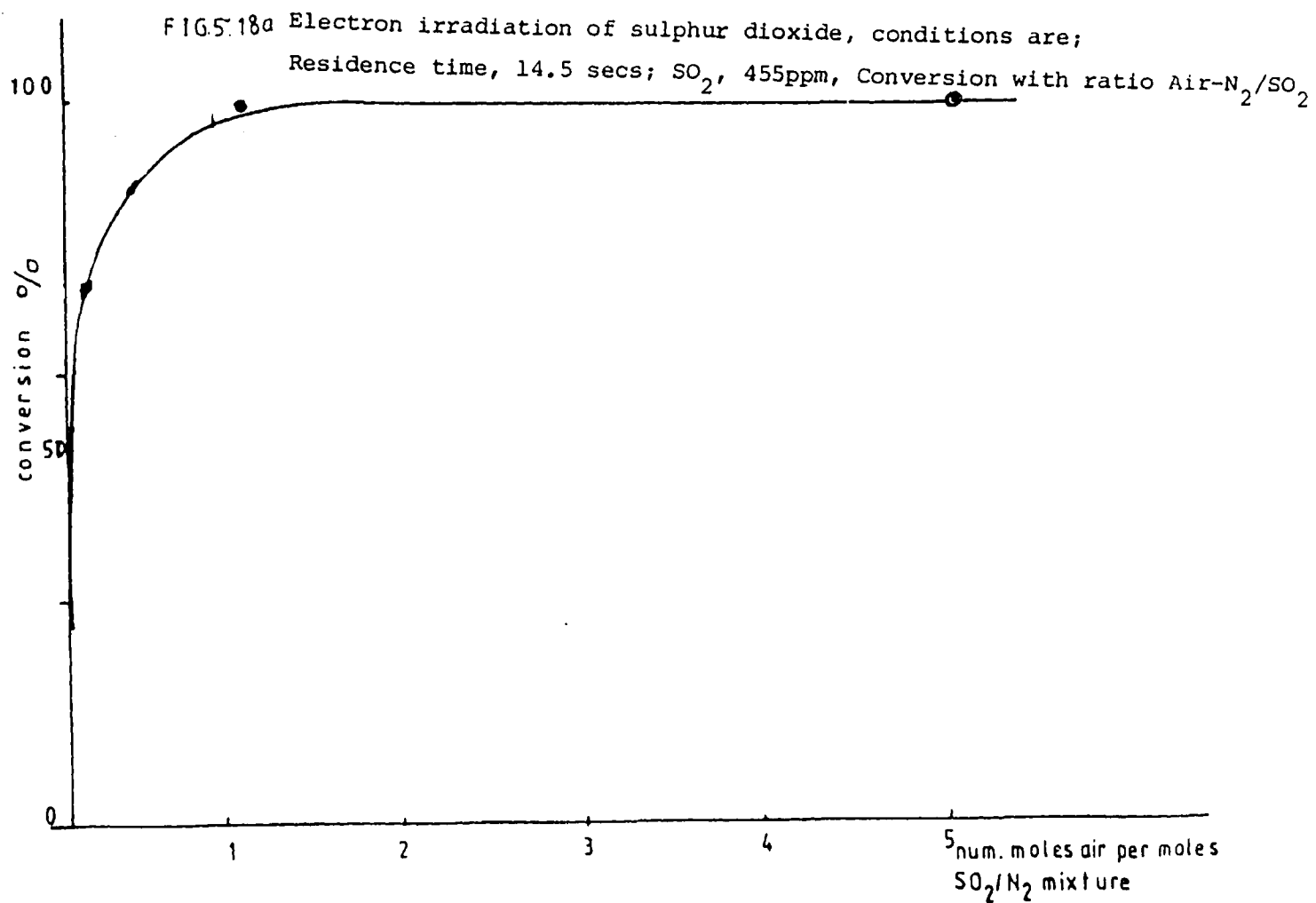


TABLE 5.5

Variation of conversion with quantity of air. Conditions are: irradiation time 10 mins.. residence time 14.5 seconds, 0.5cm diameter reactor.			
Num. moles air per mole of SO_2/N_2 mixture	Titre Iodine (10^{-3}M) mls.		Conversion %
	blank	rad.	
0	35.4	30	15.3
1.0	18.7	1.95	89.6
5.0	6.8	0.77	88.7
0.2	31.1	8.8	71.7
0.1	34.4	12.7	63.1

The conversion was plotted against moles air per mole SO_2/N_2 mixture. As seen in Fig. 5.18₃ it is exponential in shape, falling from 88% at 5 moles air per mole SO_2 , to 15% at SO_2/N_2 .

Finally, the conversions at different residence times were calculated under the conditions shown in table 5.6. A lead time of 2.2 mins. was assumed in calculating the conversions. The corrected titres and the conversions calculated from them are shown in tables (5.7 and 5.8), the titres and the conversions are plotted against residence time in

TABLE 5.6

Variation of conversion with τ , conc. $\text{SO}_2 = 455 \text{ ppm}$

Residence time (Seconds)	Flow rates (cm^3/min)		Titre I_2 $10^{-3}\text{M}(\text{cm}^3)$		Corrected titre (cm^3)		Conversion %
	SO_2	Air	Blank	Irradiated	Blank	Irradiated	
3.6	500	50	89	68	69.4	48.4	33.3
8.0	225.5	22.5	41.2	27.2	32.1	18.1	45.0
14.5	125.5	12.5	23.4	10.9	18.3	5.8	60.0
20.0	91.0	9.0	16.7	9.0	13.0	5.3	65.4

T A B L E 5.6 (continue)

Variation of conversion with τ , conc. SO_2 = 910 ppm

Residence time (Seconds)	Flow rates (cm^3/min)		Titre I_2 $10^{-3}\text{M}(\text{cm}^3)$		Corrected titre (cm^3)		Conversion %
	SO_2	Air	Blank	Irradiated	Blank	Irradiated	
3.6	500	50	204	156	159.0	114.1	28.3
8.0	225.5	22.5	91	60	71.0	40.0	42.8
14.5	125.5	12.5	54.9	35.8	42.8	23.7	51.9
20.0	91	9.0	21.5	13.6	16.8	8.9	63.2

T A B L E 5.7

Variation of titre with length of run, to discover lead time

a) 1000 ppm SO₂ ,

$\tau = 20$ secs. ,

No air

Length of run (Minutes)	Titre I ₂ 10 ⁻³ M (cm ³)		Corrected Titre (cm ³)		Conversion %
	Blank	Irradiated	Blank	Irradiated	
5	13.6	9.8	7.0	4.5	35.7
10	25.1	20.2	19.7	12.9	34.5
15	36.7	31.8	32.3	21.1	34.7
20	50.2	38.5	45.0	29.4	34.7
25	65.6	39.5	58.6	37.7	35.7
Lead time = 2.25 minutes = 6.3cm ³					

T A B L E 5.8

b) 455 ppm SO₂ , τ = 14.5 seconds , 5 parts N₂/SO₂: 1 part air

Length of run (Minutes)	Titre I ₂ 10 ⁻³ M (cm ³)		Corrected Titre (cm ³)		Conversion %
	Blank	Irradiated	Blank	Irradiated	
2	8.0	8.0	-	-	-
5	14.2	13.3	7.8	3.8	51.3
8	22.0	16.8	16.1	8.0	50.3
10	25.0	15.5	21.3	10.8	49.3
15	42.3	22.5	34.9	17.7	49.3
Lead time = 2.2 minutes = 6.5 cm ³					

figures 5.19, 5.20 and 5.21.

The order of the reaction was confirmed to be one as shown in Figure 5.22 and the values of k derived from the slopes are in table 5.9.

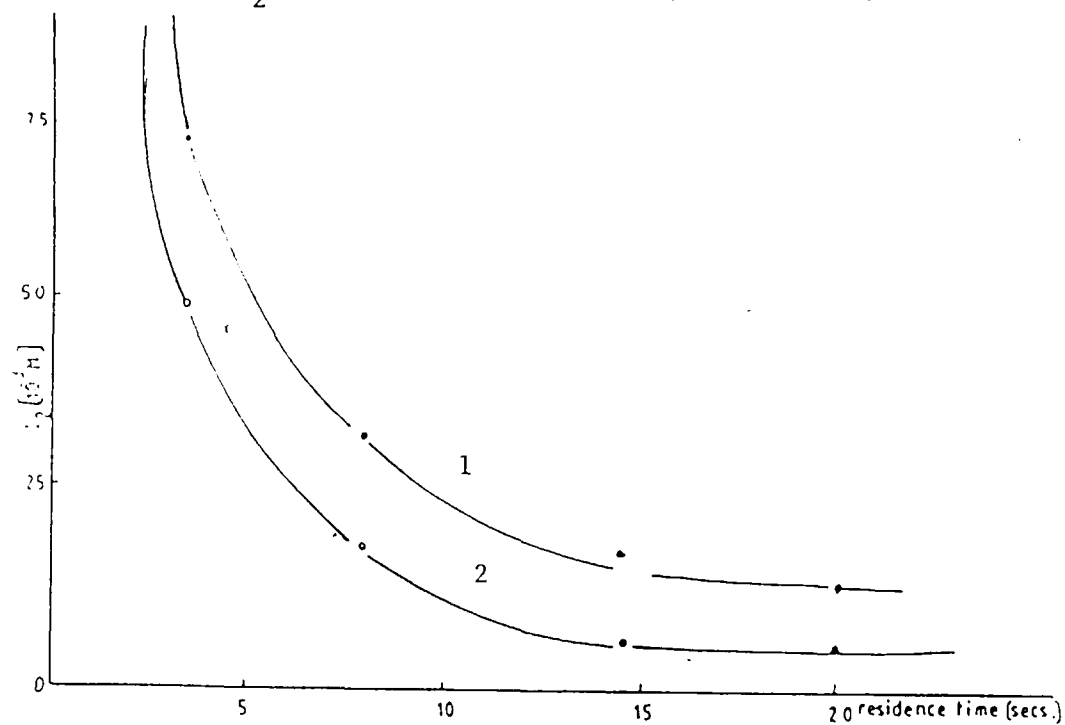
TABLE 5.9

Typical conditions and values of the rate constant

SO ₂ /N ₂ mixtures composition	SO ₂ conc- entration in reacting mixture	ratio SO ₂ /N ₂ mixture : Air	lead time (mins)	Rate constant k (seconds ⁻¹)
0.05%	455	10:1	10	0.042
0.1%	910	10:1	10	0.038

It was also observed that aerosol formation occurred at all residence times, confirming the sulphuric acid aerosol theory. Aerosol was not observed when humid air was not added.

FIG.5.19. Electron irradiation of SO_2/N_2 , at 10min. irradiation time
 SO_2 , 455ppm 1) unirradiated 2) irradiated.



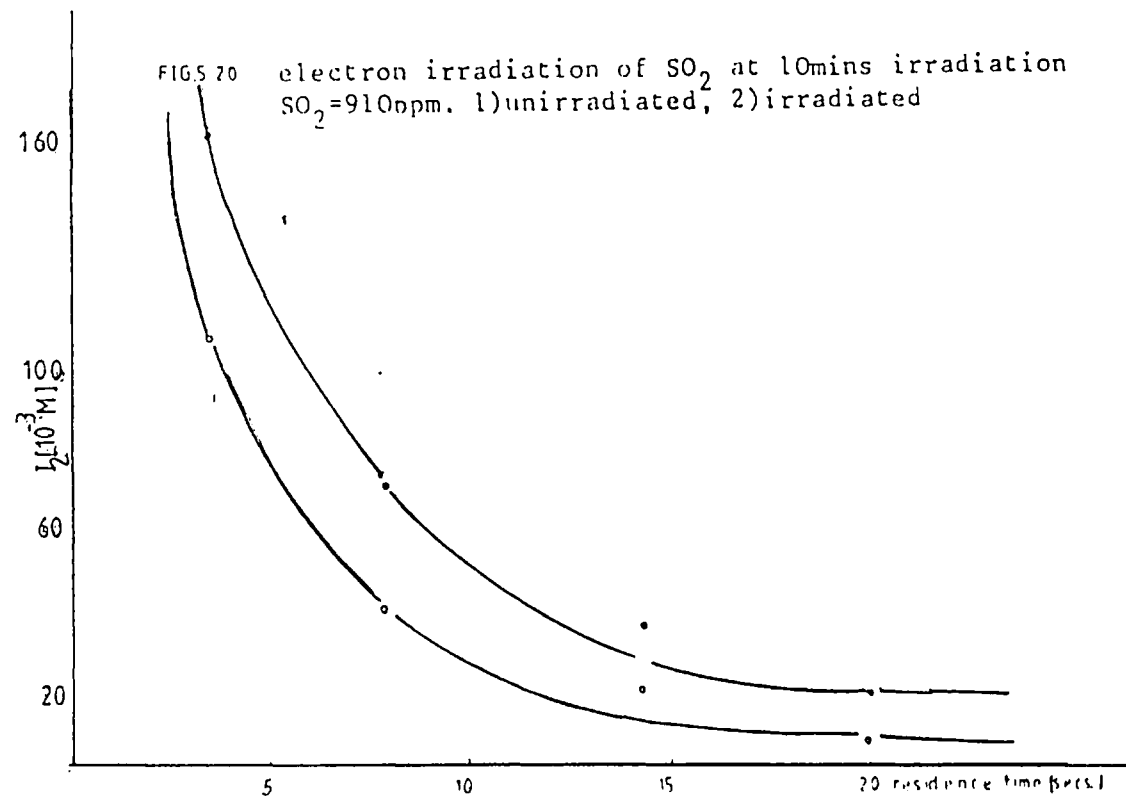


FIG. 5.21. CONVERSION OF SULPHUR DIOXIDE/NITROGEN AT 455ppm AND 910ppm BY ELECTRON IRRADIATION

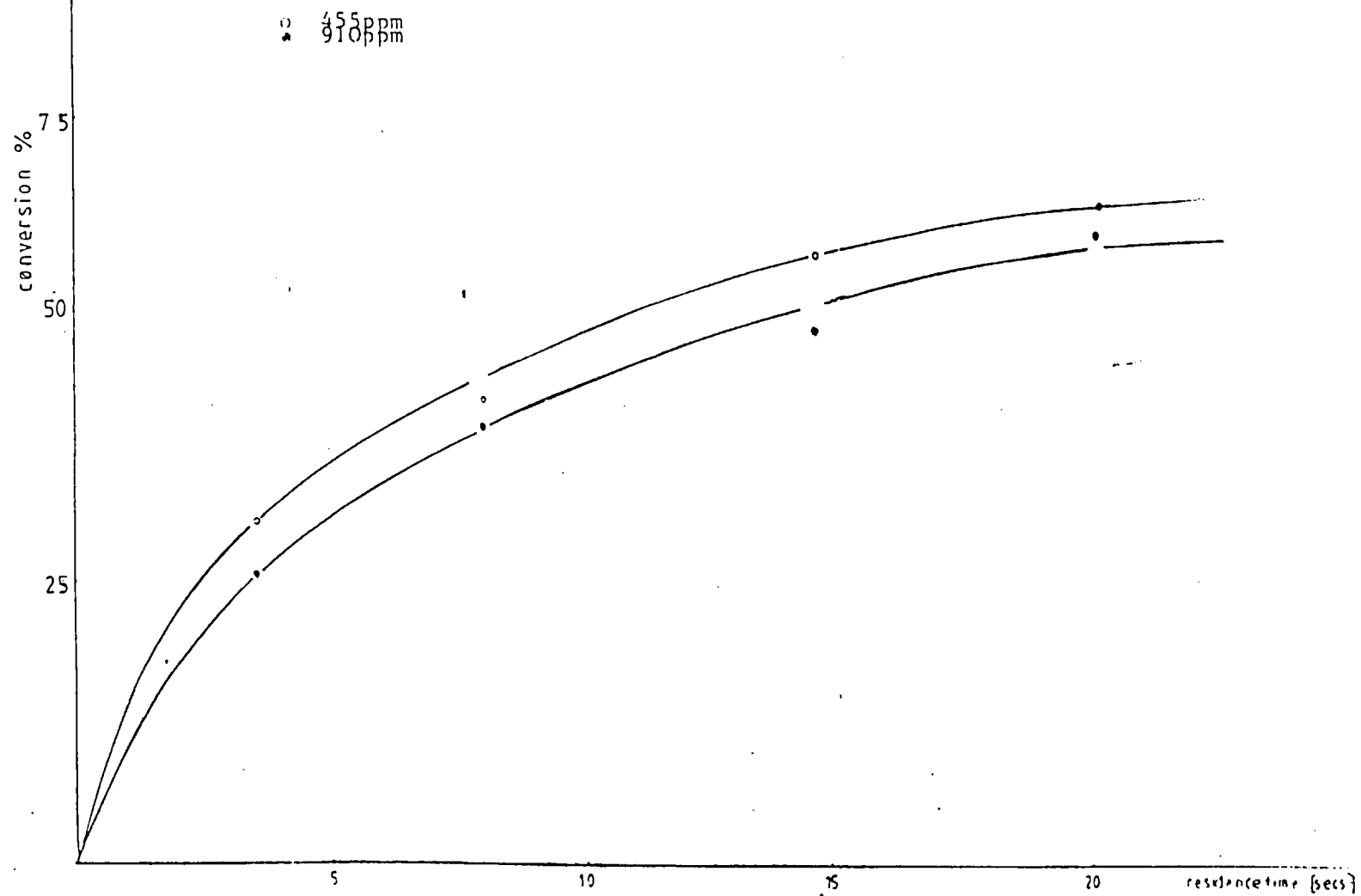
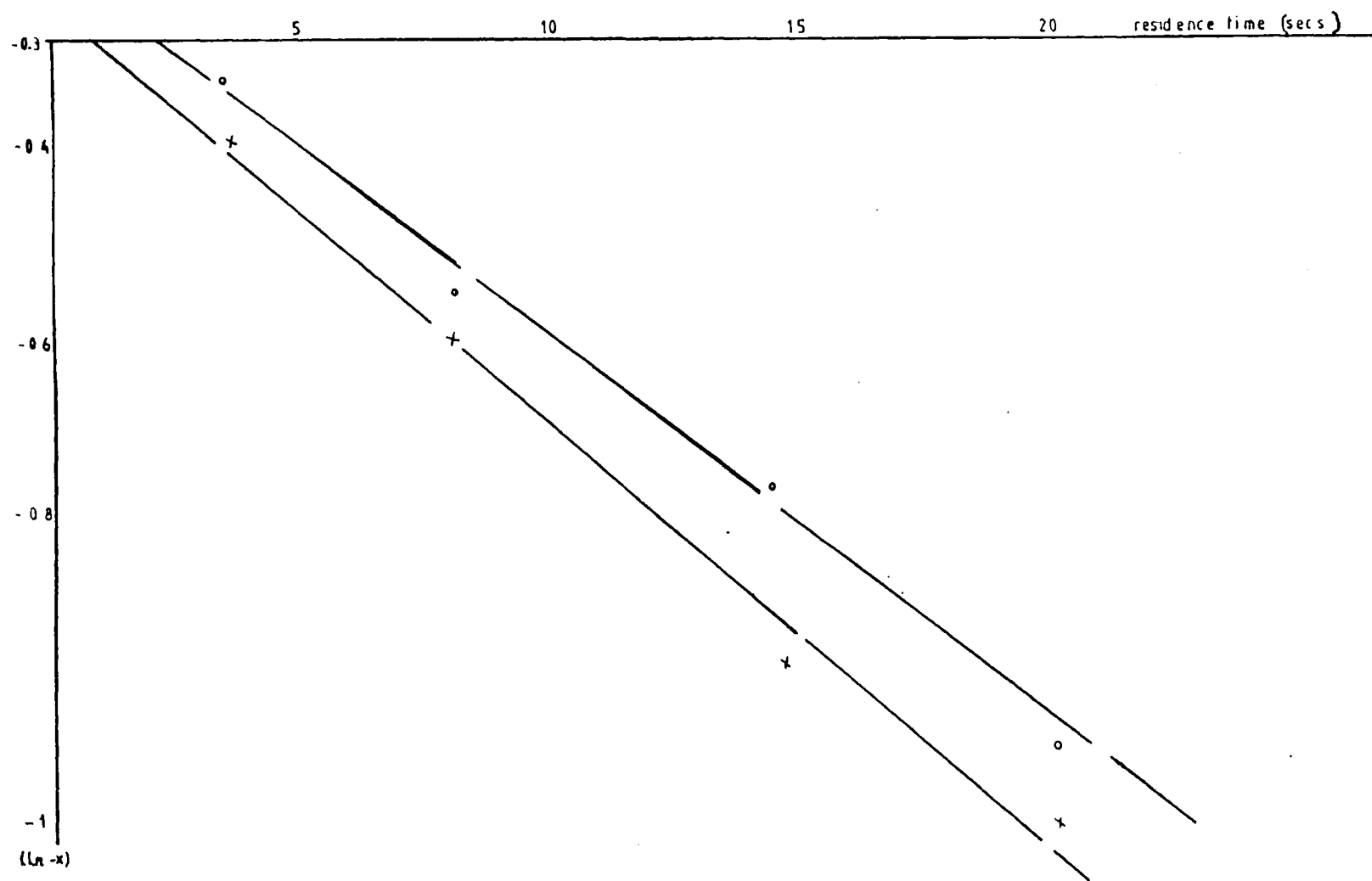


Fig.5.22 Kinetic order of sulphur dioxide oxidation at 455ppm and 910ppm, by irradiation



Errors

The efficiency of the mixer is difficult to quantify, but as it relies on diffusion and eddy currents it is unlikely to be above 97%, and may be much lower.

Accuracy of flow meters - $\pm 0.1\text{cm}$ in 4cm = $\pm 2.5\%$

Accuracy of titration (max) - $\pm 0.1\text{cm}$ in 10cm = $\pm 1.0\%$

Error in mixer - 3%

Error in titre = $3 + 2.5 + 1 = \pm 6.5\%$

Error in calculation of conversion = $2 \times 6.5 = \pm 13\%$

(calculation of conversion involves taking difference of 2 titre readings).

CHAPTER 6

RESULTS OF ELECTRON BEAM RADIATION: AEROSOLS

6.1 Introduction

In this chapter are described the measurement of size distributions by light scattering techniques in aerosols which have been produced from the $\text{SO}_2/\text{N}_2 + \text{Air}/\text{H}_2\text{O}$ system, irradiated by the electron beam.

These submicron aerosols, which are of narrow size distribution, can be prepared quite reproducibly when appropriate precautions in operating the collector are taken. Such experiments have the advantage that rapid measurements can be made without otherwise disturbing the particles.

6.2 The problem of inversion of scattering intensity data to produce a size distribution presents itself in two parts: (S. Polychronakis Ref. (90) Appendix 1.)

a) Information required: to define a size distribution of random form and range requires the determination of the number fraction of particles falling within consecutive size intervals covering the range, and the interval width. (In practice a histogram may require the determination of about eleven variables).

b) Information available: scattering pattern analysis can usefully be applied with particles which are large enough for the scattering pattern to vary with size (or the extinction coefficient to vary not simply as a constant power of size), but which are too small for size analysis by

geometric optical methods such as holography, diffraction, or interference fringe scattering. B.J. Thompson Ref. (99); J.H. Chin et al. Ref. (21); N.S. Hong and A.R. Jones Ref. (48).

A lower limit of particle size parameter, $\alpha = \frac{\pi d}{\lambda}$, for the method is thus introduced at a value of about 0.5. For example, if the helium neon laser with wavelength $\lambda = 0.6328 \mu\text{m}$ is used as the light source, the diameter limit $d = 0.1 \mu\text{m}$. Geometric optical methods can only be used when α is larger than, say 30, i.e. $d > 4.7 \mu\text{m}$ with the same light source. Within the range specified, the scattering pattern and extinction coefficient are complicated oscillatory functions of particle size. Thus different size distributions may give rise to similar scattering behaviour and evaluations may be ambiguous. So more intensity measurements have to be made than there are size distribution parameters to be determined.

In the present work an assumed form of size distribution was used in the data inversion, and in common with numerous previous investigations, the form preferred was the zeroth order logarithmic distribution (ZOLD). It is characterised by the two parameters, model diameter, d_M ; and spread parameter σ_0 Ref. (90).

For this work the parameters chosen were a set of intensities measured at about 15 angles, with monochromatic (laser) illumination. We used the polarised light with alignment perpendicular to the plane of observation, because it was more effective in previous work. Maddock Ref. (77), Moore Ref. (83).

The choice of inversion method is described later in this chapter.

6.3 Review of *in situ* methods of measuring particle size

Most measurements of the composition and amount of atmosphere particulate matter have been accomplished with methods involving the removal of the particles from the air. There are some advantages in such methods. The acquisition of large samples makes it possible to use ordinary chemical techniques for analysis and analytical balances for determination of mass. The apparatus needed for removing particles from air, such as impinger, filters, etc. are simple to operate.

However, there are many disadvantages to this dependence on removal methods. Firstly, the particles are probably subjected to gross physical and chemical changes of their "micro-environment", thus possibly changing their composition and properties. Secondly, some particles may volatilize after removal, as suggested by Goetz et al. (1961) Ref. (37), leading to errors in amount as well as composition. Other particles may react with the sampling surface or with other collected particles to form molecular species that did not exist in the atmosphere. For example CaO and CaCO_3 dust could react with the deposited sulphuric acid mist to neutralize the acid even though the constituents might have come from different air samples, collected hours apart. Thirdly, contamination of the sampled material by handling is possible. Ammonia gas in the laboratory could easily react with H_2SO_4 on a filter or impactor slide, altering the composition and mass.

One major problem exists in that most standard analytical procedures provide elemental or ionic information, not the molecular or crystalline composition. Since many of the important properties of particles are due to molecular rather than elemental character (for instance: toxicity; refractive index; density; particle shape and physical state) more elaborate sampling techniques and sample handling procedures are still

under investigation. Since these methods are all relatively, new, they are mentioned in the next paragraph.

ION MOBILITY:

The size of atmospheric aerosol particles in the range $0.00075 \leq D_p \leq 0.6 \mu\text{m}$ may be measured by subjecting them to a charge of controlled magnitude followed by removal in the electrical field of a mobility analyser. Such an instrument is depicted in Figure 6.1

OPTICAL SINGLE PARTICLE COUNTER:

The scattering efficiency factor Q_{scatt} may be defined by

$$Q_{\text{scatt}} = S/A$$

where:

Q_{scatt} = scattering efficiency

S = scattering cross section (cm^2)

A = cross-sectional area.

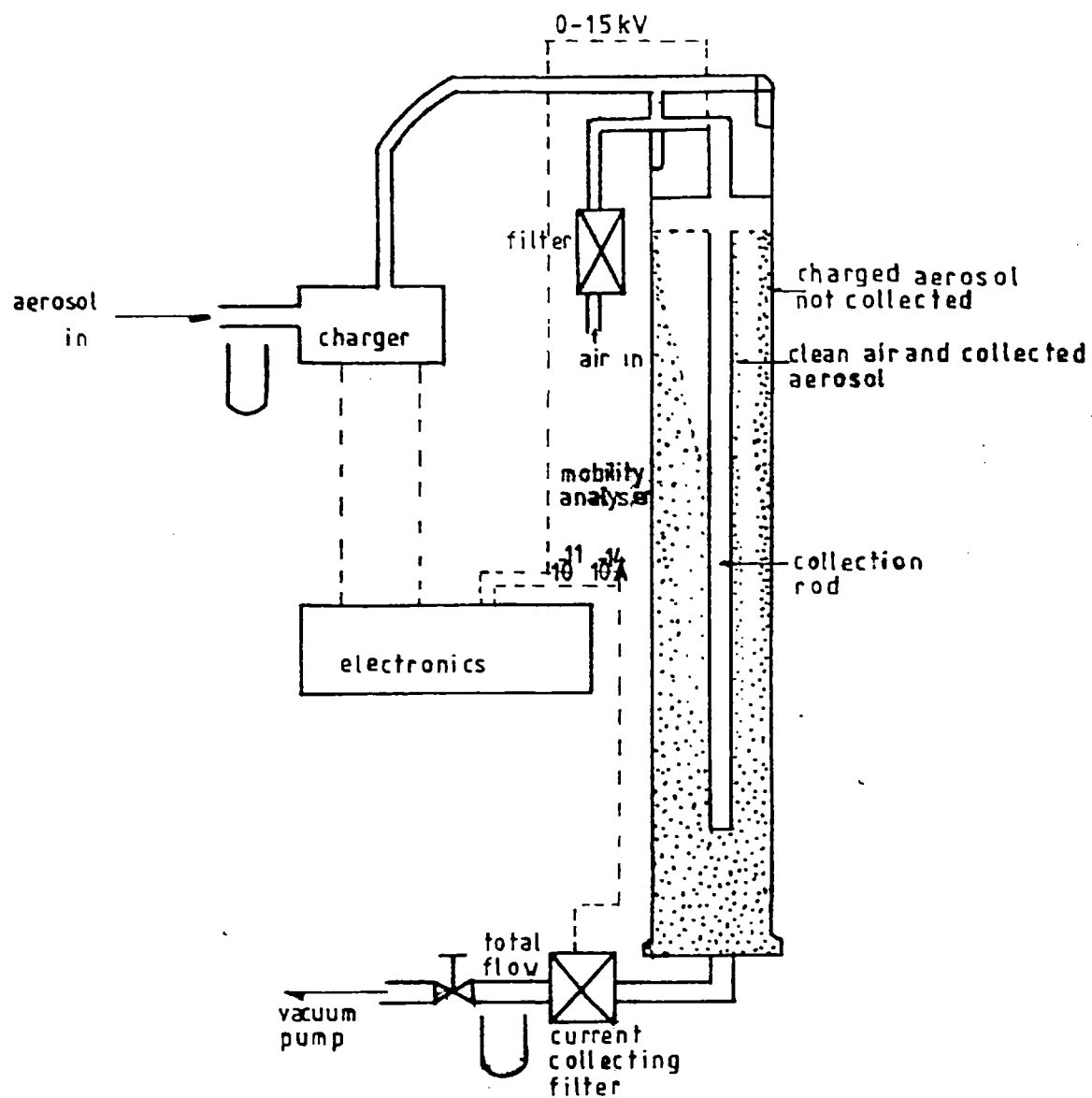
It is a strong function of size parameter, (Ensor et al. 1972 Ref{30}).

Replotting the graph as actual scattering cross section at a fixed wavelength as a function of size, gives an approximately monotonic increase of scattering with particle size. In practice, however, several different particle sizes can produce the same amount of light scattering if the instrument is constrained to the use of measurements at one angle, a size distribution is then obtained by analysis or segregation by a multichannel analyser of pulse-heights (corresponding to particle size). Detection is done by a multiplier phototube receiving light scattered from individual particles in a sample.

ANGULAR INTEGRATING NEPHELOMETER:

This is an instrument which senses the scattering component of extinction by both particle and gas molecules Ref. (38). The integrating nephelometer

FIG. 6.1 The mobility analyser



$$b_{\text{scatt}} = 2\pi \int_0^\infty b^1(\phi) \sin \phi \, d\phi$$

senses the scattering

component of extinction b_{scatt} by a particular geometry that provides the sine function in the integrand without lenses or mirrors. This circumvents the lack of linearity in the responses of the usual sensor, the human eye. In fig. 6.2 is shown a simple nephelometer, indicating the key elements of geometry. A UV cut-off filter and the normal response of an S-11 photocathode provide wavelength definition. Porch et al. (1970) Ref. (92) suggest a background aerosol mass concentration of 1.6 to $16 \mu\text{g}/\text{m}^3$ based on the relation $1.5 < b_{\text{scatt}}/b_{\text{Rayleigh}} < 1.9$. This ratio represents the geometric mean at 500 nm.

Polar nephelometer:

An instrument providing the same information as the integrating nephelometer, though by measuring $b^1(\phi)$; where ϕ = scattered angle as a function of ϕ and integrating this quantity over angle, a manipulation requiring more data handling.

This has been used, mainly for measurements on single particles, suspended in a Millikan apparatus Blau et al (1970) Ref. (9). Its main advantage lies in the simultaneous estimation of size distribution and refractive index, though this assumes knowledge of particle shape, often a limiting factor.

Too few atmospheric studies have been carried out to assess whether refractive index determination is possible. Bullrich (1964) Ref. (13).

Flame Scintillation method:

An aerosol entering a flame is heated, partly or wholly vaporised and raised to an excited electronic state. This is followed by emission of light which may be used for chemical identification and particle sizing. Size determination depends on knowledge of particle composition which

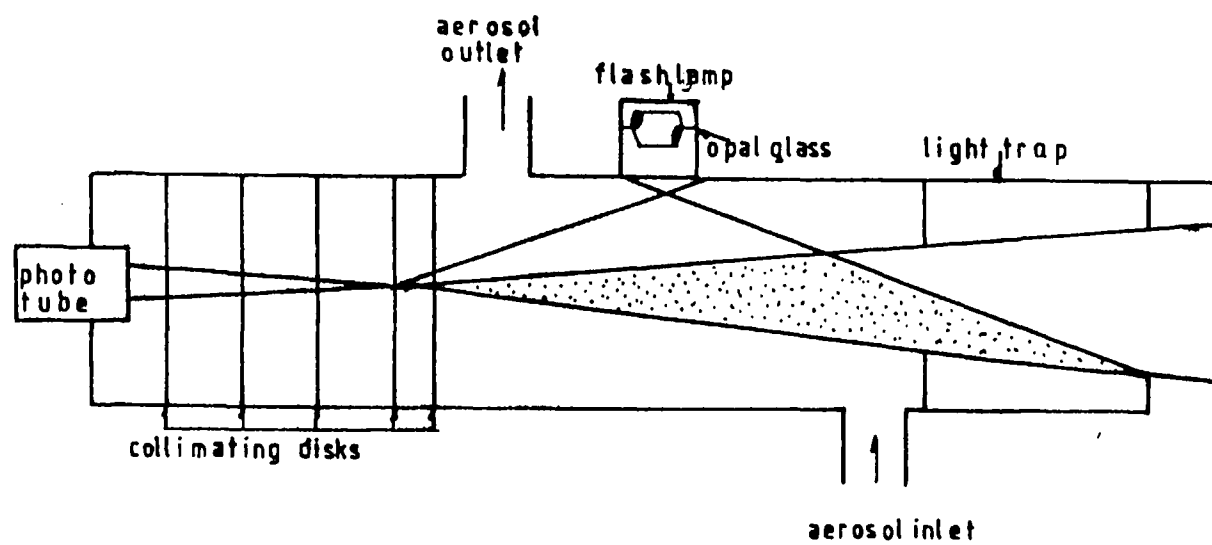


FIG. 6.2 Integrating nephelometer

is changed rapidly during the process. This factor being frequently unknown, the method is of limited applicability in the atmosphere, though useful for sea salt aerosols (90% NaCl).

Light scattering instrument:

In the course of earlier studies by Sinclair and La Mer et al. Ref. (95) on the preparation of liquid aerosols, light scattering has been used for many physical studies of laboratory aerosols in the submicron range. There are many subsequent examples in the literature of the use of light scattering with a wide range of types of light source, choice of angles at which to record data, etc. Our particular interest has been in a suspension of hygroscopic acid droplets growing in a humid atmosphere, on a suspension of solid particles formed by interaction of gases such as sulphur dioxide (SO_2) and nitrogen oxides (NO_x), usually the main sources of the pollution. The background and basis of the method used here are described in the following section.

6.4 Determination of particle size by light scattering

The presence of molecules and particulate matter in air results in an interaction with light called scattering. This phenomenon is one of the most common consequences of atmospheric aerosols, resulting in effects ranging from the very ordinary visibility degradation in cities to the appearance of rare optical occurrences such as the blue moon. Our purpose in this section is to provide a general description of the most important mathematical aspects.

Rayleigh scattering:

Light interacts with particles in a gas by virtue of the electromagnetic wave nature of light and the presence of electrons and positive

charges in matter.

Particles which are small relative to the wavelength of light , experience the same electric field throughout their entire dimensions. This external electric field establishes a dipole in the small particle that is a function of its polarizability. This emission of light results in the removal of energy from the incident beam and a redirecting of the radiation in the characteristic dipole pattern. Lord Rayleigh established the basic nature of this scattering process, and it is known as Rayleigh scattering. This theory is represented by the equation (1)

$$\frac{I_o}{E} = \frac{8\pi^4 r^6}{R^2 \lambda^8} \frac{M^2 - 1}{M^2 + 2} (1 + \cos^2 \phi) \quad (1)$$

Where:

I_o = intensity of scattered light

E = luminous energy per unit area and time

M = refractive index of the scattering particles

ϕ = scattering angle (measured from the transmitted beam)

λ = wavelength of light

r = particle radius

R = distance of observation from the point where scattering occurs

One valuable consequence of this relationship is that the scattering by gases, including air, has the same wavelength dependence independent of viewing angle. Rayleigh scattering by the molecules in air is sometimes dominant, especially in clean air. In haze, smoke, smog etc., the scattering by molecules is usually dominated by Mie scattering

by the aerosol method.

Mie scattering

Discussions of the Mie theory are given by Van de Hulst (1957) and Kerker (1969) Ref. (106). The theory describes the process of scattering for particles of any size (including the Rayleigh case). As the particles become larger relative to wavelength of light, it is no longer possible to consider the dipole to be exactly in synchrony with the external wave. Rather, it is necessary to consider the wave inside the particle along with the external wave. The theoretical description of this situation was first developed by Mie (1908).

The general character of these solutions for particles where $r \geq \lambda$, is the result of constructive and destructive interference by the internal and external waves, leading to complicated mathematical formulations. For example in fig.6.3 are shown the calculated scattered intensities in both planes of polarization (i_1 and i_2) as functions of scattering angle ϕ for a particle with $r/\lambda \approx 10$.

If, instead of a single particle, an aggregation of particles of different sizes (such a atmospheric aerosol) is considered, much of the complexity shown in fig.6.3 disappears. In fig.6.4 is shown typical measured intensity in the atmosphere as a function of angle. The large amount of scattering at small angles (called "forward" scattering) clearly dominates in this typical case.

It is important to note that "Mie" scattering often dominates the Rayleigh scattering by the air molecules in haze or smog, so that the angular scattering diagram is very nearly that of the particles alone. For very clean situations, both the gas molecules and aerosol particles contribute to the observed scattering.

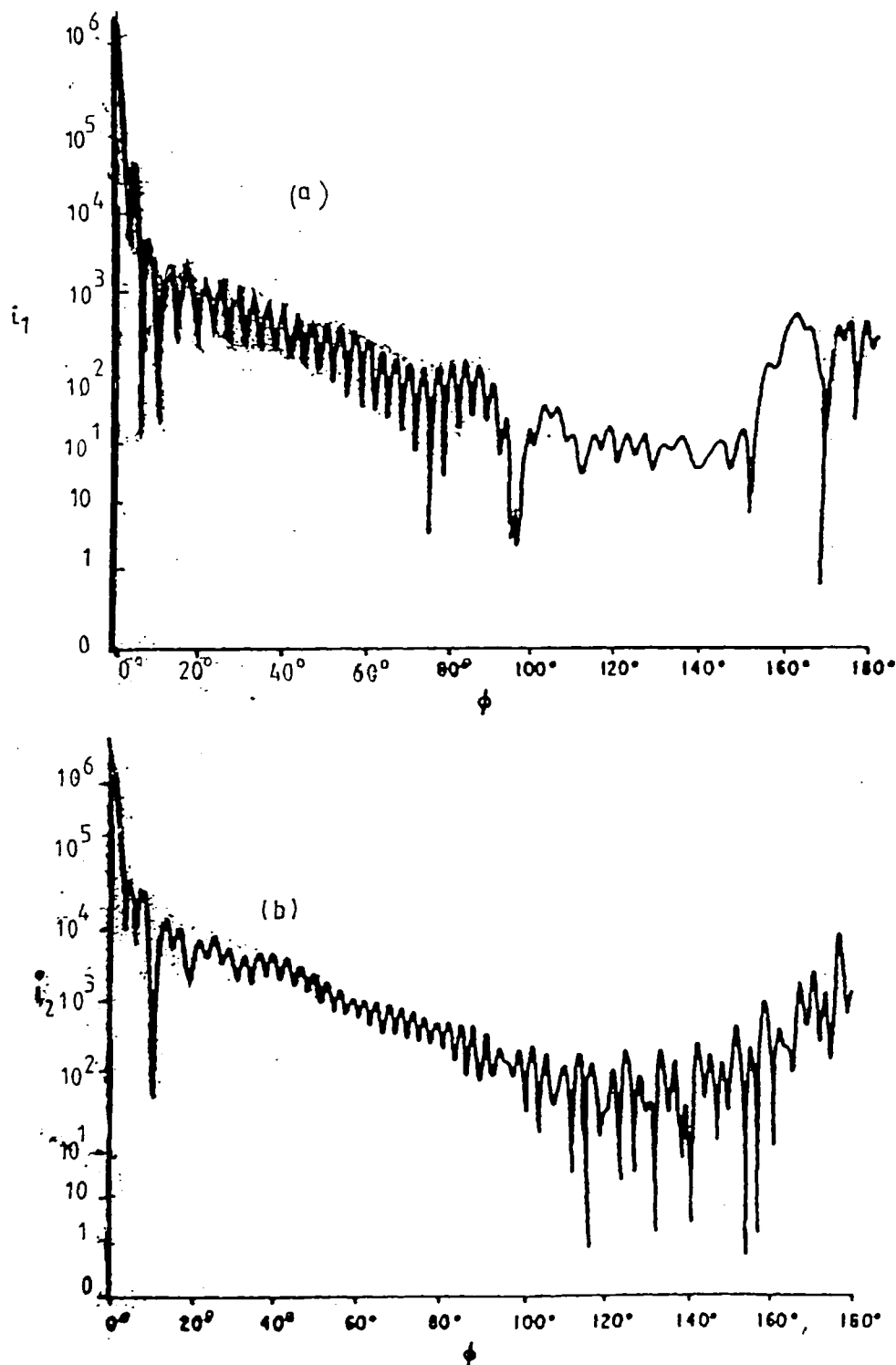


FIG.6.3. Scattered intensity in one plane of polarization (i_1) as a function of scattering angle θ for $x = 60$ ($r/\lambda = 10^1$). The calculation assumes spherical particles of refractive index, $n = 1.5$. i_1 is in arbitrary units (Bullrich, 1964). (b) The same as (a), but for i_2 the other plane of polarization.

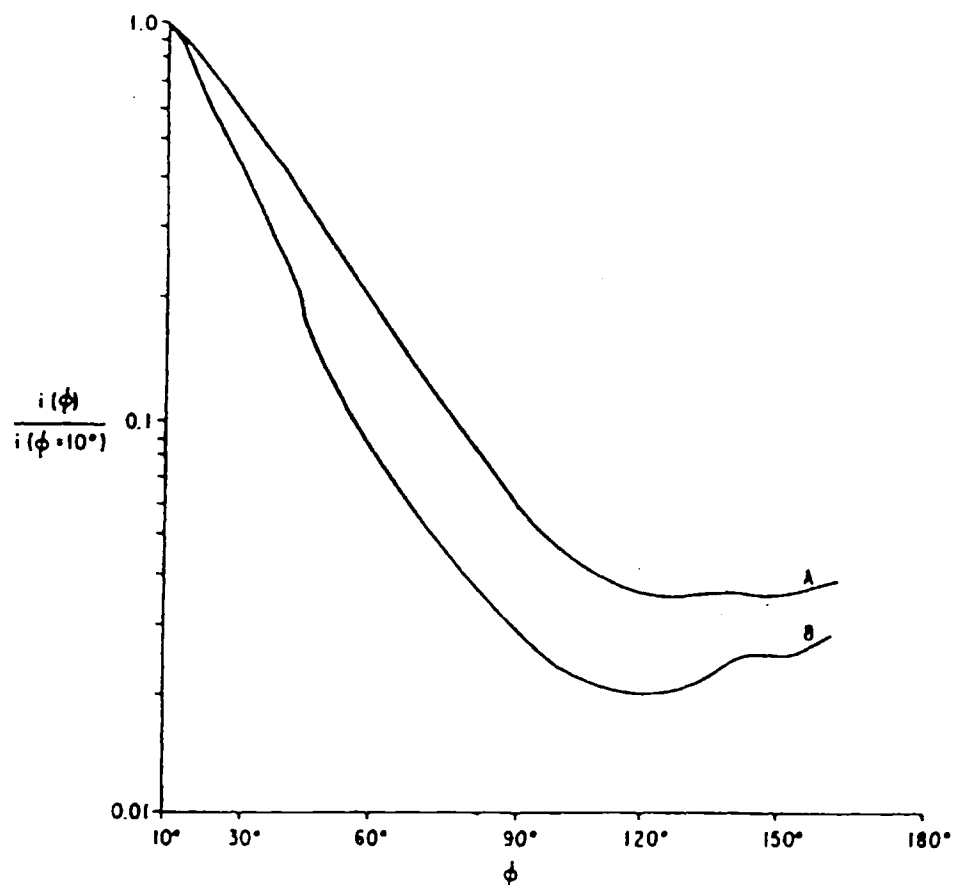


FIG. 6.4. Measured scattered intensity as a function of angle relative to scattered intensity at 10° , including both planes of polarization using blue light. The ratio $i(\phi)/i(\phi = 10^\circ)$ is plotted versus ϕ for two different times: A, December 19, 1961; and B, November 23, 1961 in Mainz, Germany (Bullrich, 1964).

6.5 Experimental procedures in the present work

Apparatus: In fig. (4.2) is shown a general view of the apparatus for light scattering measurements in the study of sulphuric acid aerosol formation obtained by irradiation of electron beam "2MeV". The SO_2/N_2 - air mixtures were passed through the 0.5cm diameter reactor at a constant flow rate. The aerosol was collected in a polyethylene bag (D) and analysed by these techniques, as described below.

Measuring procedure: Before being run, the laser (L) and associated electronic equipment were switched on to warm-up for the manufacturer's recommended period (e.g. 1-2 hours for the laser). Having aligned the light beams and checked the scattering angles, for the pre-selected scanning sequence, there remained only the setting-up of the scattering cell (C).

The particles produced by the electron beam accelerator were released from the sampling bag, the flow rates were adjusted to achieve as nearly as possible constant and stable flow of aerosol through the center of the cell (C). It is quite evident that the reaction of the SO_2 was influenced by changes in the humidity of the air. If the humidity was decreased, an appreciable distribution did not form and a weak aerosol production was observed. In another typical experiment moist air was used to partially fill the collector bag and irradiated aerosol then flowed into the collector (D) fig. (4.2) and analysed by light scattering technique. The results are shown in tables (1 and 2).

6.6 Light scattering determination of particles size SO_2 -Air system aerosol

In fig. 6.5 is shown the photomultiplier (PM) which was used for light scattering intensity measurements. The photomultiplier, an EMI tube

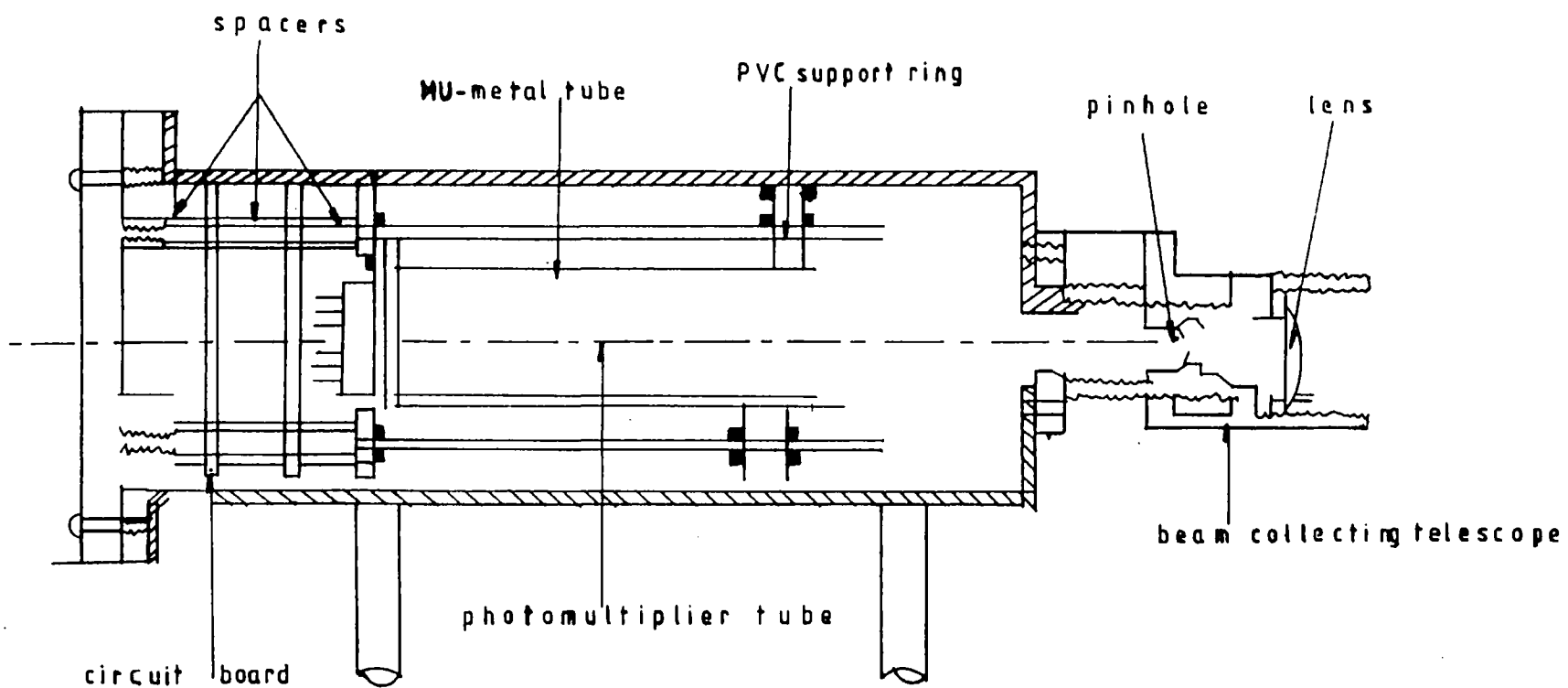


FIG.65 SCATTERED LIGHT RECEIVING, SYSTEM

with a SIO cathode, was housed in a special case incorporating a collecting telescope which received the scattered light and directed it on the photosensitive area. It was operated according to specifications by a regulated DC power supply, usually at 900 V. The signal from the photomultiplier tube was measured by a digital volt meter (supplied by Digital Measurements Ltd.) used as an integrating digital voltmeter, and recorded by a IBM typewriter machine for further analysis.

The whole instrumentation as seen in fig. (6.6) was set on a solid structure adjustable to a level plane, which is the plane of light-scattering observation. During the experimental runs a dark room principle was followed, the only light source being the laser itself. The helium-neon laser used during the experiments was a Spectra Physics 638.8 nm wavelength. To the end of the laser beam route a Rayleigh horn was installed to act as a black-hole. A narrow band-pass interference filter, passing 632.8 nm was fixed to the front of the photomultiplier housing. During the light scattering measurements, the aerosol continuously passed through the specially designed cell (C) fig. (6.5). The inner part of the cell (C,d) was designed in order to maintain a steady flowrate. Signals corresponding to the scattering intensities of the perpendicular polarized components of the scattered light wave were measured at 9° intervals (M) fig. (6.6) for a range of angle θ $9^\circ - 126^\circ$, then also at 130.5° where θ is the angle between the directions of the incident and the scattered beam. During each run, readings at 130.5° were repeated after measurements at 15 consecutive angles had been taken, in order to test the constancy of the aerosol and the flow-rate. It was standard practice to record again in a reverse traverse of the angles.

All the experimental aerosol particles were analysed using SEARCH, an

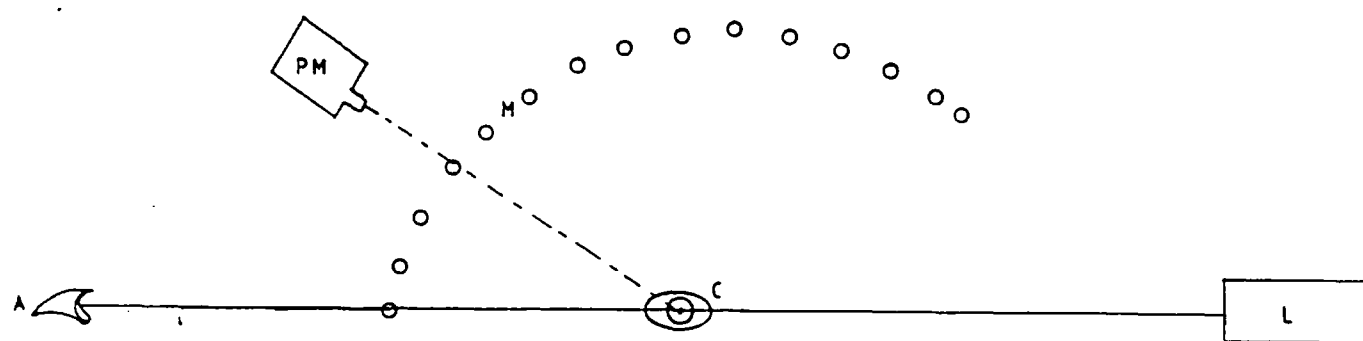


FIG. 6.6 Schematic plan view of the optical system

PM. photomultiplier
 C. scattering cell
 A. fibre glass light trap
 M. angular positions of the PM

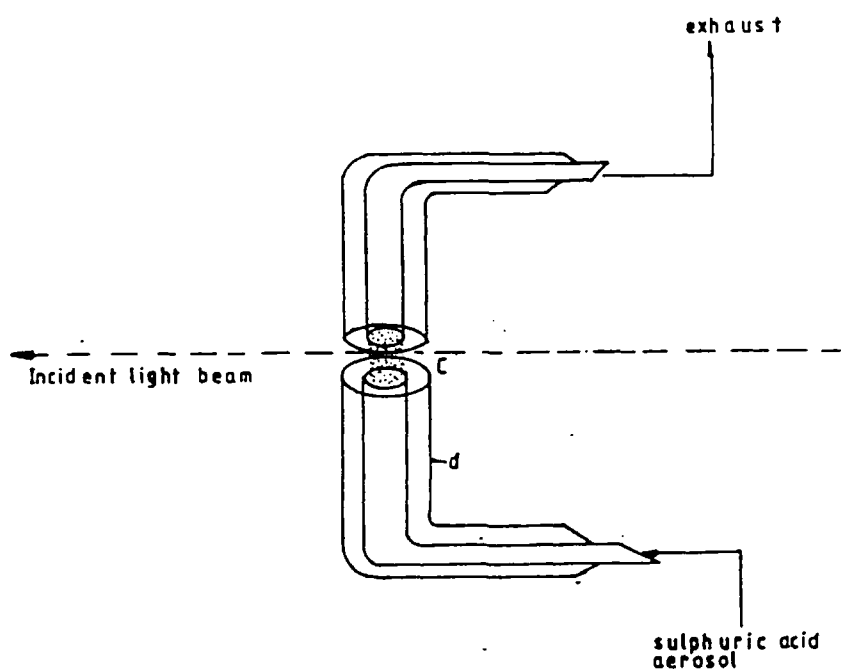


FIG. 6.7 The light scattering cell.

inversion programme (See appendix 1), with intensity coefficients for a relative refractive index of 1.0007 for sulphur dioxide and 1.0003 for air and 1.38 for the sulphuric acid liquid (A.P. Moore Ref. (82)).

6.7 Results of the light scattering analysis.

Typical results under various conditions are summarised in Tables 6.1, 6.2, and graphs were drawn from the parameters evaluated in the analysis, to show the size distribution which gives the best fit to the light scattering data. Examples of these are to be found in figure 6.7a,b

The reproducibility of the light scattering analysis is illustrated in figure 6.8. These curves are for aerosols produced in nominally identical runs with a reactor of diameter 0.5cm and flowrates of 500cc min^{-1} . The modal particle size varies from $d_m = 0.38$ to $0.424\mu\text{m}$ at a relatively constant value of σ_0 .

The standard procedure involved a delay of $5 \pm 1\text{min.}$ to transport the collector bag from the van de Graaff laboratory to the light scattering equipment and to complete the analysis. To investigate any possible effect on the aerosols several runs (marked in the tables) were repeated after 45 mins. The effect of this exaggerated delay is seen to be minimal in figure 6.9.

Particle size distributions were investigated as functions of sulphur dioxide concentration and residence time. A summary of results collected for this purpose is shown in Table 6.3.

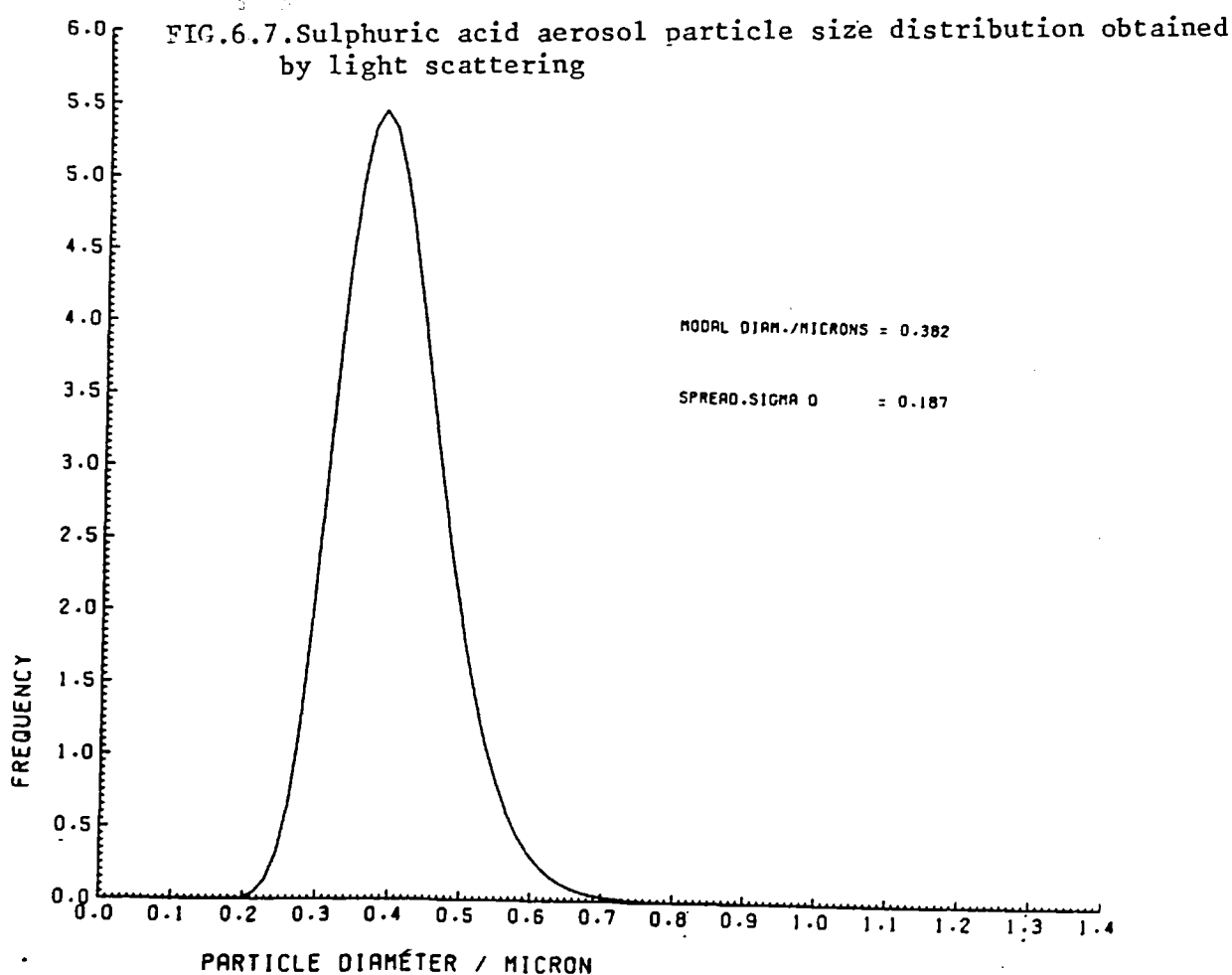
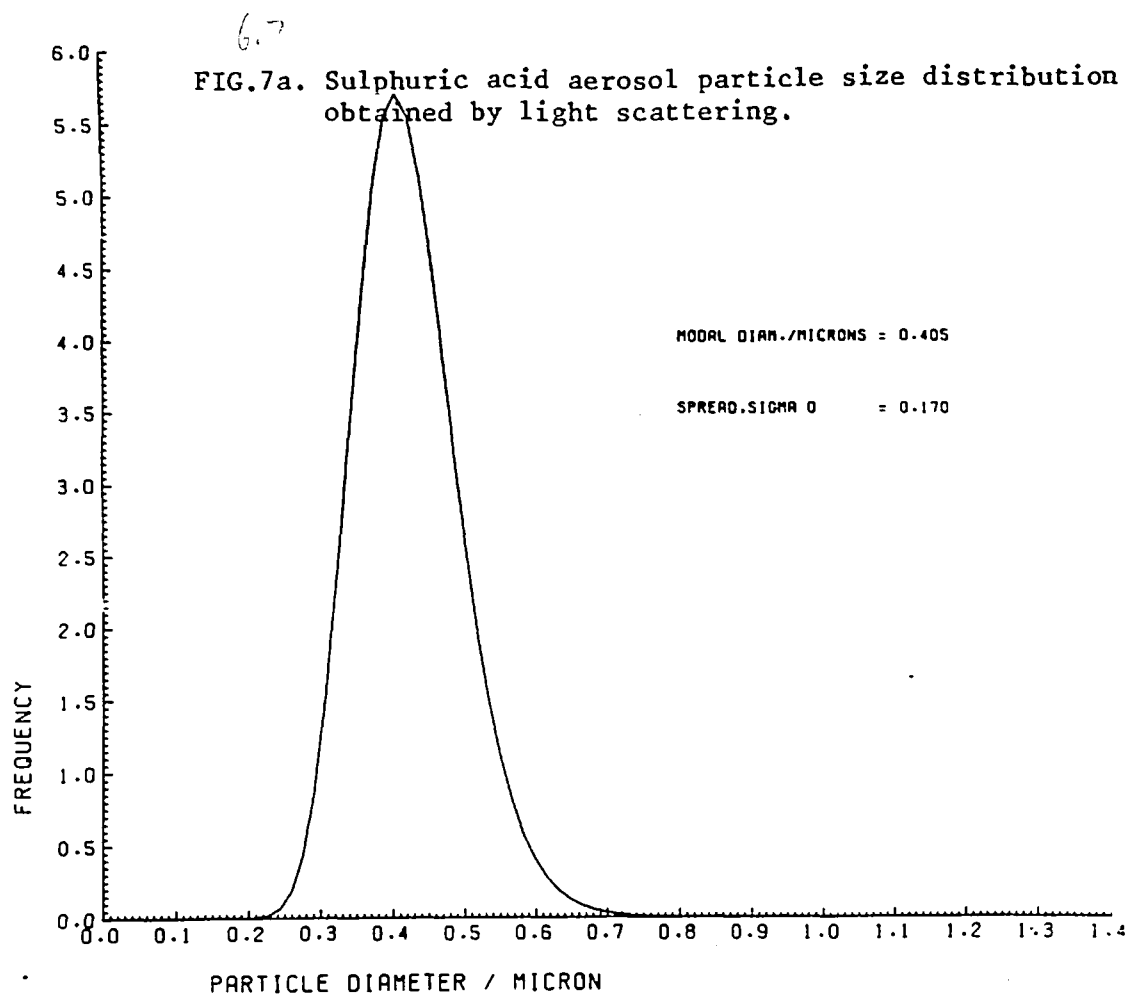


FIG. 6.8 REPRODUCIBILITY of the sulphuric acid aerosol particle size obtained in light scattering experiments.

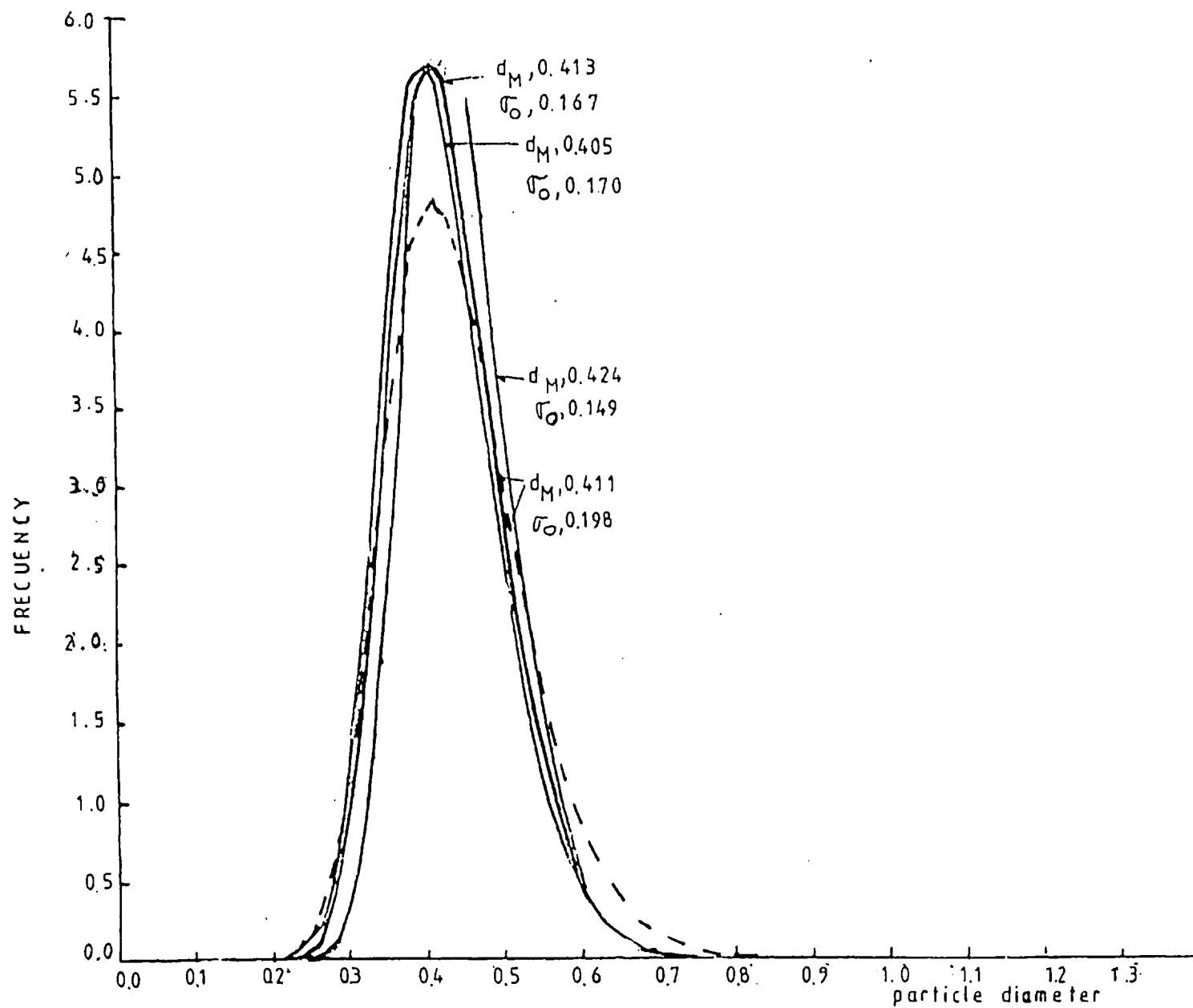


FIG.6.9.comparison of aerosols size distribution with 45 mins. delay before analysis.

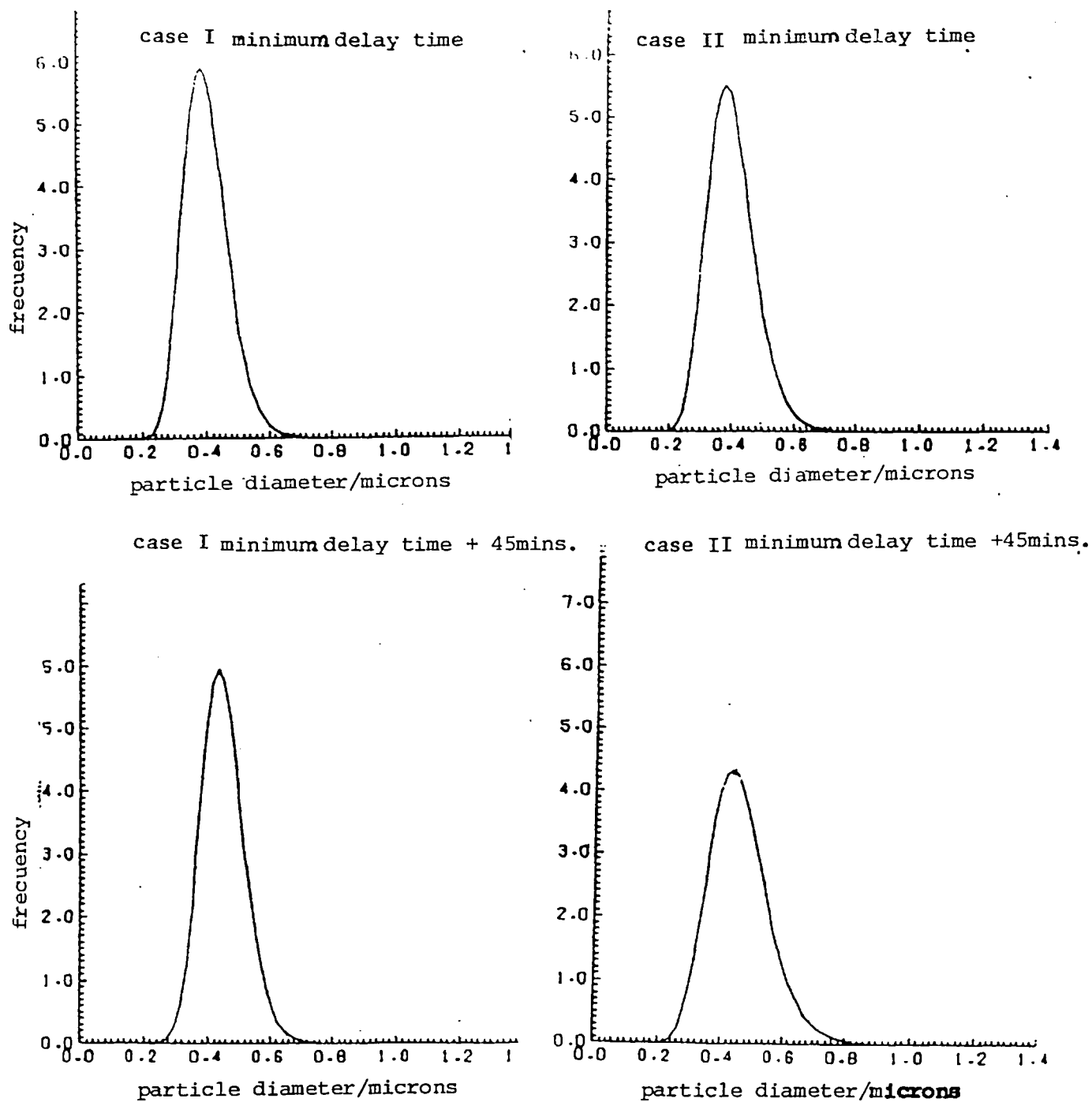


TABLE 6.1

Particle size distribution in SULPHUR DIOXIDE - AIR stream
from van de Graaff accelerator using 0.5 cm diameter reactor

Experiment Run number	SO ₂ (vpm)	Particle size		residence time in the reactor (s)
		d _M (μm)	σ _O (μm)	
1	18	0.459	0.252	3.6
2		0.475	0.233	
3		0.468	0.257	
4		0.476	0.243	
5	15	0.054	0.530	
6		0.414	0.197	
7		0.335	0.179	
8		0.119	0.463	
9	10	0.294	0.449	
10		0.440	0.169	
11		0.504	0.265	
12		0.423	0.254	
13		0.452	0.203	
14	7.4	0.388	0.202	
15		0.364	0.215	
16		0.362	0.220	
17		0.335	0.297	
18		0.363	0.256	
19		0.339	0.331	
20	29	0.307	0.408	
21		0.366	0.147	
22		0.352	0.235	
23		0.351	0.235	
24		0.421	0.150	
25	19	0.456	0.215	
26		0.426	0.213	

TABLE 6.2

Particle size distribution in sulphur dioxide - air stream from van de Graaff accelerator using 1.0 cm diameter reactor.

Experiment run number	SO ₂ vpm	Particle size		residence time in reactor (s)
		d _M (μm)	σ _o (μm)	
1	18	0.424	0.149	11.5
2		0.405	0.170	
3		0.413	0.167	
4		0.414	0.197	
5		0.411	0.198	
6	23	0.487	0.280	
7		0.519	0.285	
8	22	0.450	0.250	
9		0.493	0.222	
10*		0.450	0.256	
11*		0.552	0.249	
12*		0.586	0.250	
13*		0.501	0.083	
14		0.613	0.195	
15		0.654	0.166	
16	19	0.386	0.173	11.7
17*		0.435	0.153	
18		0.382	0.187	
19*		0.430	0.210	
20		0.423	0.213	
21*		0.424	0.222	
22		0.420	0.261	
23		0.326	0.008	

* Were running at the same conditions and measured after a lapse of time (45mins).

TABLE 6.3

EFFECT of the sulphur dioxide concentration on the particle size distribution.

SO ₂ (vpm.)	particle size		reactor diam.(cm.)	residence time seconds.
	d _M (μm)	σ _o (μm)		
7.4	.335	.297	0.5	3.6
	.362	.220		
10	.423	.254		
15	.414	.197		
18	.459	.215		
19	.456	.215	1.0	11.7
18	.413	.167		
19	.386	.173		
19	.435	.153		
22	.613	.195		

In this table is shown the effect of the sulphur dioxide concentration on the particle size distribution at constant residence times. The size distribution are actual values closest to the average in their category, and these were also chosen for display in the size distribution graphs Fig. 8.2 in Chapter 8.

CHAPTER 7

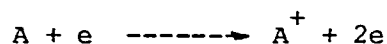
PLASMA IRRADIATION

7.1 Introduction

It has been previously stated that various alternative means exist of injecting electrical energy to promote oxidation of sulphur dioxide in a gas stream. The main source used in this work has been the Van de Graaff accelerator, but in this chapter a small number of exploratory experiments are described, using a plasma jet to introduce active species and energy.

The plasma jet used was one developed for its potential applications to chemical processes, especially in the field of fuel utilisation, and it will be described in more detail below (7.5)

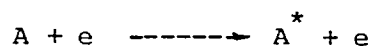
7.2 A plasma may be induced in a gas under laboratory conditions by a number of methods: electrical discharges (the most commonly used); shock; irradiation at high energy, or bombardment by high energy particles. Chemical consequences in the gas can be linked with the active species produced in the primary plasma, and hence vary with the kind of energy supply used. The types of active species which can potentially be formed comprise ions, electrons, and excited molecules and atoms. It is convenient to classify the processes which lead to these as IONISING COLLISIONS, and EXCITATION COLLISIONS. In an ionising collision, an energetic species, (usually an electron) ejects from a substrate molecule a further electron which retains some kinetic energy, and leaves a positive ion. The process depicted in Fig. 7.1 is:



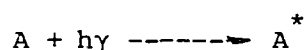
The initial kinetic energy of the impinging particle is accounted for in four ways after the collision.

(a) The energy required to eject the electron (b) The recoil energy of the ion and (c) of the electron and (d) the kinetic energy of the detached electron. In an excitation collision (see Fig. 7.2) an atom or molecule A is excited by collision with an electron, an ion, a neutral particle of high kinetic energy, or a quantum ($h\nu$) of radiation energy.

eg.

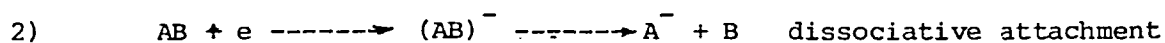
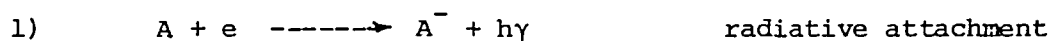


or



When electrons are fired through a gas, there is no excitation if the kinetic energy is insufficient; in these circumstances they exhibit a high probability of being trapped by neutral atoms, to form a negative ion.

So a special case of ionising collision is an electron attachment. There are two distinct types exemplified by:



Collisions of a further type (3) that result in ionization are those between two metastable atoms or molecules (A^M). In the collision process part of all of the excitation energy is transferred from one to the other, and if the total energy available is sufficient, ionisation may result.

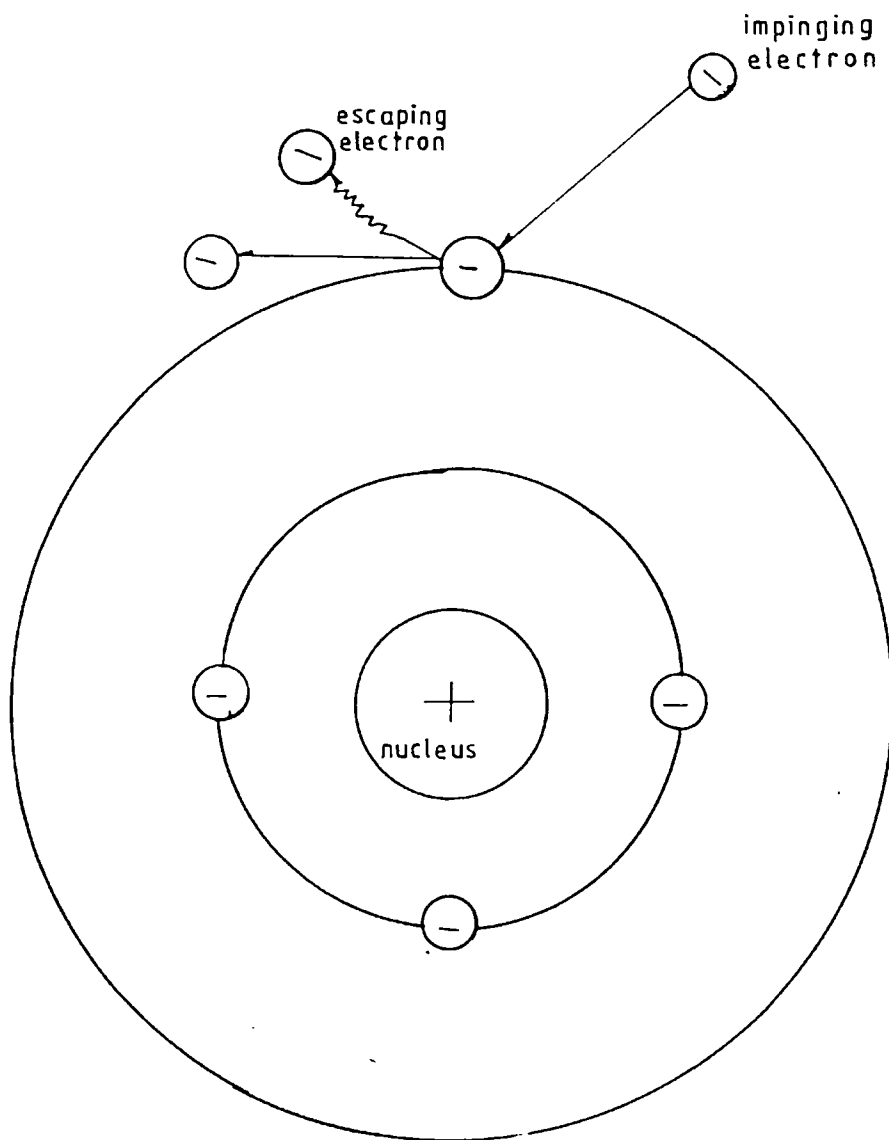
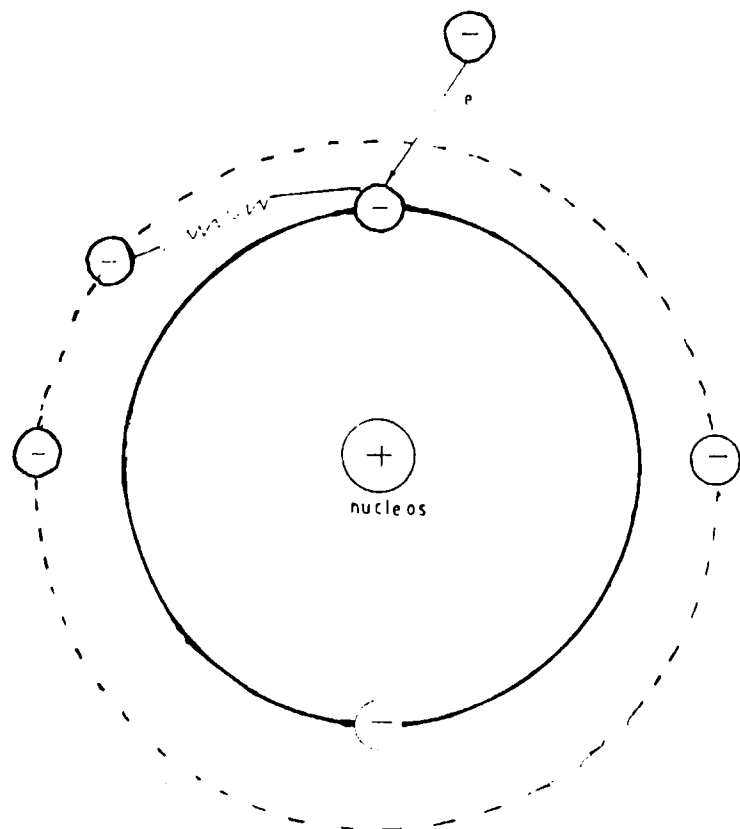
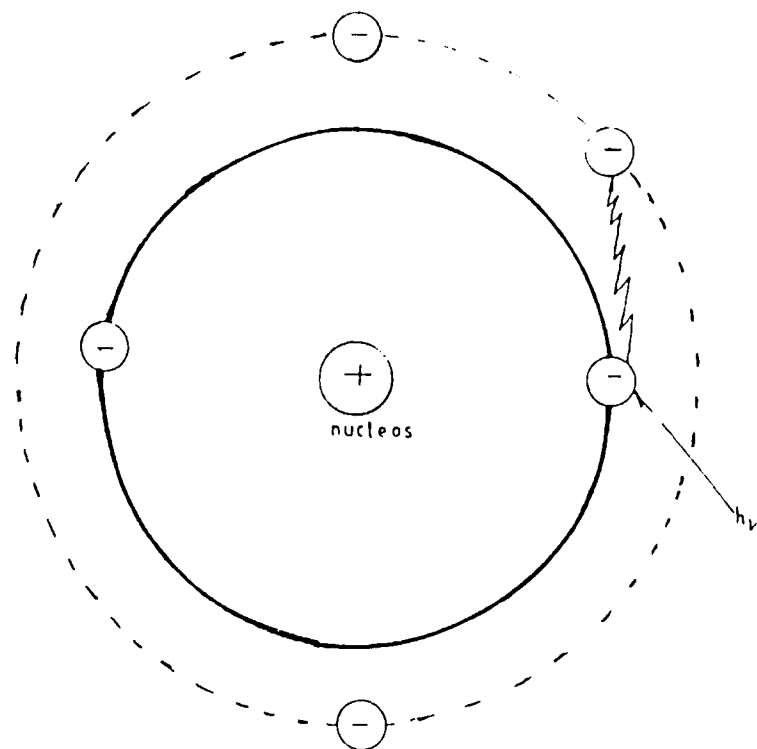


FIG.7.1 IONISATION BY COLLISION OF AN ATOM WITH AN ELECTRON.

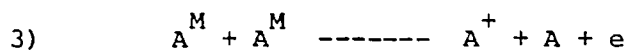


a) collision with an electron



b) collision with a photon

FIG 7 2 EXCITATION COLLISIONS



In order to produce an "avalanche" of electrons, it is necessary that the electric field applied to the gas be large enough so that the energy imparted to the electrons during their free flight between collisions is sufficient to eject at least one electron from a neutral species on impact. Hence under the right voltage conditions, only a small number of free electrons will be necessary to produce an avalanche. Information on such multiplication of electrons in plasmas is available in, for example, Massey et al. (1969) Ref. (80), A.K.F. Chan et al. Ref. (20), Hilliard, J.C. Ref.(46) and Weinberg, F.J. Ref. (111).

7.3 Chemical Processes in plasma jets.

The application of plasma to convert chemicals has been reviewed, at an early stage by Venugopalan Ref. (107), and more recently in several monographs. Ref. (105,107). Some of the processes under non equilibrium conditions described in the literature are summarized as:

- 1) Synthesis of ammonia from nitrogen and hydrogen
- 2) Oxidation of nitrogen
- 3) Dissociation of carbon dioxide
- 4) Decomposition of nitrous oxide
- 5) Oxidation of hydrogen
- 6) Oxidation of carbon dioxide
- 7) Cracking of methane
- 8) Formation of acetylene
- 9) Decomposition of ethylene
- 10) Production of ozone

The plasma jet described by Weinberg and co-workers is one with unusual temporal stability, and with such relatively weak quenching, that active species from the plasma can persist for several centimetres distance, and can hence be "fixed" into gases containing a chemical substrate.

An early application was that by J.C. Hilliard (1976) Ref. (46) which demonstrated that it was possible to reduce NO using nitrogen atoms generated in such a plasma jet. In addition to its academic interest, such a process of removal for this noxious gas would be of potential practical importance. In the light of this previous work, the same type of plasma jet recommended itself as a device to promote sulphur dioxide oxidation, and perhaps also as a means for removal of SO₂ from the gas stream. In the following sections, tests will be described using alternatively nitrogen, or argon, or air in the plasma jet itself, with sulphur dioxide and air in the secondary stream into which plasma was injected.

7.4 The main chemical properties of nitrogen, argon and air plasmas

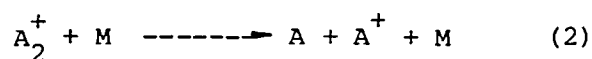
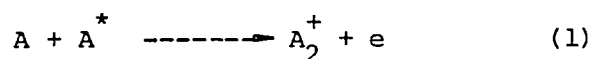
Nitrogen Production of "active" nitrogen by electrical discharges has been investigated by many workers over the last sixty years. A review by Mannella Ref. (79), summarises the physical and chemical results of these investigations.

"Active nitrogen" contains a variety of species, the relative ^(p.122) abundance of which are shown in table 2a for a plasma jet of nitrogen at equilibrium Ref. (32). The species included electrons, ions, excited atoms as well as ground state ⁴S atoms, and of course molecules. However the great complexity of results using active nitrogen is probably due to the large cross section for vibrational excitation of the nitrogen

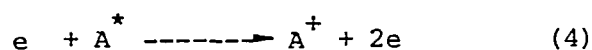
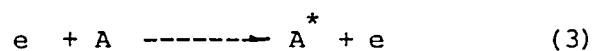
molecule: Work done by H.F. Behbahani Ref. (49) indicates that the active species in their rotating are N_2 plasma are carried in hot pockets of dissociated nitrogen, at temperatures around 20000°K.

Argon The main components at equilibrium are tabulated in (Table 1-a). The chemical reactions that can occur in the plasmas of monoatomic noble gases are of course far more limited in number than those in other gases and gas mixtures.

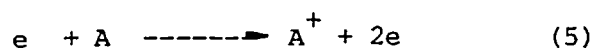
Molecule ions can be formed, but since their dissociation energy is low they will be expected to dissociate rapidly by comparison with their rate of formation:



Once a few electrons have been produced in the gas excitation and ionising collisions can proceed.



Direct formation of ions A^+ is of course also possible with energetic electron-atom encounters.



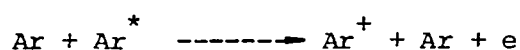
Where :

A = monoatomic species

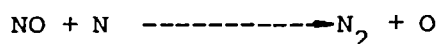
M = third body

Reactions (3) and (5) are important in the study of noble gas plasmas, and they have also been studied in other types of experiments: flame stabilization J. Harrison and Weinberg Ref. (41), NO formation and sooting of flames J.C. Hilliard and Weinberg Ref. (47).

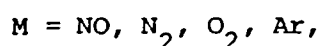
In an argon plasma no radicals can be generated; there is evidence that some highly reactive species are formed at the interface between an extremely hot argon jet and flame reactants (Harrison and Weinberg (1971) Ref. (41)). Harwell and John Ref. (43) in previous work have concluded that the ionization was due to the atomic excitation processes, followed by ionization in a faster atom reaction, as for example in the following:-



Air In an air plasma various oxygen species are produced (see table 3a). Oxygen atoms and ions are likely to be present, the former being strong oxidising agents. A summary of their reactions has been compiled by McTaggart Ref. (84). Nitrogen and nitric oxide would generate oxygen atoms by the fast reaction Ref. (43):



There will be enough oxygen in the air plasma jet used in this work to play a role in the oxidation of sulphur dioxide as seen in the next reaction.



7.5 The Apparatus

The central feature of the experimental set up was the plasma-jet, schematically shown in Fig. 7.3. As described elsewhere, the geometrical arrangement of the anode and cathode, and the rapid rotation of the arc around the cathode confer on the device exceptional stability over time. It has been shown that "pockets" or "slugs" of exceptionally hot gas (20000°K) emerge through the anode orifice and travel outwards for some tens of millimeters in a stream of otherwise cooler gas (at say 800°K). These pockets will be the carriers of the active atoms and other species, which may of course diffuse out into the surrounding gas.

The experiments with sulphur dioxide were planned so as to collect samples of product aerosol, and to measure their size distributions. It was not practicable in the short time available to investigate the SO_2 conversion directly. This was principally due to the much greater flow rates which have to be employed in a plasma jet, as compared with those in the reactor under the Van de Graaff accelerator. (The factor was about 50 times).

The overall experiment is schematically shown in Fig. 7.4. The plasma was generated in a "primary" flow of argon, nitrogen, or air at a flow rate of several hundred $\text{cm}^3 \cdot \text{s}^{-1}$, dissipating power in the range 300 - 1500 Watts. The flow was directed upwards into a central quartz tube (1.5 cm. diam.).

The gas mixture to be processed was admitted at a high flow-rate (upwards of $2 \text{ dm}^3 \cdot \text{s}^{-1}$) at the top of the outer cylindrical tube. It was drawn down to the plasma zone by the jet momentum. This system has been investigated by A.M. Warris Ref. (109) for use in the reduction of NO . After passage upwards through the inner tube, the reactor products were

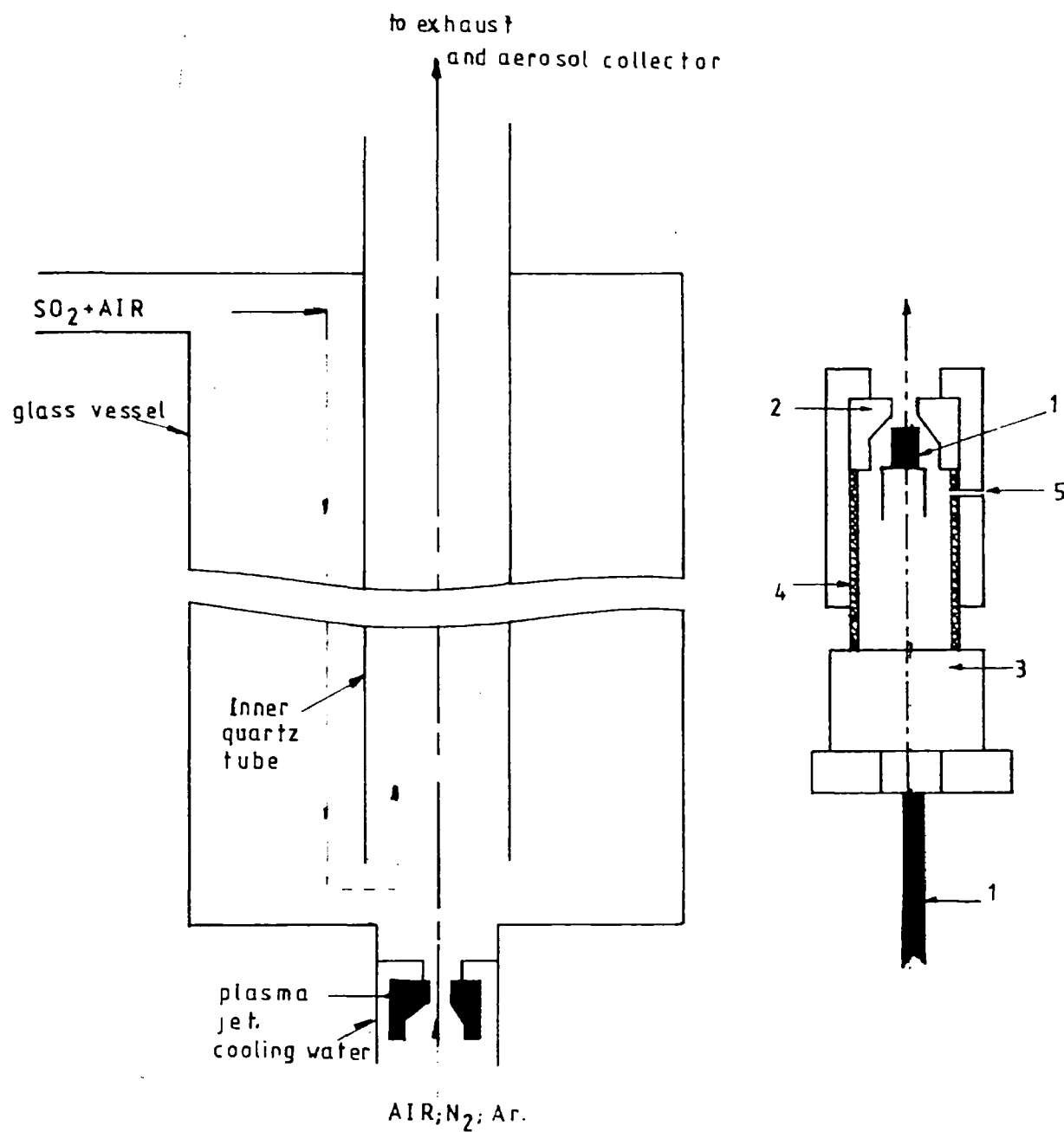


FIG.7.3 AERODYNAMICALLY SPUN PLASMA JET.

1. anode
2. cathode
3. spark plug body
4. fine thread for gap adjustment
5. tangential gas inlet

split partly to exhaust, and partly to a collecting bag of similar type to that used in the Van de Graaff experiments (see page 39).

The aerosols were analysed for size distribution by the conventional laser-light scattering technique. In addition to the gas flow rates in the primary and secondary flows, the power in the plasma jet, and the temperatures at the collector, and at the exit from the quartz tube were monitored. The former temperature was typically about 70°C and the latter about 110 - 120°C.

7.6 Experimental performance and results

The conditions of typical runs are depicted in tables 7.1, 2 and 3 for the respective feedstock gases to the jet, argon, nitrogen, and air.

Where sufficient aerosol for light-scattering analysis was produced, the particle size parameters are also tabulated. The principal observations can be summarised as follows.

1. With the argon plasma jet, no aerosol was produced and there were no obvious reactions in the gas present (compared with the nitrogen oxide production reported below). The jet power was in the range 330 - 530 W, the low values reflecting the comparative case of arc operation in argon. The flow-rates of sulphur dioxide (0.1 % mixture in nitrogen) at the inlet were 60 and 260 cm³ s⁻¹, and the implied concentrations were 23.4 vpm and 94.2 vpm.
2. With the nitrogen plasma jet the conditions reported in table 2 resulted in no aerosol formation, but in the gas mixture there was considerable formation of nitrogen oxides, clearly recognisable by the odour and the yellow-brown colour of NO₂.
3. With the air plasma jet, aerosol formation was immediate and resulted

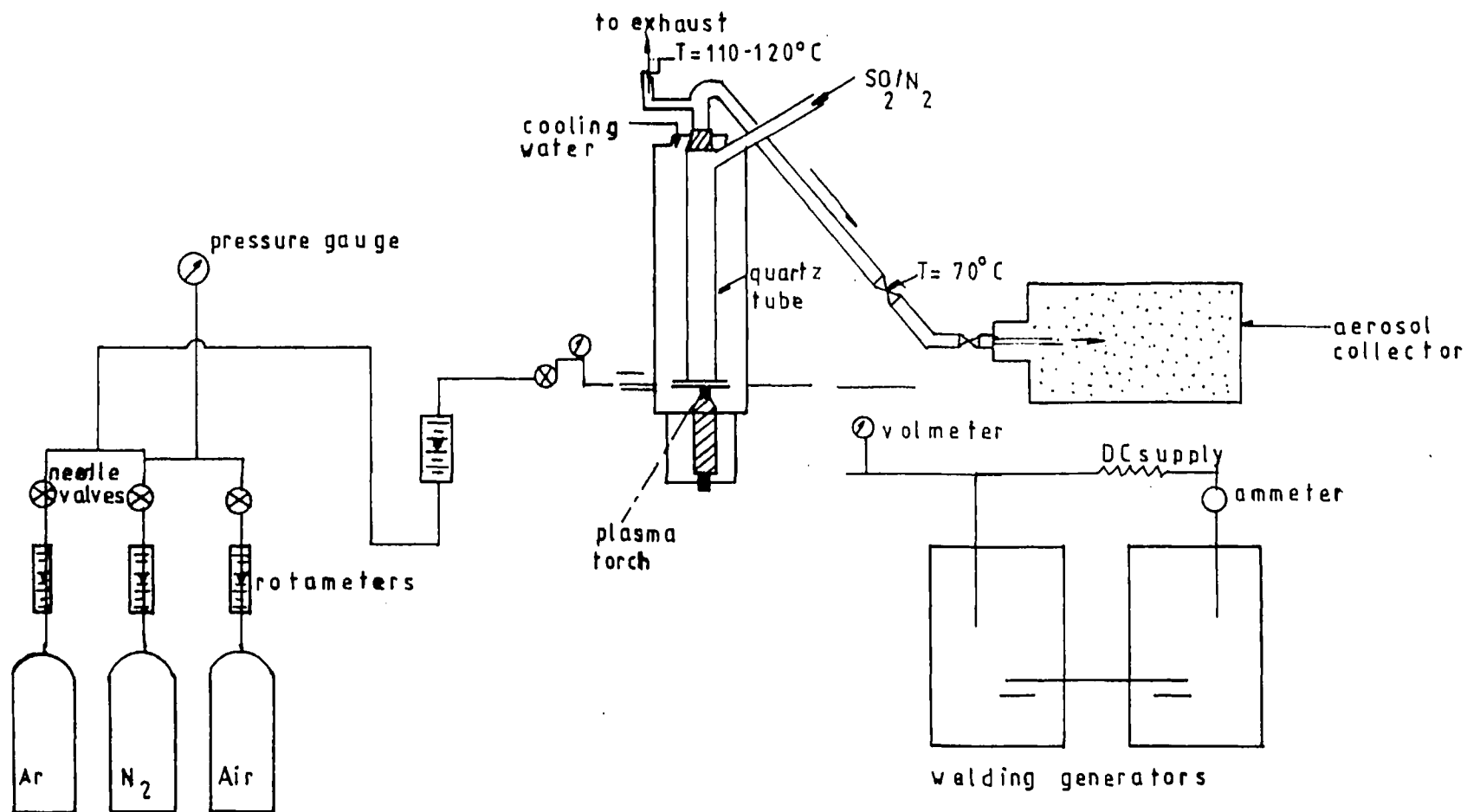


FIG.7.4 Apparatus for SO_2 reduction by O atoms generated by plasma jet

in high particle concentrations, using inlet concentrations in the range 11.8 vpm to 60 vpm. There was also a high yield of nitrogen oxides in these experiments.

Preliminary experiments with the nitrogen plasma jet also gave aerosols at readily detectable concentrations and size analysis was carried out. The results are shown in table 7.4, but no conclusions can be drawn since the results were not consistent with later numerous runs producing no aerosol.

7.7 Discussion of results

The main object of the experiments described in this chapter was to obtain a set of exploratory results to test the feasibility of using plasma irradiation to remove sulphur dioxide in polluted gases. As before in the Van de Graaff experiments, removal of product aerosols by precipitation was envisaged, so the questions of primary concern were (a) positive formation of aerosols, and (b) the particle size distributions in them.

The experiments with air fed to the plasma have clearly shown that with this means it is possible to induce sulphur dioxide oxidation and aerosol production in gas at quite high volumetric flow rates.

The particle sizes produced are in the 0.3 - 0.5 μm range (modal diameter) and hence just as conveniently suited for precipitation as those produced by Van de Graaff irradiation.

There is an interesting trend of size distribution as the sulphur dioxide concentration is varied (Table 7.5). For runs at roughly equivalent power (the first three columns) there is a decrease of d_M as concentration increases. The relevant curves depicting the size distributions are shown in Figs. 7.6, 7.7

It may be that the dominant process in determining the final aerosol is the nucleation at very early times, since a high value of nucleation rate (appropriate to high SO_2 concentration) would be expected to lead to lower ultimate sizes (other processes such as growth and coagulation being assumed equal).

Table 7.1OPERATIONAL CONDITIONS AND RESULTS OBTAINED BY ARGON PLASMA JET

ARC-CHARACTERISTICS POWER (W)	528	330	330	330
ARGON FLOWRATE cm^3s^{-1} through plasma	200	200	200	200
AIR FLOWRATE l min^{-1} external	150	150	150	150
$0.1\% \text{ SO}_2 \text{ cm}^3 \text{ s}^{-1}$	260	260	60	60
Concentration of SO_2 at the start of reaction above the plasma (vpm)	94.2	94.2	23.42	23.42
$d_M/\mu\text{m}$	-	-	-	-
σ_o	-	-	-	-

TABLE 7.2

Operational conditions and results obtained by nitrogen plasma jet.

ARC-CHARACTERISTICS POWER (W)	1050	960	960	913	863
NITROGEN FLOWRATE cm^3s^{-1} through plasma	250	165	160	170	170
AIR FLOWRATE l min^{-1} external	150	150	150	150	150
0.1% SO_2 cm^3s^{-1}	800	180	180	180	180
concentration of SO_2 at the start of reaction above the plasma (VPM)	242	68.0	68.0	68.0	68.0
$d_M/\mu\text{m}$	-	-	-	-	-
σ_o	-	-	-	-	-

Table 7.3

OPERATIONAL CONDITIONS AND RESULTS OBTAINED BY AIR PLASMA JET

ARC-CHARACTERISTICS POWER (W)	1600	1495	1495	1330	980	980	980
AIR FLOWRATE cm^3s^{-1} through plasma	270	250	270	210	270	230	230
AIR FLOWRATE l min^{-1} external	140	150	150	80	150	150	270
0.1% SO_2 cm^3s^{-1}	35	40	30	118	160	160	180
Concentration of SO_2 at the start of reaction above the plasma (vpm)	13.0	14.3	11.0	71	55	55	37
$d_M/\mu\text{m}$	.388	.302	.409	.388	1.108	.093	.450
α_o	.450	.100	.119	.115	.095	.515	.282
T_{EXHAUST} $^{\circ}\text{C}$	110 - 120						
T_{SAMPLE} $^{\circ}\text{C}$	70 - 72						

Table 7.4PARTICLE SIZE OBTAINED BY NITROGEN PLASMA

Concn. of SO ₂ (vpm)	90.9	94.2
d _M /μm	.053	.279
σ _O m	.547	.291
POWER/W	1210	1210

TABLE 7.5

PARTICLE SIZE VALUES OBTAINED BY AIR PLASMA.

POWER/W	1600	1495	1495	1300	980	980	980
Concentration of SO ₂ at the start ² of reaction above the plasma (vpm)	13	14.3	11	71	55	55	55
d _M μ m	.388	.302	.409	.388	.450	.093	1.108
σ ₀ μ m	.450	.100	.119	.115	.282	.515	.095

TABLE 1a

Concentration of the argon plasma components at $p=1$ atm [6], cm^{-3}

T, °K	Ar	Ar ⁺	Ar ⁺⁺	α	α_z
4000	1.835 (18)*	1.272 (10)	—	1.272 (10)	1.835 (18)
4500	1.631 (18)	1.673 (11)	—	1.673 (11)	1.631 (18)
5000	1.468 (18)	1.313 (12)	—	1.318 (12)	1.468 (18)
5500	1.331 (18)	7.158 (12)	—	7.158 (12)	1.331 (18)
6000	1.223 (18)	2.938 (13)	—	2.938 (13)	1.223 (18)
6500	1.129 (18)	9.727 (13)	—	9.727 (13)	1.129 (18)
7000	1.048 (18)	2.719 (14)	—	2.719 (14)	1.048 (18)
7500	9.773 (17)	6.637 (14)	—	6.637 (14)	9.786 (17)
8000	9.146 (17)	1.450 (15)	—	1.450 (15)	9.175 (17)
8500	8.577 (17)	2.893 (15)	2.586 (5)	2.893 (15)	8.635 (17)
9000	8.949 (17)	5.344 (15)	2.336 (6)	5.344 (15)	8.156 (17)
9500	7.542 (17)	9.242 (15)	1.656 (7)	9.242 (15)	7.727 (17)
10000	7.040 (17)	1.508 (16)	1.605 (8)	1.508 (16)	7.342 (17)
10500	6.526 (17)	2.339 (16)	5.084 (8)	2.339 (16)	6.994 (17)
11000	5.986 (17)	3.462 (16)	2.230 (9)	3.462 (16)	6.679 (17)
11500	5.411 (17)	4.965 (16)	8.638 (9)	4.905 (16)	6.392 (17)
12000	4.798 (17)	6.665 (16)	2.993 (10)	6.665 (16)	6.131 (17)
12500	4.153 (17)	6.656 (16)	9.442 (10)	8.696 (16)	5.893 (17)
13000	3.493 (17)	1.09 (17)	2.726 (11)	1.09 (17)	5.674 (17)
13500	2.884 (17)	1.313 (17)	7.284 (11)	1.313 (17)	5.471 (17)
14000	2.235 (17)	1.524 (17)	1.814 (12)	1.524 (17)	5.284 (17)
14500	1.699 (17)	1.704 (17)	4.242 (12)	1.704 (17)	5.108 (17)
15000	1.253 (17)	1.844 (17)	9.371 (12)	1.844 (17)	4.942 (17)
15500	9.046 (16)	1.940 (17)	1.566 (13)	1.94 (17)	4.786 (17)
16000	6.441 (16)	1.956 (17)	3.938 (13)	1.927 (17)	4.637 (17)
16500	4.568 (16)	2.019 (17)	7.567 (13)	2.020 (17)	4.497 (17)
17000	3.253 (16)	2.017 (17)	1.399 (14)	2.020 (17)	4.364 (17)
17500	2.341 (16)	1.998 (17)	2.500 (14)	2.503 (17)	4.238 (17)
18000	1.710 (16)	1.967 (17)	4.327 (14)	1.976 (17)	4.119 (17)
18500	1.327 (16)	1.926 (17)	7.267 (14)	1.940 (17)	4.006 (17)
19000	1.015 (16)	1.891 (17)	1.187 (15)	1.925 (17)	3.899 (17)
19500	7.911 (15)	1.831 (17)	1.885 (15)	1.859 (17)	3.798 (17)
20000	6.278 (15)	1.776 (17)	2.918 (15)	1.824 (17)	3.702 (17)

*In brackets is given the power to which the factor 10 must be raised, for example, $1.835(18) = 1.835 \cdot 10^{18}$.

TABLE 2a

Concentration of components of the nitrogen plasma, cm^{-3}

T, °K	N ₂	N	N ₂ ⁺	N ⁺	N ⁻	α
3000	2.45 (18)	3.45 (13)	5.40 (7)	3.99 (3)	—	5.40 (5)
4000	1.84 (18)	3.30 (15)	1.10 (10)	3.50 (8)	1.50 (3)	1.1 (10)
5000	1.42 (18)	4.70 (16)	9.70 (11)	3.10 (11)	2.5 (6)	1.3 (12)
6000	9.70 (17)	2.60 (17)	1.50 (13)	2.10 (13)	4.30 (8)	3.60 (13)
7000	4.10 (17)	6.40 (17)	5.70 (15)	3.40 (14)	1.40 (10)	3.90 (14)
8000	8.60 (16)	8.30 (17)	7.30 (15)	2.60 (15)	9.00 (10)	2.10 (15)
9000	1.60 (16)	7.90 (17)	6.60 (13)	6.90 (15)	3.40 (11)	7.00 (15)
10000	3.40 (16)	6.00 (17)	3.10 (13)	1.80 (16)	7.20 (11)	1.80 (16)
11000	8.50 (15)	5.90 (17)	3.30 (13)	3.70 (16)	1.30 (12)	3.70 (16)
12000	2.30 (16)	4.60 (17)	2.65 (13)	6.20 (16)	1.80 (12)	6.20 (16)
13000	—	1.70 (17)	—	1.30 (17)	—	1.3 (17)
14000	—	6.30 (16)	—	2.00 (17)	—	2.00 (17)
15000	—	1.20 (16)	—	2.00 (17)	—	2.00 (17)
16000	—	4.00 (16)	—	1.30 (17)	—	1.30 (17)

TABLE 3 a

Concentration of components of the air plasma, cm^{-3}

T, °K	N_2	O_2	NO	N	O	N^+	N^-
3000	1.80 (18)	3.50 (17)	1.01 (17)	—	1.08 (17)	—	—
4000	1.19 (18)	5.31 (15)	7.50 (16)	2.52 (15)	4.70 (17)	—	3.98 (5)
5000	8.95 (17)	3.43 (15)	2.53 (16)	3.67 (16)	1.89 (17)	—	6.20 (7)
6000	6.22 (17)	3.08 (14)	9.92 (15)	2.06 (17)	3.81 (17)	2.55 (12)	2.03 (9)
7000	2.57 (17)	4.18 (13)	2.99 (15)	5.10 (17)	2.73 (17)	1.65 (14)	1.67 (10)
8000	5.45 (16)	8.76 (12)	7.54 (14)	6.82 (17)	2.68 (17)	1.51 (15)	7.70 (16)
9000	9.92 (15)	2.93 (12)	2.12 (14)	6.20 (17)	1.72 (17)	5.53 (15)	1.95 (11)
10000	2.12 (15)	1.21 (12)	7.03 (13)	5.45 (17)	1.49 (17)	1.44 (16)	5.55 (11)
11000	5.25 (14)	5.45 (11)	2.57 (13)	4.62 (17)	1.28 (17)	3.05 (16)	9.98 (11)
12000	1.40 (14)	2.52 (11)	9.68 (12)	3.77 (17)	1.07 (17)	5.45 (16)	1.37 (12)
14000	—	—	—	1.85 (17)	6.00 (16)	1.08 (17)	1.25 (12)
16000	—	—	—	6.18 (16)	2.47 (16)	1.48 (17)	5.65 (11)
18000	—	—	—	1.90 (16)	8.15 (15)	1.49 (17)	1.02 (11)
20000	—	—	—	6.50 (15)	2.82 (15)	1.49 (17)	—
				5.83 (15)	2.57 (15)	1.40 (17)	—

(cont. of Table 3a)

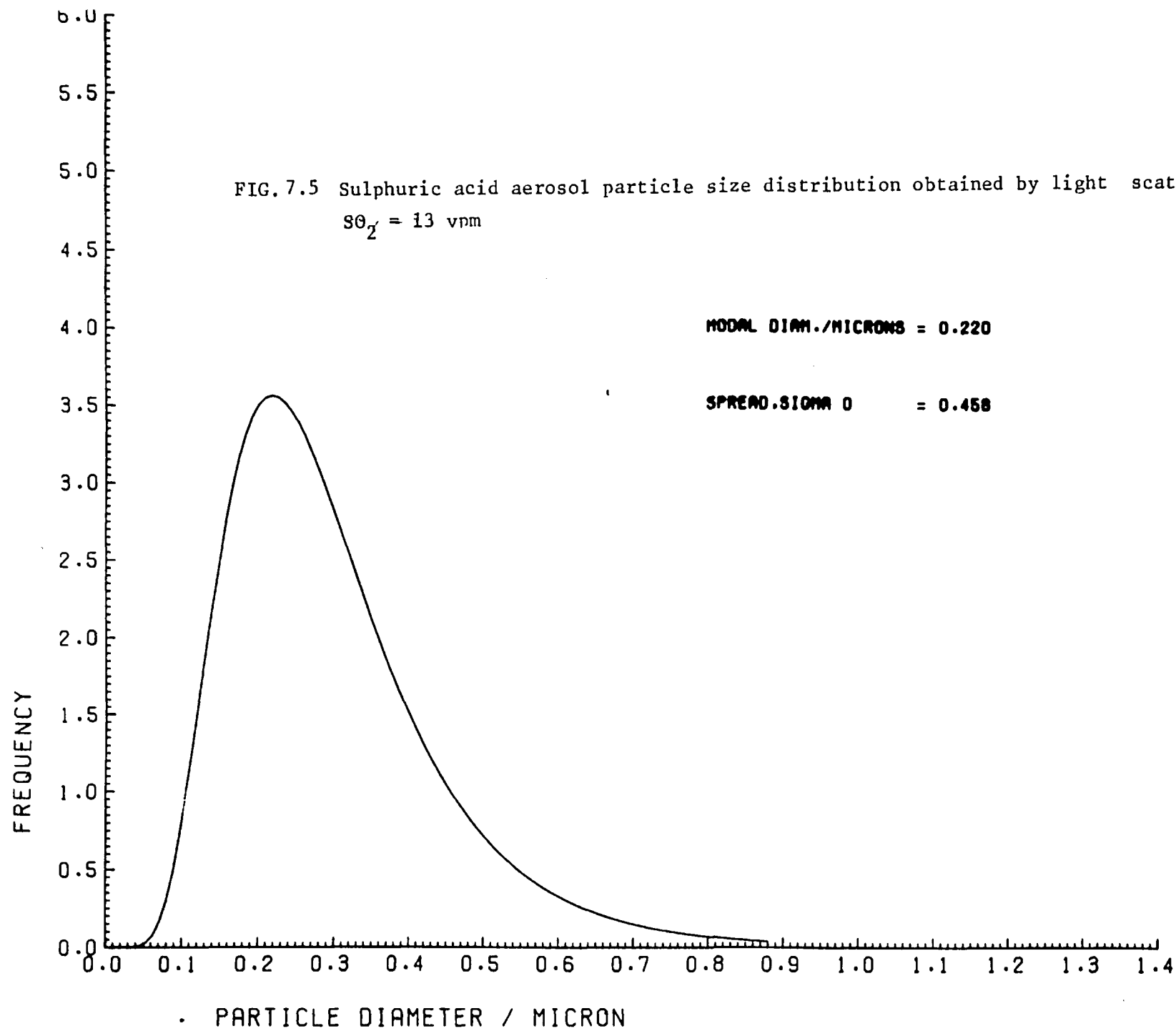
o^+	o^-	N_2^+	O_2^+	NO	Ar^+	ϵ
—	—	—	—	—	—	—
—	1.09 (11)	1.00 (9)	—	—	—	6.30 (12)
—	3.19 (11)	1.00 (11)	—	—	—	5.90 (13)
6.53 (12)	4.30 (11)	1.56 (12)	1.45 (11)	2.02 (14)	3.00 (10)	2.14 (14)
8.57 (13)	4.70 (11)	2.17 (13)	2.40 (11)	3.55 (14)	7.03 (11)	0.20 (14)
2.82 (14)	5.96 (11)	4.50 (13)	2.21 (11)	2.27 (14)	4.96 (12)	2.16 (15)
1.10 (15)	1.01 (12)	4.12 (13)	1.95 (11)	1.13 (14)	2.03 (13)	6.82 (15)
3.59 (15)	1.97 (12)	3.25 (13)	1.85 (11)	6.05 (13)	6.25 (13)	1.72 (16)
5.21 (15)	2.56 (12)	2.44 (13)	1.09 (11)	3.41 (13)	1.55 (14)	3.53 (15)
9.29 (15)	2.01 (12)	1.71 (13)	1.46 (11)	1.97 (13)	3.20 (14)	6.42 (16)
2.65 (16)	—	—	—	—	—	1.29 (17)
3.35 (16)	—	—	—	—	—	1.82 (17)
3.60 (16)	—	—	—	—	—	1.87 (17)
5.67 (16)	—	—	—	—	—	—
—	—	—	—	—	—	—

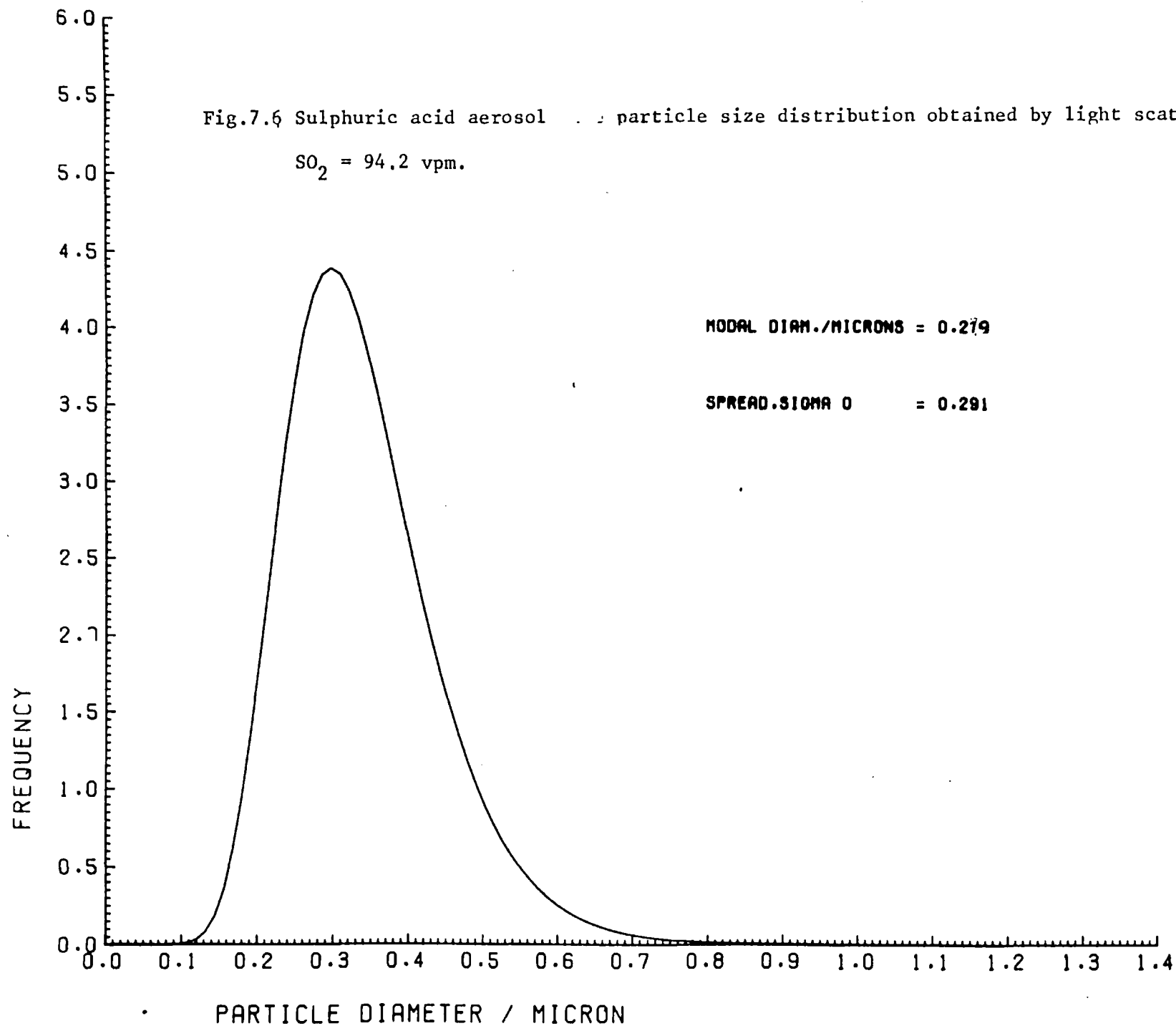
TABLE 4 a

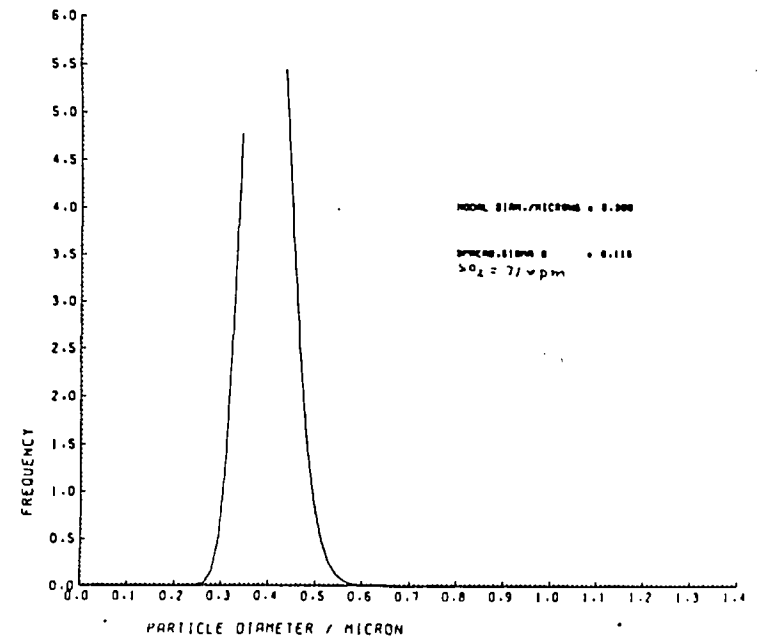
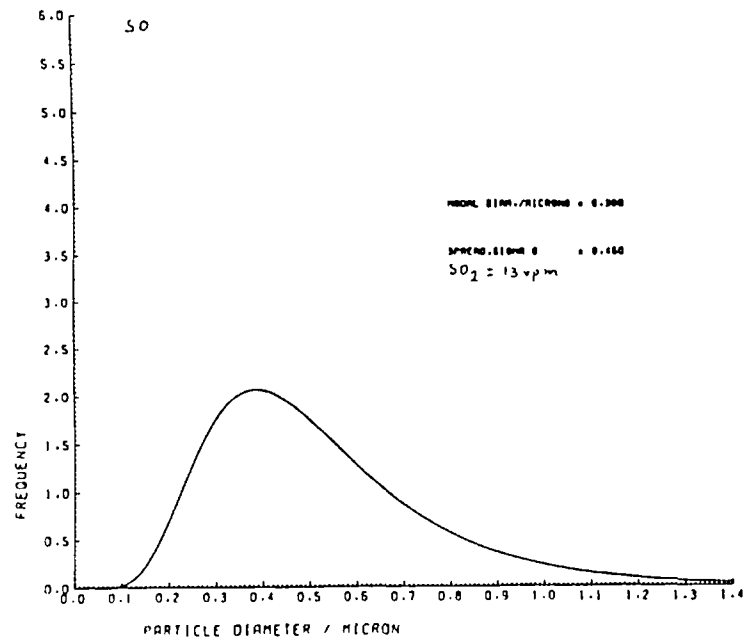
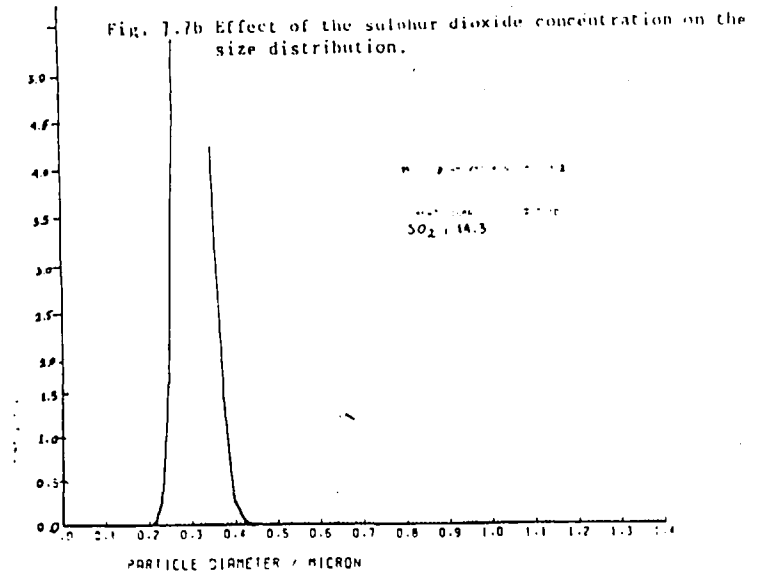
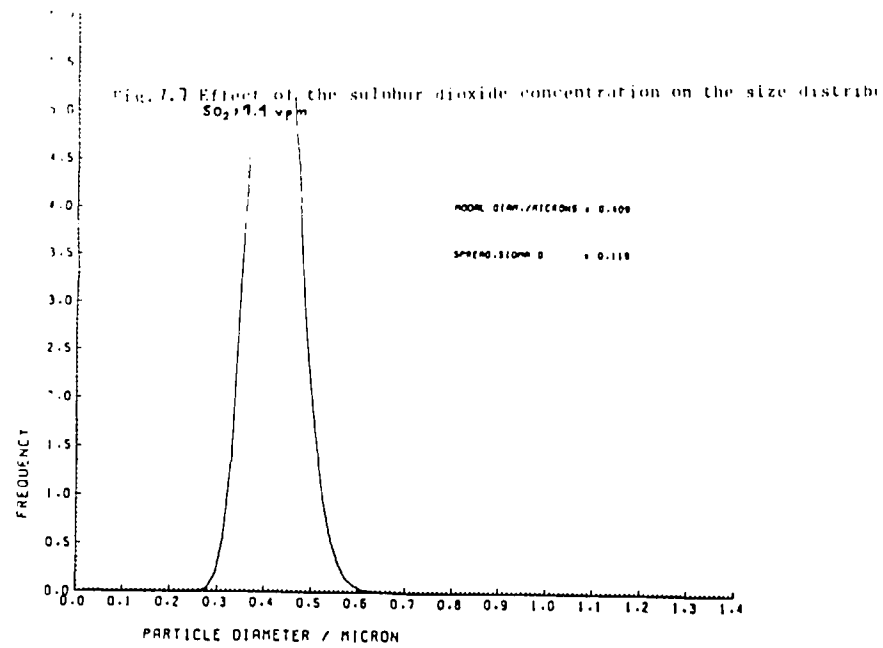
Concentration of components of the oxygen plasma, cm^{-3}

T, °K	O_2	O	o^+	o^-	ϵ	N_2
3000	2.18 (18)	2.72 (17)	—	—	—	2.46 (18)
4000	4.47 (17)	1.39 (18)	—	—	—	1.84 (18)
5000	2.73 (16)	1.44 (18)	—	—	—	1.47 (18)
6000	2.96 (15)	1.24 (18)	2.20 (13)	4.02 (11)	9.16 (13)	1.23 (18)
7000	5.83 (14)	1.045 (18)	4.54 (14)	1.25 (13)	4.53 (14)	1.05 (18)
8000	1.65 (14)	9.14 (17)	2.04 (15)	2.44 (12)	2.04 (15)	0.92 (18)
9000	6.00 (13)	8.05 (17)	6.41 (15)	5.35 (12)	6.40 (15)	0.82 (18)
10000	2.63 (13)	7.65 (17)	1.59 (16)	7.32 (12)	1.59 (16)	0.735 (18)
12000	—	4.84 (17)	5.95 (16)	1.25 (13)	5.95 (16)	0.615 (18)
14000	—	2.57 (17)	1.27 (17)	8.65 (12)	1.27 (17)	0.524 (18)
16000	—	9.60 (16)	1.73 (17)	—	1.78 (17)	0.458 (18)
18000	—	2.50 (16)	1.87 (17)	—	1.87 (17)	0.408 (18)
20000	—	9.50 (15)	1.78 (17)	—	1.78 (17)	0.367 (18)

All tables from Physics and Technology of Low Temperatures Plasma
S.V. Dresvin, (editor) pp. 21; 23. Ref. 27







CONCLUSIONS AND DISCUSSION

8.1 Conclusions.

Radiolysis of sulphur dioxide in gaseous mixtures with nitrogen or air was investigated in a dynamic flow reactor. The following conclusions are drawn.

1. Sulphur dioxide in a nitrogen atmosphere was removed with conversions of 30 to 80% by irradiation. The products were not chemically analysed but are presumably decomposition and oxidation products.
2. In the radiolysis of sulphur dioxide/nitrogen-oxygen mixtures about 97% of the sulphur dioxide was removed. The decrease in sulphur dioxide was much larger for the mixture containing oxygen than for the mixture without oxygen.
3. Sulphur dioxide is not easy to convert to sulphur trioxide by irradiation in a dry system. This is perhaps a consequence of the equilibrium, under irradiation, between sulphur dioxide and sulphur trioxide.
4. We have studied the oxidation of sulphur dioxide in moist air and the results are reported in Chapter 5. With moist air the conversion to sulphur trioxide and sulphuric acid was almost complete (97%), and numerous experimental results have been presented in Chapter 5.
5. The order of the reaction was found to be first order with respect to sulphur dioxide concentration, with a rate constant of 0.045^{-1}

6. The reaction mechanism of sulphur dioxide has not been completely elucidated. The radiolysis of the mixtures sulphur dioxide/Nitrogen/air/water seems to indicate that the oxidation species formed from oxygen, nitrogen and water react with the sulphur dioxide to form HSO_3^- and sulphuric acid with the aid of water.

7. Under favourable conditions, (with air and water vapour present) the removal efficiency of sulphur dioxide was 70 to 97% with an irradiation voltage of 2MeV. a low voltage in comparison with that used by other workers.

8. The product simultaneously formed in all gas mixtures which included water vapour, already reported in Chapter 5, is a suspension of fine particles of sulphuric acid.

9. The aerosol product from the sulphur dioxide/nitrogen-air system was analysed by light scattering techniques and several effects have been observed. a) The signal strength decreases with increasing age of the sample. Since this decrease is always accompanied by unstable aerosol as observed visually, it appears that the effect is associated with the generation of a larger number of agglomerated droplets. b) The effect of more rapid measurements was to give reproducible results, scattering pattern remaining constant within the time of measurement.

10. These experiments were carried out using the Zeroth Order Logarithmic Distribution (ZOLD) method. The modal diameter and the logarithmic standard deviation given in Chapter 6 are the average of duplicate runs, the diameter typically lying in the range 0.35 to 0.6 μm .

11. Measurements carried out at angles between 9 to 130° were of light scattered by each particle over a cone of finite but small solid angle. It is of general interest to point out the way in which the results vary with the angles. The angles used in the preceding experiments were tested by previous workers.

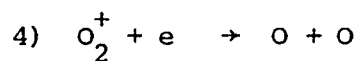
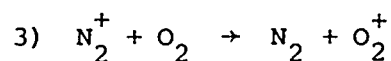
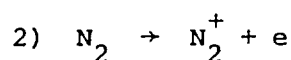
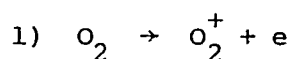
12. Further more, as shown in Chapter 7 the plasma irradiation experiments also result in sulphuric acid aerosol formation. The plasma supported in air is of the type which contains a high concentration of oxygen atoms and nitrogen atoms.

8.2. DISCUSSION

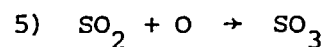
a) Effects of experimental variables on removal of sulphur dioxide.

1. The role of oxygen in removing SO₂

Previous workers Ref. (57, 100, 110) have suggested that oxygen atoms are produced in radiolysis of mixtures containing O₂ and N₂ by a group of reactions shown below (1 - 4). That is, an oxygen atom can be produced via the oxygen ion O₂⁺ (or from excited oxygen molecules). These in turn would be formed by either direct effect of radicals, or by energy transfer from nitrogen ions.



In the present work with sulphur dioxide the oxygen atoms expected to be present via this mechanism would readily produce oxidation to SO₃



A secondary effect might occur with radiation-excited sulphur dioxide molecules transferring energy to augment the production of O_2^+ . The exponentially-shaped curve of conversion against the number of moles of air per mole of N_2/SO_2 (Fig. 5.18a) is to be expected if it is accepted that the rate depends on the concentration of oxygen. A higher concentration will lead to a faster overall rate of reaction, and so in a given period of time, the conversion will be higher. The figure suggests that the maximum rate of reaction occurs when there is a high concentration of oxygen in the mixture i.e. 300 moles of oxygen per mole of sulphur dioxide.

In summary, the effect of oxygen in the mixture in producing large conversions of sulphur dioxide can be consistent with the scheme of radiolysis.

1a. Role of nitrogen in removing sulphur dioxide

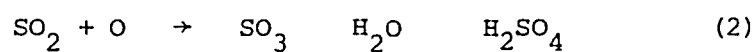
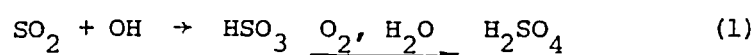
In experiments with oxygen absent there is a reduced, but nevertheless measurable sulphur dioxide conversion. It would be logical to expect some oxidation although there is no aerosol evidence to support this. The absorption of energy from the beam by nitrogen and by sulphur dioxide could nevertheless be sufficient to decompose sulphur dioxide, i.e. by disproportionation to sulphur trioxide and to lower states of oxidation (based on, say, SO).

2. Role of water vapour

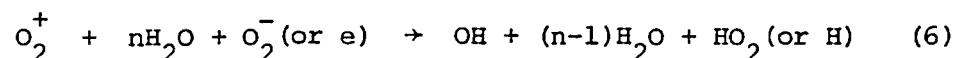
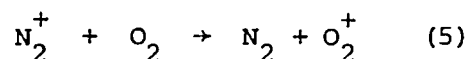
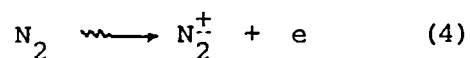
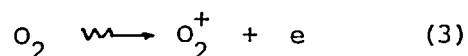
In this work, the amount of OH which can be generated by the direct absorption of radiation by water is relatively negligible (being

roughly in proportion to the mass fractions in the gas of water and of the important absorbers such as nitrogen).

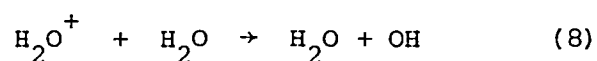
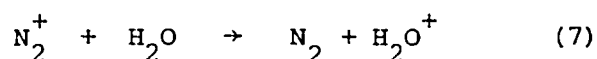
The SO_2 in the mixture sulphur dioxide-Air- H_2O was irradiated at 2MeV, with relative humidities of up to 96%. Processes for the generation of sulphuric acid OH and O may be written as follows:-



OH radicals are mainly made Ref. (100, 110), by the neutralization reaction of O_2^- or e (reaction 6) with O_2^+ and with several H_2O molecules (reaction 6 below). O_2^+ are made directly (3), or indirectly through the charge transfer reactions from N_2 to O_2 (4) and (5).



In this work, the OH· can be made by the direct action of radiation light on H₂O. OH can also be produced by the reaction of H₂O with H₂O⁺, which is in turn generated by the charge transfer reactions from N₂⁺, as seen in reactions (7) and (8)



When SO₂ without O₂ was irradiated, relatively smaller decreases were observed. SO₂ was the effective acceptor of OH and O. Consequently, the contribution of OH made by reaction (7), (8) is negligible. Water will play an essential role for the formation of H₂SO₄ from SO₃, and for the formation of OH and HO₂.

3. Effect of temperature

The temperature was controlled by blowing compressed air system over the radiation vessel. By this means it was possible to keep the reactor wall at 70-80°C. No experiments were done to vary the reaction temperature.

4. Effect of beam current and voltage

It can be seen that over 97% of sulphur dioxide is removed in a few seconds irradiation at 2MeV. The conversion was virtually independent of beam current in the range 20 - 100 μA.

5. Properties of the product aerosol

Physical aspects: Aerosol formation in the sulphur dioxide-air-water system was induced by electron beam irradiation with the experimental arrangement as seen in fig. 4.2.

For a physical explanation of the aerosol we can refer to other experimental work Ref. (9) in which the end product of photochemical aerosol formation was sulphuric acid.

The irradiation induced reaction product condenses as an aerosol. After reaching a sufficient saturation, the sulphuric acid condenses to drops Ref. (39,77). Reactions on the wall of the reactor probably do not induce aerosol formation and are disregarded.

Because of the continuing influence of the radiation, more reaction product condenses on these drops, bearing in mind that the necessary saturation is smaller than that needed for spontaneous condensation. The result is the continued growth of the drops at constant temperature and pressure, with an increasing number of drops being deposited through sedimentation.

However, as the reaction continues new condensation nuclei will also be produced. After some time there is reason to suppose there will be a balance between renewal and removal of condensed drops, - a phenomenon described by various authors as the "self-preserving" distribution.

The results observed in the present work will now be discussed against the above hypotheses.

- (a) The reaction product which manifested itself as an aerosol was positively identified as sulphuric acid. (litmus and BaCl_2 tests).
- (b) The size distributions showed certain trends with (i) residence time in the reactor, and (ii) concentration of sulphur dioxide.

Size distribution as a function of residence time

The series of curves shown in figure 6.8 are derived from similar experiments at various intervals of time and show the very acceptable reproducibility of the measurements. In figure 8.1 are shown representative distributions from two residence times. It was also observed that the aerosols produced at long residence times were intrinsically much less dense and much less obvious visually.

At 11.5 s residence time we have narrower distributions with particles larger than $\sim 0.6 \mu\text{M}$ "missing" when compared with the distributions at 3.6 secs residence time.

It is reasonable to ascribe both these observations to a greater extent of deposition in the mixture with the larger residence time (since obviously the deposition is preferential in removing larger particles).

Size distribution as a function of sulphur dioxide concentration

As shown in figures 3.2, Table. 6.3 there is a gradual increase of modal diameter and spread when experiments with increasing sulphur dioxide concentration are compared (all at one residence time). The trend of modal diameter is also depicted in the curve of Figure. 3.3. Factors which could produce this effect would be increasing growth of droplets at higher SO_2 concentrations, and increasing co-agulation of more numerous droplets; it is not practicable to distinguish these simultaneous processes in these experiments.

6. Practicability of removing the aerosol by electrostatic precipitator.

The experimental work of this thesis was carried out in the main without using an electrostatic precipitator. (It was not necessary to so treat the effluent gases). However, electrostatic precipitators are widely used to collect solid and liquid particles in the size range encountered in this irradiation work. Unfortunately, due to time constraints, it was not possible to achieve any quantitative results except in a very preliminary way. It can however be asserted that the particles produced are such that could be removed in this way with relative ease and efficiency.

7. Limits of potential for sulphur dioxide removal; further investigations required.

A great deal of work is currently being conducted on various methods such as chemical processing in the gases and in the furnace itself, and improvement of burners and combustion chamber design to decrease sulphur dioxide emission. In comparison with these methods the process using electron beam accelerator has shown the following features.

Effectiveness: Strong efficient removal of sulphur dioxide is obtained by irradiation with short residence times (e.g. 10 sec). The power source (Van de Graaff system) typically required beam current of 20 μA . The ratio of power/ SO_2 removal rate was 7.10^9Jmol^{-1} in the Van de Graaff system and 5.10^9Jmol^{-1} in the plasma-jet system.

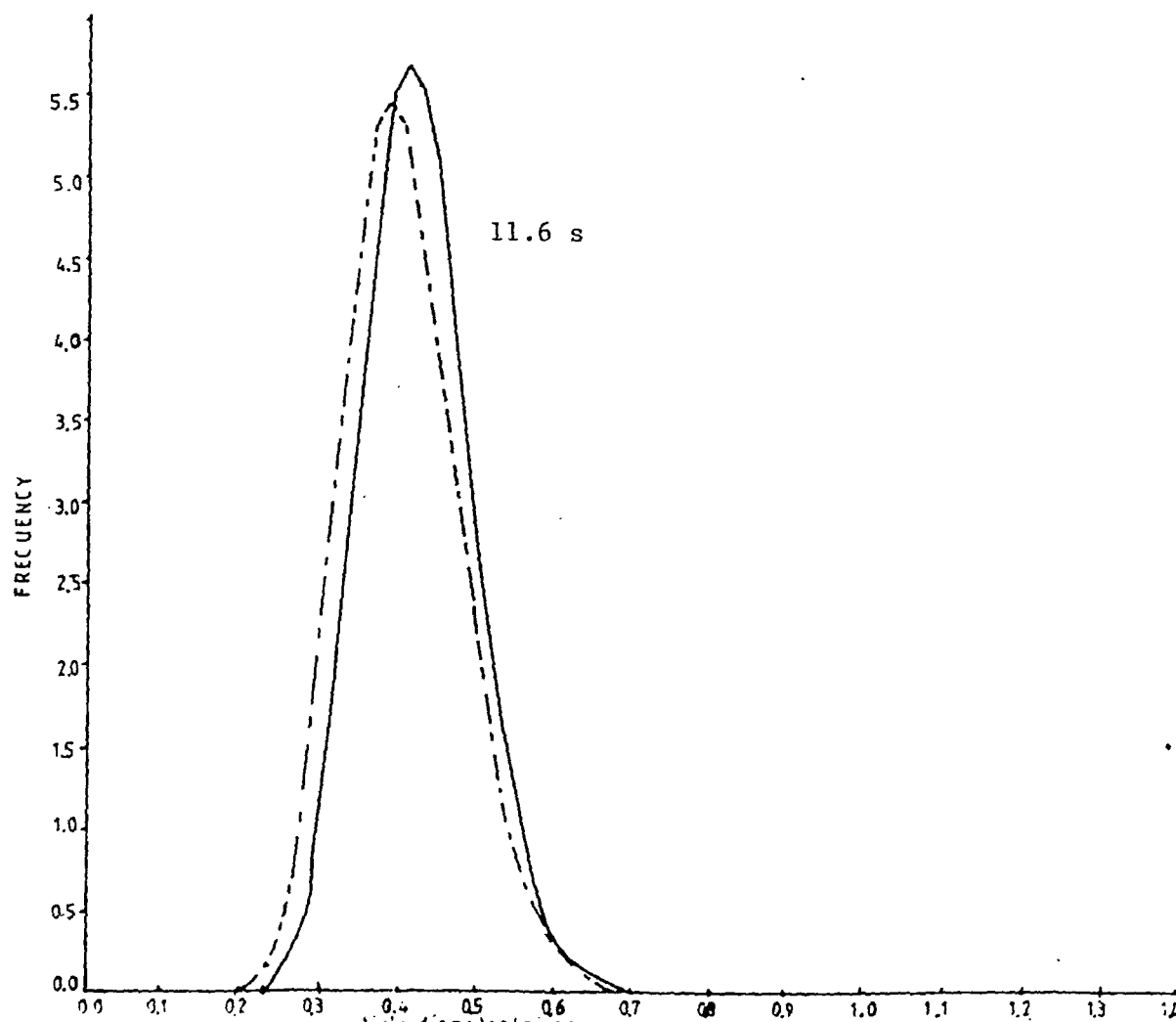
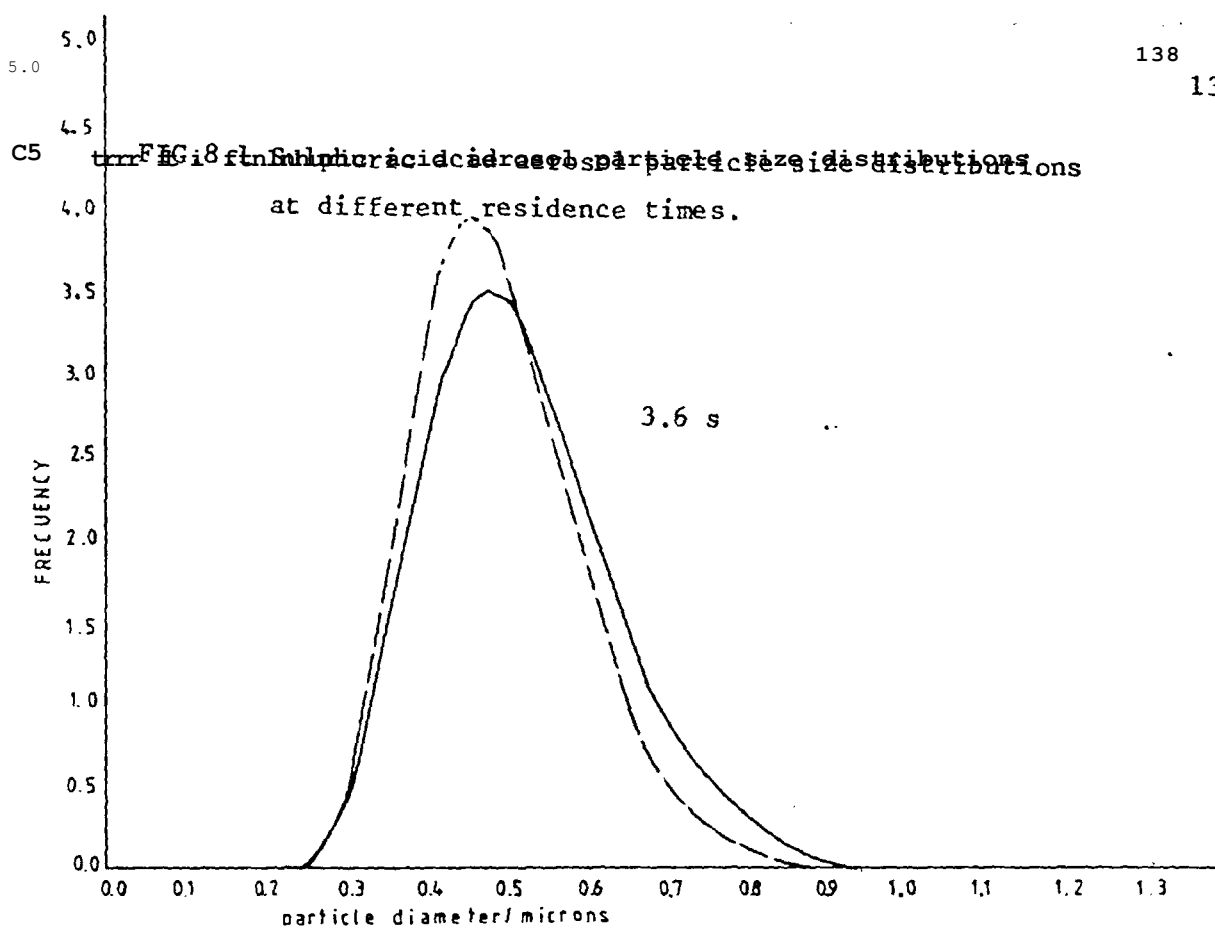
Dry process: The product should be capable of easy collection as "dry" material using an electrostatic precipitator, this is in contrast to slurry addition in the alkali flue gas treatment processes.

Simplicity: The process equipment could consist of high energy sources such as an electron beam accelerator, or, more probably, a plasma-jet, and an electrostatic precipitator.

8.3. Recommendations for future work.

An air plasma could be used instead of the Van de Graaff accelerator to remove noxious compounds from combustion gases. This method could be in future developed to guarantee the removal of sulphur dioxide and NO_x on an industrial scale.

Further studies of the reaction mechanisms are needed to develop the process for industrial use. If developed, the process might offer significant economic advantages over alternative processes.



concentrations.

Fig.8.2. Comparison of sulphuric acid aerosol size distribution at different SO_2 concentrations.

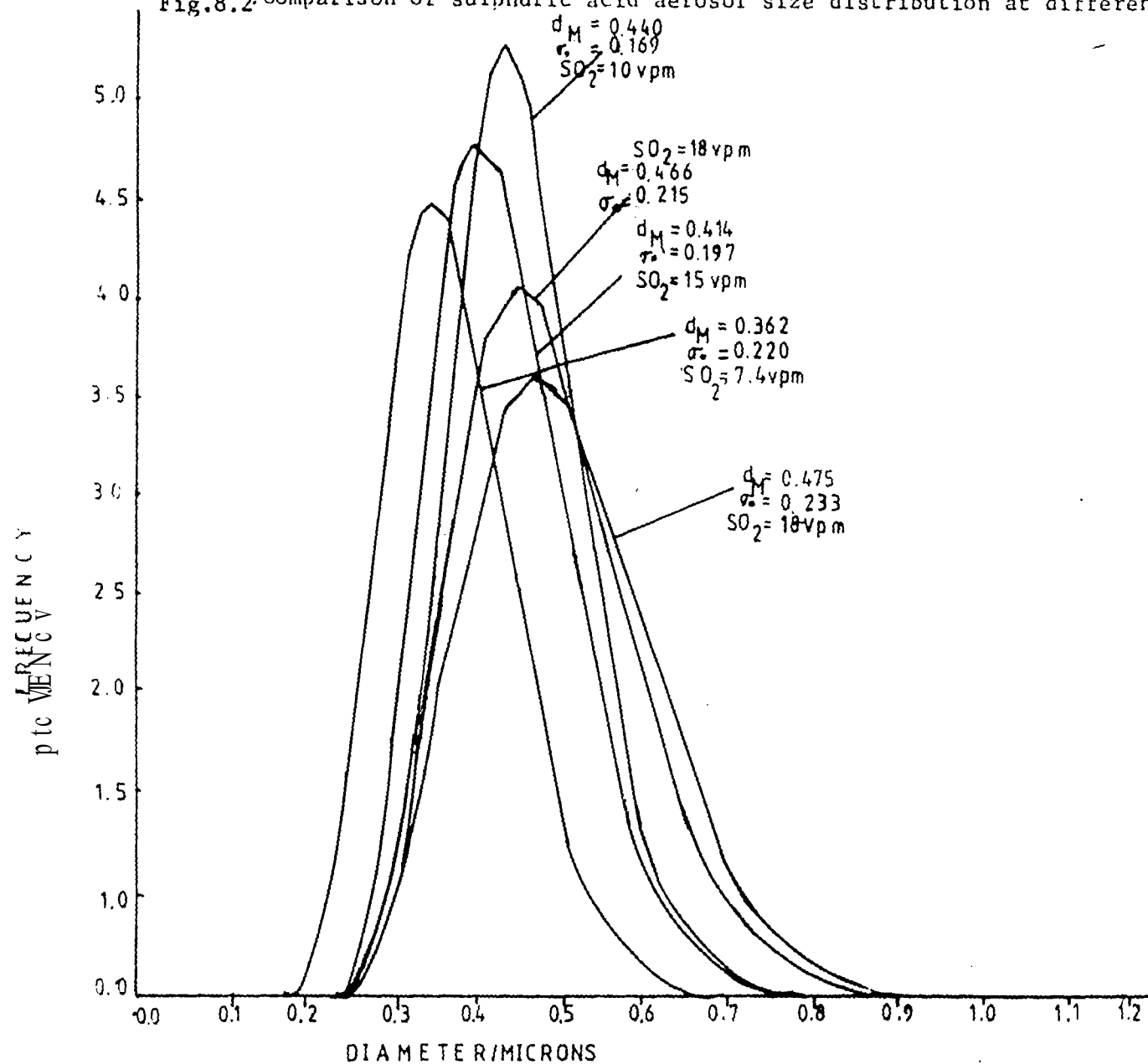
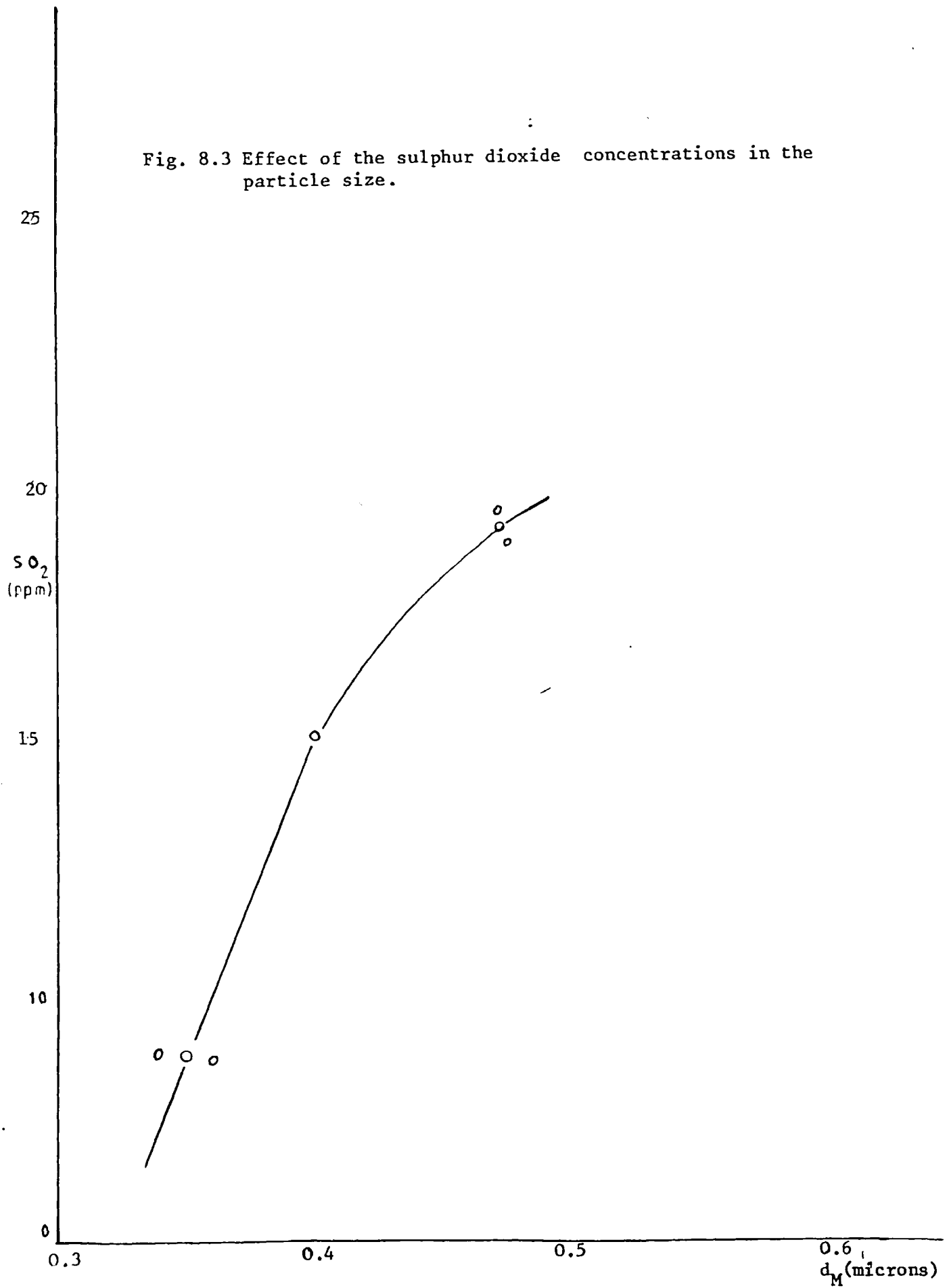


Fig. 8.3 Effect of the sulphur dioxide concentrations in the particle size.



REFERENCES

1. ARNOLD, F. and FABIAN, R., 1980, Nature 283, 5742, 3.1, 55.
2. ARNOLD, F. and FABIAN, R. 1979, J. Atmos. Sci. 36, 699.
3. ALLEN, E.R., McQUIGG, R.D. and CADLE, R.D., 1972, Chemosphere, 1, 25.
4. BAILY, R. and BROWN, S.C., 1959, Rad. Res., 11, 745.
5. BALLANTINE, D.S., MILLER, L.A., BISHOP et al., 1969, J. Water Pollution Control Fed., 41, 445.
6. BADDOUR, R.F. and TIMMINS, R.S., 1967, The application of plasmas to chemical processing, Pergamon Press.
7. BARRETT, R.E., HUMMELL, J.D. and REID, W.T., 1966, J.Eng. Progress 23, 165.
8. BATES, 1954, The Earth as a planet. Chap. 12, 576. Univ. Chicago Press.
9. BLAU, H.H. et al., 1970, Appl. Opt., 9, 2522.
10. BRAND, J.C.D., JONES, V.T. and DiLAURO, C., 1971, J. Molec. Spectr., 40, 616.
11. BROWN, S.C., 1959, "Basic data in plasma physics"., M.I.T. Press.
12. BROWN, R.D., DONDES, S., HARTECK, P., 1966, Rep. AD.642579.
13. BULLRICH, K., 1964, Advan. Geophys., 10, 99.
14. CADLE, R.D. and MAGILL, 1956, "Air Pollution Handbook" McGraw-Hill, N.Y.

15. CADLE, R.D. and POWERS, J.W., 1966, *Tellus* 18, 176.
16. CAINS, P.W., 1975, Ph.D. Thesis, Univ. London.
17. CAINS, P.W. and CARABINE, M.D., 1978, *J. Chem. Soc., Faraday I*, 74, 2689.
18. CALVERT, J.G. et al., 1978, *Atmospheric Env.* 12, 197.
19. CARABINE, M.D., MADDOCK, J.E. and MOORE, A.P., 1971, *Nature, Phys. Sci.*, 231, 18.
20. CHAN, A.K.F. et al. 1980, *J. Phys. D. App. Phys.*, 13, 2309.
21. CHIN, J.H., SLIEPCEVICH, C.M. and TRIBUS, M., 1955, *J. Phys. Chem.*, 59, 841.
22. CHEREMISINOFF and YOUNG, 1975, *Production Eng. Practice Handbook*.
23. CHUAN, R.L., 1957, U.S.C.E.C. Rept. 68-202.
24. COMPTON, D.M.J. et al. 1969, *Proc. Symp., Munich, IAEA, Vienna*.
25. COX, R.A.J. , 1976, *J. Phys. Chem.* 76, 814.
26. COX, R.A.J., 1964, *Int. J. Chem. Kinet.* 7, 379.
27. DRESVIN, S.V. (editor) *Physics and technology of low temperature plasma, Moscow, Atomisdat* .
28. DIXON, R.S., 1970, *Radiat. Res. Rev.* 2, 237.
29. ECKER, P. and KROLL, U., 1963, *Phys. Fluids.* 6, 62.
30. ENSOR, D.S. et al., 1972, *J. Colloid Interface Sci.*, 39, 242.

31. VON ENGEL, A. and STEENBECK, R., 1944, Elektrische Gasentladungen., Edwards Brothers, Ann Arbor, Mich.
32. FIELDER, R.D., MORGAN, C.H., 1960, Anal. Chim. Acta, 23, 538.
33. GERHARD, E.R., 1954, Dissertation Abst. Ann. Arbor, Mich., 14, 321. (Univ. Microfilms, Num. 6949).
34. GERHARD, E.R. and JOHNSTONE, H.F., 1955, Ind. Eng. Chem., 47, 972.
35. GOOD, A., DURDEN, D.A., and KEBARLE, A., 1970, J. Chem. Phys. 52, 222.
36. GRIEM, H.R., 1964, Plasma Spectroscopy, McGraw-Hill, N.Y.
37. GOETZ, et al., 1961, Geofis. Pura.Appl. 50, 67.
38. GROBLICKI, P.J. and NEBEL, G.J., 1971, The photochemical formation of aerosols in urban atmospheres, Elsevier Publishing Co., p. 241.
39. GÜSTEN, H. und PENZHORN, R.D., 1974, Naturwissen., Rundschau, 27, 56.
40. HALL, T.C. Jr. , 1953, Photochemical studies of NO₂ and SO₂, Ph.D. Thesis. U.C.L.A.
41. HARRISON, A.J. and WEINBERG, F.J., 1971, Proc. Roy. Soc. London, A321, 95.
42. HARTECK, P., REEVES, R.R. and MANNELLA, G.G., 1958, J. Chem. Phys. 29, 608.
43. HARWELL, K.E. and JOHN, R.G., 1964, Phys. Fluids., 7, 214.
44. HEALY, T.V. et al., 1970, J. Geophys. Res., 75 2317.
45. HERZBERG, G., 1966, Molecular spectra and molecular structure III, Van Nostrand., Princeton New Jersey.

46. HILLIARD, J.C., 1980, Ph.D. Thesis Univ. of London.
47. HILLIARD, J.C. and WEINBERG, J.J., 1976, Nature, 259, 556.
48. HONG, N.S., JONES, A.R., 1976, J. Phys.D, 9, 1839.
49. H0USHANG, F. BEHBAHANI, Et al. 1982, Comb. Sci. and Techn., 27 123.
50. HOWARD, C.J., 1972, J. Chem. Phys., 57, 3491.
51. JOHNSTONE, H.F., LEPLA, P.W., 1934, J. Am. Chem. Soc. 56, 1169.
52. JOHNSTONE, H.F., COUGHANOUR, D.R., 1958, Ind. Eng. Chem. 50, 1169.
53. JOHNSTONE, H.S. and K. Dev JAIN, 1960, Science, 131, 1523.
54. JOHNSTONE, H.F. and CADLE, R.D., 1952, Proc. 2nd Nat. Air Pollution Symp., Stanford Research Inst. Los Angeles, Cal.,
55. JOHNSON, G.R.A. and WARMAN, J.M., 1964, Disc. Fraaday Soc. 37, 87.
56. JACOBS, M.B., 1960, Chem. Anal., 10, Interscience.
57. JUNGE, C.E. and RYAN, T.C., 1958, Quart. J.R. Meteor. Soc., 84, 46.
58. JUNGE, C.E. and MAISON, J.E., 1961, J. Geophys. Res., 66, 2163.
59. KAWAMURA, K. et al., 1975, IAEA-SM-194/707.
60. KAWAMURA, K. et al., 1972, J. Atom.Energy Soc. Japan 414, 11, 597.
61. KAWAMURA, K., et al., 1979, Rad. Phys. Chem., 13, 5.
62. KERKER, M. et al., 1972, J. Colloid Interf. Sci., 38, 460

63. KETTANI, M.A., and HOYAMX, M.F., 1973, Plasma Engineering, Butterworth & Co.
64. KNEWSTUBB, P.F. et al., 1962, J. Chem. Phys., 36, 674, 37, 2941, 1963, 38, 464.
65. KNOLL, M., OLLENDORF, F., ROMPE, R., 1944, Gasentladunstabellen. Edwards Brothers, Ann Arbor. Mich.
66. KEITH, TEORCE, 1973, Ind. Pollution Control., Business Books Ltd., London.
67. LA MER, V.K., INN, E.C.Y., and WILSON, J.B., 1950, J. Colloid Sci. 5, 471.
68. LEIGHTON, P.A., 1961, Treatment of exhaust gases by irradiation. Photochemistry of air pollution, Academic Press, N.Y., London.
69. LEIGHTON, P.A. and PERKINS, A., 1958, Photochemical secondary reactions in urban air. Air Pollution Foundation, San Marino, California.
70. JUERGEN, W. Leonhardt, et al., 1981, I.J.A.R.I., 32, 487.
71. LEVENSPIEL, O., 1962, Chemical reaction engineering, John Wiley & Sons, Inc.
72. LEVY, A. and MERRYMAN, E.L., 1966, Comb. and Flame, 9, 299.
73. LIJTI, G., 1969, Nuclear Appl., 6, 494.
74. LIN, S.C. and TEARE, J.D., 1963, Phys. Fluids, 6, 355.
75. LUHR, O., 1933, Phys. Rev., 44, 459.
76. MACHI, S. et al., 1977, Rad. Phys. Chem., 9, 371.
77. MADDOCK, J.E.L., 1974, Ph.D. Thesis. Univ. of London.

78. MACHI, S., 1973, Proc. 11th Japan Conf. on Radioisotopes, 213.
79. MANNELLA, G.G., 1963, Chem. Rev. 63, 1.
80. MASSEY, Et al, 1969, I, II; 1971, III; 1974, IV, Electronic and ionic impact phenomena, Oxford University Press.
81. MEISELS, G.G., 1964, J. Chem. Phys., 41, 54.
82. MOORE, A.P., 1974, Ph.D. Thesis, University of London.
83. MOORE, Ch.E, 1949, Atomic Energy Levels, Vol., I, II, III, Nat. Bur. Stand., 467.
84. McTAGGART, F.K., 1967, Plasma chemistry in electrical discharges, N.Y., Elsevier Publish. Co.
85. MATIJEVIC, E., KITANI, S. and KERKER, M., 1964, J. Colloid Sci. 19, 223.
86. OGATA, Y., ISAWA, Y. and TSUDA, T., 1965, Tetrahedron, 21, 1349.
87. PRAGER, M.J., STEPHENS, E.R., and SCOTT, W.E., 1960, Ind. Eng. Chem., 52, 521.
88. PENZHORN, R.D., STIEGLIETZ, L., FILBY, W.G. and GÜNTER, K., 1973, Chemosphere Num., 3 111.
89. PHAZMORAJAN, Thomas V., 1975, Science of the total environment, 4 (3), 279.
90. POLYCHRONAKIS, S. 1978, Ph.D. Thesis, University of London
91. RAO, T.N., CALLIER, S.S. and CALVERT, J.G., 1969, J. Am. Chem. Soc., 91, 1609, 1616.
92. PORCH, W.M., CHARLSON, R.J. and RADKE, L.F., 1970, Science 170, 315

93. RENZETTI, S., and DOYLE, D.J., 1960, Int. J. Air Pollution, 2, 327.
94. SCOTT, W.D. and HOBBS, P.V., 1967, J. Atmos. Sci., 24, 54.
95. SINCLAIR, D. and LA MER, V.K., 1949, Chem. Rev., 44, 245.
96. STEPHENS, E.R., 1961, Treatment of exhaust gases by irradiation Interscience Publishers, N.Y.
97. SWALLOW, A.J. 1973, Radiation chemistry, Longman.
98. TAKAHASHI, K., KASAHARA, M., and ETO, H., 1975, J. Aerosol Sci., 6, 45.
99. THOMPSON, B.J., 1974, J. Phys., E 7, 781.
100. TOKUNAGA, O. et al., 1978, I.J.A.R.I., 29, 81, 87.
101. TOKUNAGA, O., MACHI, S. et al., 1977, Rad. Phys. Chem. 9, 371.
102. TOKUNAGA, O., et al., 1978, Rad. Phys. Chem., 11, 117, 229.
103. UMAN MARTIN, A., 1964, Introduction to plasma physics, McGraw-Hill, N.Y., London, Tokyo.
104. UNSÖLD, A.Z., 1948, Astrophysics, 24, 355.
105. VAN DEN HEUVEL, and MASON, 1963, Quart. J. Royal Meteorol. Soc. 89, 271.
106. VAN DE HULST, H.C., 1957, Light scattering by small particles. Wiley, New York.
107. VENUGOPALAN, M., 1980, Topics in Current Chemistry, 90, Plasma Chemistry II.

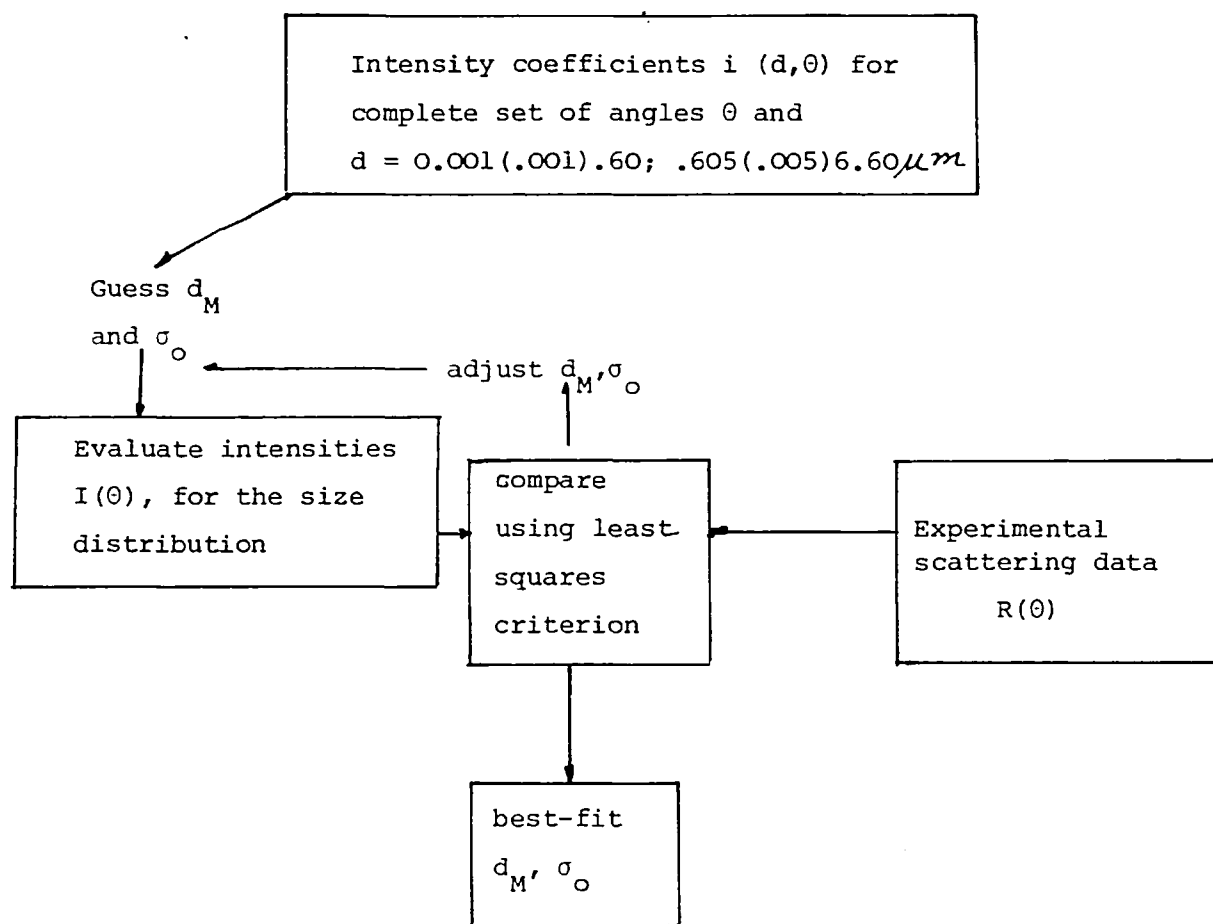
108. VENUGOPALAN, M., 1971, Reactions under plasma conditions
Vol. I, II, Wiley Interscience.
109. WARRIS, A.M., 1983, Ph.D. Thesis, Univ. of London.
110. WASHINO, M., TOKUNAGA, O., et al. 1975, Proc. Symp. Munich.
111. WEINBERG, F.J., 1968, Inaugural Lecture, Imperial College,
London.
112. WHITTINGHAM, G., 1948, Trans. Faraday Soc., 44, 141.
113. WOOD, W.P., CASTLEMAN, A.W. Jr., and TANG, J.N., 1975,
J. Aerosol Sci., 6, 367.
114. YOUNG, R.A., 1966, Can. J. Chem., 44, 1171.

SUMMARY

1. Sulphur dioxide removal from SO_2/N_2 - Air mixtures was investigated in a Van de Graaff electron beam.
2. A method for guaranteed complete sulphur dioxide removal from combustion gases was developed.
3. The reaction mechanisms of oxidation of sulphur dioxide in air, was studied.
4. Aerosol particle size distributions were analysed by light scattering techniques.
5. Further experiments were carried out with air plasma irradiation and a method proposed for further industrial applications.
6. Further investigations into the SO_2/N_2 - Air system were carried out with particular reference to effect of moisture on sulphur dioxide removal.

APPENDIX 1

Simplified Flowchart for SEARCH Refs.(83,90)



In the iterative programme described by this chart (Refs. 83, 90), a comparison is made between experimental scattering data and data which are calculated for an assumed size distribution, using single particle intensity coefficients derived by Mie theory. If optimum fit between empirical data and predicted is acceptable, the ZOLD distribution closest to the aerosol's distribution has been identified.

APPENDIX 2

ELECTRON BEAM DOSIMETRY AND G-VALUES CALCULATIONS

Three vessels, diameters 0.5cm, 1cm, and 2cm were used in these studies.

1cm. diameter

a) Calibration:

0.5cm³ of H₂ at ambient temperature and pressure gave a signal on the gas chromatograph a (peak height x attenuation) = 19200.

b) Irradiated sample:

2cm³ of irradiated ethylene was injected into the gas chromatograph and gave a signal at the same retention time (peak height x attenuation) = 3008.

Hence a 0.5cm³ sample would have given a signal of magnitude 752.

This is equivalent to a yield = $\frac{752}{19200}$ x 0.5cm³ of H₂ (ambient).

$$= 1.958 \times 10^{-2} \text{ cm}^3 \text{ H}_2 = 0.0196 \text{ cm}^3$$

hence dose per 2. cm³ of irradiated gas is given by

$$G = 1.2 = \frac{\text{Yield} \times 100}{\text{Dose}}$$

Taking $G(\text{H}_2) = 1.2$

$$1.2 = \frac{\text{Yield} \times 100}{D} = \frac{1.96 \times 10^{-2}}{22400} \times \frac{6.23 \times 100}{D}$$

$$\begin{aligned}\text{Dose (0.5cm}^3) &= 4.35 \times 10^{19} \text{ eV} \\ &= 8.70 \times 10^{19} \text{ eV cm}^{-3} \text{ ethylene}\end{aligned}$$

Calculation of $G(\text{SO}_2)$.

The SO_2 was irradiated in a 1% mixture with N_2/Air . It is assumed that all the energy is absorbed in the N_2 component.

Hence dose is

$$\begin{aligned}\text{N}_2 &= \text{dose in ethylene} \times \frac{Z_{\text{N}_2}}{Z_{\text{C}_2\text{H}_4}} \\ &= 8.7 \times 10^{19} \times \frac{14}{16} = 7.6 \times 10^{19} \text{ eV cm}^{-3} \text{ N}_2\end{aligned}$$

In a typical experiment the flow rate of the SO_2/N_2 -air mixture was $550 \text{ cm}^3 \text{ min}^{-1}$. The sample (flowing) was irradiated for 10 minutes and 80% of the SO_2 destroyed, $\approx$ to

$$0.8 \times 5500 \times 0.01 = 44 \text{ cm}^3$$

hence

$$G(-\text{SO}_2) = \frac{\frac{44}{22400} \times 10^{23} \times 100 \times 6.23}{7.7 \times 10^{19} \times 5500}$$

$$G(-\text{SO}_2) = \underline{\underline{0.28}}$$

APPENDIX 3All runs were of 10 minute duration3.a) Variation of conversion with quantity of Air, $\tau = 14.5$ seconds

CONCENTRATION SO_2 vpm	No. moles air per mole SO_2 in N_2	Titre $\text{I}_2 10^{-3}\text{M}(\text{cm}^3)$		Conversion %
		Blank	Irradiated	
1000	0	35.4	30.0	15.3
910	0.1	34.4	12.7	63.1
830	0.2	31.1	8.8	71.7
500	1.0	18.7	1.95	89.6
167	5.0	6.8	0.77	88.7

3.b) 5000 ppm SO₂, $\tau = 14.5$ seconds, 1 part N₂/SO₂: 1 part air

Length of run (Minutes)	Titre I ₂ 10 ⁻³ M (cm ³)		Corrected Titre (cm ³)		Conversion %
	Blank	Irradiated	Blank	Irradiated	
2	45	45	-	-	-
5	87	71	58	27	53.4
10	157	137	155	72	53.5
15	301	152	253	119	53.0
20	408	206	350	165	52.9
25	475	231	448	212	52.7