

THE EFFECT OF PLASMA CONSTITUTION
ON LASER IGNITION ENERGIES

by

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ABSTRACT

The main object of this research was to investigate, using focussed laser pulses, the extent to which the minimum ignition energies of flammable gas mixtures depend on the species which carry the plasma energy, with particular reference to inhibitors and to the usual constituents of electrodes used in conventional spark ignition.

The fundamental limitations which apply to ignition by laser beams focussed into initially transparent gases were avoided by using minute targets in the form of wires or fibres of the order of 10^{-5} m in diameter placed at the focal spot. The use of these targets also enabled the amount of target material in the plasma, its chemical constitution and its initial volume to be varied by changing the target size, the material of which it is made and its position in the beam relative to the focal spot, respectively. The energy of the plasma was measured, independent of its composition, by a specially developed suction microcalorimeter.

It was found that, for Q-switched pulses of approximately 40 ns duration, minimum ignition energies are independent of the plasma constitution both as regards different substances and different amounts of the same substance within the plasma. For free-running pulses of much longer duration (approximately 1 ms) however, the effect of plasma constitution was that expected from each different target material.

The essential difference between the Q-switched and free-running pulses was investigated using double Q-switched pulses and by applying high speed

laser schlieren cine photography to the free-running events. This yielded the velocities of the relevant expanding fronts and revealed the reason why the free-running pulse duration is long enough to enable the plasma constitution to affect minimum ignition energies. It transpires that if energy continues to be fed to the target then, so long as the plasma cloud remains dense enough, the latter continues to absorb energy for the duration of the pulse. This enables the cloud to expand rapidly, eventually becoming turbulent as it overtakes the flame front, breaking through it locally and producing the effect expected from the target material used, e.g. extinction, in the case of an inhibitor.

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TABLE OF CONTENTS

	ABSTRACT	2
	ACKNOWLEDGEMENTS	4
	LIST OF FIGURES	8
1	INTRODUCTION	10
1.1	Definitions of Ignition Parameters	10
1.2	Ignition Theory	11
1.3	Inhibitor Background	23
1.3.1	The Mechanism of Inhibition	26
1.4	Previous Work	29
1.4.1	Electrical Spark Ignition	29
1.4.2	Laser Induced Ignition	34
1.5	Objectives and Purpose of Research	37
2	DESCRIPTION OF APPARATUS	40
2.1	Ruby Laser	40
2.1.1	Alignment of Laser	40
2.1.2	Outputs available	42
2.2	Construction of Reinforced Beam Energy Calorimeter	45
2.3	Calibration of Copper-constantan Thermocouples	49
2.4	Beam Energy Reproducibility and Number of Pulses in Q-switched Output	52
2.5	Mixing System and Ignition Cell	54
2.5.1	Accuracy of Mixture Composition	58

3	DEVELOPMENT OF MICROCALORIMETER FOR PLASMA	
	ENERGY MEASUREMENTS	62
3.1	Introduction	62
3.2	Thermocouple Thickness Investigation	64
3.3	Construction of Calibration Source	66
3.4	Development of Microcalorimeter	69
3.5	Calibration of Microcalorimeter	77
3.5.1	Variation of Aspiration Rate	77
3.5.2	Variation of Energy Release Rate	80
3.5.3	Linearity of Calibration	80
4	PRODUCTION AND USE OF SMALL LASER TARGETS	84
4.1	Introduction	84
4.2	Production of Targets	85
4.3	Use of Targets	87
5	RESULTS: VARIATION OF IGNITING PLASMA	
	COMPOSITION	91
5.1	Experimental System and Technique	91
5.2	Preliminary Investigations	95
5.3	Use of Q-switched Output	101
5.3.1	Variation of Target Mass	102
5.3.2	Variation of Target Material	104
5.3.3	Discussion	104
6	RESULTS: VARIATIONS OF PLASMA DIMENSIONS,	
	MIXTURE STRENGTH AND PULSE DURATION	107
6.1	Variations of Plasma Dimensions and Mixture Strength	107

6.1.1	Plasma Extension	107
6.1.2	Variation of Mixture Strength	108
6.1.3	Discussion	113
6.2	Variation of Pulse Duration	114
6.2.1	Discussion	115
6.3	High Speed Cine Photography	116
6.3.1	Discussion	118
7	CONCLUSIONS	119
	REFERENCES	123
	LIST OF SYMBOLS	126

LIST OF FIGURES

Fig. 2.1	Ruby laser head	41
Fig. 2.2	1 ms free-running pulse	43
Fig. 2.3	Pen recorder trace of free-running pulses	44
Fig. 2.4	Beam energy calorimeter in polished metal cavity	48
Fig. 2.5	Beam splitter, condensing lens and beam energy calorimeter	50
Fig. 2.6	Copper-constantan thermocouple calibration	51
Fig. 2.7	Mixing system	56
Fig. 2.8	Ignition cell (containing target)	57
Fig. 3.1	Thin thermocouple responses for various temperatures and time intervals	65
Fig. 3.2	Calibration source	70
Fig. 3.3	Calibration source during construction	70
Fig. 3.4	Microcalorimeter designs	72
Fig. 3.5	Final microcalorimeter design	73
Fig. 3.6	Assembled microcalorimeter	73
Fig. 3.7	Radiation shield	74
Fig. 3.8	Microcalorimeter during construction	76
Fig. 3.9	Effect of aspiration rate	78
Fig. 3.10	Effect of energy release rate	81
Fig. 3.11	Linearity of microcalorimeter calibration	82
Fig. 4.1	Quartz fibre (80 μm diameter) coated with NaCl	88

Fig. 4.2	NaCl-coated fibre used as target	89
Fig. 5.1	Layout of experimental system	92,93
Fig. 5.2	Rotatable polaroid, iris and lens assembly, ignition cell containing target, and sighting microscope	94
Fig. 5.3	He-Ne laser and schlieren system	96
Fig. 5.4	Hitachi high speed cine camera	97
Fig. 5.5	Copper wire (12 μm diameter) used as target	103
Fig. 6.1	Effect of extent of plasma	109
Fig. 6.2	Comparison of laser results with electrical spark minimum ignition energies	112
Fig. 6.3	Cine and schlieren records of expanding kernel	117

CHAPTER 1

INTRODUCTION

The earliest research work in the field of ignition of flammable gas mixtures was carried out by Davy^{10,11} and others^{12,13} in consequence of the need to avoid fire-damp explosions in coal mines. Also, early work by Morgan^{14,15} was concerned with the production of a reliable electric spark ignition source for use in internal combustion engines.

1.1 Definitions of Ignition Parameters

Most studies of the ignition of premixed combustible gases involve the determination of the minimum ignition energy. This is defined as the minimum amount of energy required to ignite a system of given composition and usually varies with the composition of the flammable gaseous mixture. Ignition of the mixture may be possible only between certain composition limits known as the limits of flammability. Due to statistical fluctuations in the experimental methods used to measure minimum ignition energies, the latter are usually associated with certain ignition probabilities. In studies concerned with ensuring reliable ignition, high ignition probabilities are taken to be significant. Other work - notably that of Lewis and von Elbe - has attached useful meaning to ignition probabilities as low as 0.01. The choice of such a low value in situations where ignition is to be avoided e.g. in coal mines, is readily appreciated.

Determinations of ignition parameters have been confined mainly to premixed gaseous systems. However, ignition of gases by hot gas jets has

been studied^{16,17} and the hot gas technique has been applied successfully to the ignition of diffusion flames. Also, ignition parameters of heterogeneous systems i.e. suspensions of solid or liquid particles in gases, have been studied.¹⁸⁻²¹ Recently, Ballal and Lefebvre²² have proposed a model for the ignition of quiescent multidroplet fuel mists. Expressions have been derived for ignition parameters and experimental results have shown these to be strongly dependent on droplet size and other factors such as fuel volatility.

Along with both the minimum ignition energy and the limits of flammability, an ignition parameter important for safety with explosive atmospheres is the quenching distance. This is most conveniently defined for a flammable gas mixture by means of two parallel flat solid surfaces of large dimensions, as the smallest distance between the surfaces that permits flame propagation to take place in the space between them. Studies of ignition by electric spark discharge² have shown that the minimum ignition energy varies with the spark gap width and increases as the gap width falls below the quenching distance of the mixture under study. This increase is particularly rapid when flanged electrodes are used. Blanc et al.²³ determined the quenching distances of various methane - oxygen - inert gas mixtures using electrodes fitted with flanges 25 mm in diameter. The fact that a flame cannot propagate through a wire gauze of mesh size smaller than the quenching distance was utilized by Davy¹¹ in the construction of the miner's safety lamp.

1.2 Ignition Theory

Ignition of a flammable gaseous mixture requires the transfer of energy

into the system by an ignition energy carrier, e.g. solid bodies, gases, plasmas, shock waves or electromagnetic radiation. Ignition may be classified according to the dimensions of the region in which the energy carrier and reaction mixture interact, e.g. line ignition, surface ignition, etc.

Studies of minimum ignition energies involve the use of "instantaneous point" initiating sources. The view of point ignition is based on the concept that for one initial composition and physical state of a flammable gas mixture, there is an absolute minimum amount of energy which will produce ignition provided that the energy source is small in comparison with a volume termed the "quenching volume". This minimum ignition energy is thought to be required to enable the small spherical flame kernel generated by the point-like source to attain a critical quenching diameter, beyond which the flame is able to propagate unaided. The minimum ignition energy is deemed to be independent of the rate of energy supply so long as all the energy is delivered in a time short in comparison with the reaction time or the time taken for the flame to travel its own thickness.

In typical spark ignition experiments, the discharge results in the formation of a small volume of hot, ionized gas which attains peak temperatures²⁴ in excess of 10^4 °K. Thermal theories on spark ignition^{2,25-27} consider only the temperature distribution within the gas. However, other theories^{28,29} such as activation and chain-thermal, consider ignition to be due to activated particles supplied by the source and attach little importance to the initially high gas temperature and its effect on the ignition process.

Most thermal theories on spark ignition have attempted to relate the minimum ignition energy, E_i , to one or more arbitrarily chosen parameters, such as a minimum "ignition" temperature or minimum volume of gas.^{25,26} Correlation with experimental results for such theories is generally not feasible. It is therefore instructive to consider in more detail the most successful thermal theory developed so far, due to Lewis and von Elbe.²

This treatment proposes two expressions which relate the minimum ignition energy to measurable or calculable flame parameters. The relationships concerned are based on separate concepts of ignition criteria and provide realistic estimates of minimum spark ignition energies.

It is first noted that an "instantaneous point" initiating source almost instantly establishes a small volume of very hot gas which cools rapidly as it loses heat to the cold, unburnt reactants. As the temperature increases in the adjacent gas layer, chemical reaction is induced which liberates heat and in this way a reaction wave is formed which propagates away from the source with approximately spherical symmetry. The temperature of the internal hot gases continues to fall but the rate of cooling decreases as the surface area to volume ratio of the incipient flame kernel, and the temperature gradient between the hot and cold gases both diminish. The decisive stage of this potential ignition is reached when the internal temperature has fallen to the order of the normal flame temperature. In order to continue to propagate, the reaction wave must by this time have travelled at least such a distance that the temperature gradient existing is approximately the same as that across a steady-state flame. If this distance has not been reached, the

gradient is too steep and the rate of heat loss to the unburned gas exceeds the rate of heat liberation within the reacting volume. Hence, the temperature decreases further and as the heat loss continuously exceeds the heat gain by chemical reaction, the reaction eventually ceases, having burnt only a small amount of gas around the original source.

The criterion for ignition is that by the time the internal temperature of the flame kernel has fallen to the normal flame temperature, the kernel must have grown to such size that the rate of heat release within the kernel just exceeds the rate of heat loss. Thus, the quenching distance is defined as this critical size to which the kernel must grow in order to propagate unaided and avert subsequent quenching by the ambient unburnt gas. The minimum amount of energy required from the point source for this critical size to be attained is defined as the "minimum ignition energy."

The first relationship proposed by Lewis and von Elbe to correlate experimental values of minimum ignition energies with certain energy values calculated from minimal flame parameters, is obtained simply by calculating the sensible heat, H_1 , in a sphere of diameter equal to the quenching distance d_0 . It is assumed that the contents of the sphere are burnt combustion products of density ρ_b at the final flame temperature T_b . Hence, the amount by which the heat content of the sphere at T_b is in excess of the content at the initial temperature, T_u , is given by

$$H_1 = \frac{\pi}{6} d_0^3 c_p \rho_b (T_b - T_u)$$

where c_p is the specific heat at constant pressure. It can be shown that H_1 is rather larger than the sensible heat residing within the minimal flame of diameter d_0 , but is well within the same order of magnitude as that value.

In recent studies concerning ignition and flame quenching in flowing gaseous mixtures, Ballal and Lefebvre³⁰ have used an expression such as that for H_1 , to define minimum ignition energy for mixtures of various composition over a wide range of flow conditions. The experimental results have indicated that under the test conditions used, the minimum ignition energy and quenching distance are indeed interrelated by a cubic expression.

The second relationship proposed is based on the concept of excess enthalpy which relates the minimum ignition energy to the burning velocity, S_u . This concept considers that in a steady-state laminar flame, cold reactants in the preheat zone acquire thermal energy by conduction from the reaction zone whilst retaining their chemical energy due to the absence of any chemical reaction. At the start of the reaction zone of the flame, the preheated reactants ignite and begin to lose enthalpy by conduction of heat, mainly into the preheat zone. Since the specific enthalpy of the cold reactants at temperature T_u is equal to that of the final flame products at temperature T_b for an adiabatic flame, it follows that an excess conductive enthalpy or energy "hump" exists in the preheat zone of the flame and travels with the front. According to the hypothesis of Lewis and von Elbe, all flames possess excess enthalpy and propagate because the latter continuously flows into the preheat zone, thereby providing the energy necessary to ignite the reactants.

It can be shown² that the total conducted heat, h , stored per unit area in a steadily propagating plane wave is given approximately by the equation

$$h = \frac{k}{S_u} (T_b - T_u)$$

where the thermal conductivity, k , is considered constant. In the case of a small spherical minimal flame, it is assumed that the thickness of the preheat zone is much smaller than the critical quenching diameter of the kernel. A measure of the width of the preheat zone is calculable from measurable data and is indeed found to be small compared with the quenching diameter d_o . The minimal-flame wave may therefore be regarded as plane, in which case the total conducted heat, H_{11} , stored in the wave is equal to the product of its area and the conducted heat, h , per unit area. Hence, H_{11} is given by the equation

$$H_{11} = \pi d_o^2 \frac{k}{S_u} (T_b - T_u)$$

This relationship is not greatly affected if the reaction zone extends significantly into the flame core as most of the conducted heat is contained in the outer layers of the flame volume.

The ignition criterion is that the point source must supply sufficient thermal energy to meet the excess enthalpy content of a minimal flame. This enables an estimate of the minimum ignition energies to be made provided data on critical quenching diameters are available. It is found that for a fairly wide range of mixture compositions, order of magnitude agreement exists between experimentally determined values of minimum

ignition energies and those predicted by the Lewis and von Elbe approach.

There are, however, arguments³¹ against the hypothesis that excess enthalpy plays an important role in flame propagation and the whole concept has been re-examined by the proposers.³² Other workers³³⁻³⁵ have found that finite propagation velocities exist for combustible mixtures in which a deficit of enthalpy may occur. Diffusion of combustion products (especially water vapour) into the preheat zone lowers the chemical potential and thus the enthalpy of the mixture. Whether or not an excess of enthalpy exists in the preheat zone depends on the relative importance of conductive heat transfer and diffusion of products and more generally it is found that

$$E_i = \text{constant} \times \pi d_o^2 \frac{k}{S_u} (T_b - T_u)$$

One of the most significant shortcomings of a purely thermal theoretical treatment of point ignition is the neglect of preferential diffusion. In addition it is not certain that the temperatures of incipient flame kernels in thermal models are in practice either spatially uniform or equal to the appropriate adiabatic flame temperature. Similarly, uncertainty exists in the validity of using laminar flame parameters such as burning velocity in calculating minimum ignition energies. The neglect of preferential diffusion is observed experimentally to be a significant factor in the propagation of incipient flame kernels as a displacement away from stoichiometry of the mixtures having the lowest minimum ignition energies. In general, the displacement from stoichiometry of the most easily ignitable mixture is proportional to the the difference in diffusivity between the fuel and oxygen, and is in the

direction in which the more readily diffusing component is deficient.

Considering the relationships proposed by Lewis and von Elbe, it is noted that in the reaction zone of the minimal flame model, the amount of conducted heat stored per unit volume gradually falls to zero as depth of entry increases. The difference between this conducted heat and the total heat in the reaction zone represents the heat gained by chemical reaction. The total amount of conducted heat stored in a minimal flame is approximately equal to H_{11} whilst the total amount of heat stored is approximately H_1 .

According to this model H_1 should always be greater than H_{11} but calculated values showed that this was not the case for all mixtures of components of different diffusivity. It was found that the value of H_{11} gradually increased and became larger than that of H_1 as the more diffusive mixture component was made stoichiometrically progressively more deficient. This was due to the fact that the values of the burning velocity, S_u , used for calculating H_{11} , had tended to be too small. These burning velocities had been determined for plane waves, whereas minimal flame kernels have surfaces of high curvature. In plane waves that do not spontaneously exhibit cellular structure - this applies to mixtures not close to the limits of flammability - the preferential diffusion of one of the mixture components does not significantly alter the relative concentrations of the components within the combustion wave. This is demonstrated by the fact that mixtures having the highest burning velocity are not greatly displaced in composition from stoichiometry. However, in curved waves, e.g., sharply curved minimal flame kernels, the effect of preferential diffusion is much more

significant and the convergence of the diffusion flow can considerably increase the concentration of the more diffusive mixture component. Hence, as previously mentioned, the most readily ignitable mixtures are displaced away from stoichiometry in the direction of deficiency of the more diffusive component. This means that the sharply curved minimal flame kernels are richer in the deficient component than plane combustion waves, making the burning velocities of the latter too low for calculating values of H_{11} . Consequently, the calculated values of H_{11} were too high. This effect increased with increasing separation from stoichiometry as the change in burning velocity with mixture composition becomes relatively larger. However, once this effect was taken into account, no inconsistency was found between the calculated values of H_1 and H_{11} and the requirement of the model that the former should always exceed the latter.

Experimentally determined values of minimum ignition energies are generally found to be lower than the calculated values of H_1 and H_{11} for the total heat and total conducted heat, respectively, contained in a minimal flame. This indicates that the heat contained in such a flame comprises contributions from both the ignition source and the chemical energy of the mixture. The relationship between the source and chemical heat contributions is the subject of the excess enthalpy hypothesis described earlier. The excess enthalpy contained in the preheat zone of a combustion wave is regarded as being necessary to maintain a temperature gradient between the hot and cold gases such that a balance is maintained between the energy liberated in the reaction zone and the conductive heat flow into the preheat zone.

In the case of an expanding spherical flame, the combustion wave is constantly increasing in surface area. Therefore, in order to maintain the required temperature gradient, a continuous supply of excess enthalpy is required from an external source in relation to the rate of surface area increase. When the wave has become plane and is no longer increasing in area, the excess enthalpy is supplied by the burnt gas itself.

However, a small spherical flame below the minimal flame size, contains insufficient burnt gas to supply the required amount of excess enthalpy. In this case, the temperature in the core falls to such a point that the reaction ceases and the flame is quenched. Thus, the minimum ignition energy is visualized as the amount of energy which must be supplied by the ignition source to just meet the excess enthalpy requirement of a minimal flame. This excess enthalpy is equal to the difference between the conducted heat in the minimal flame and the chemical energy carried forward into the flame by diffusion of unburnt reactants towards the flame core. Thus, the hypothesis predicts that the approximate values of H_{11} for the conducted heat should be greater than the minimum ignition energies, as is found to be the case experimentally. However, further attempts to use this hypothesis to correlate experimental results with theoretical predictions would be unrewarding in view of remaining uncertainties in minimum ignition energy measurements and theoretical values of combustion wave enthalpy. Nevertheless, it is true that the temperature profile of a minimal flame is not exclusively derived from the chemical energy in the gas, as would be the case in a combustion wave possessing zero excess enthalpy. The temperature profile is partly derived from energy supplied by an outside source. Hence, the enthalpy contained within a minimal flame exceeds that of the surrounding unburnt mixture.

The significance of the fact that it is necessary for an incipient flame kernel to attain a certain critical diameter before it is able to propagate unaided, can be perceived in terms of the flame stretch theory - a concept that has been found useful by others³⁶ in predicting flame stability criteria. The concept originates from considerations of combustion waves in flowing gases and divergent wave propagation. With regard to the present considerations of the ignition process, it is assumed that any velocity gradients in the reactants are small, i.e. no significant change in velocity occurs over distances comparable with the wave width. In a spherical wave the flow of heat from the burnt to the unburnt gas is divergent. Hence the heat lost by conduction is imparted to a larger volume of unburnt gas than in a plane wave. This has the effect of slowing the wave down and may cause it to be quenched altogether. This effect decreases with curvature and becomes negligible when the spherical flame has attained such size that the radius is large compared with the wave width, at which stage the wave may be considered plane.

The important difference between divergent and plane wave propagation is that per unit wave area and distance of propagation, the former activates to chemical reaction a larger volume of unburnt reactants than the latter. In a divergent wave the rate at which heat and active species are transferred from the reaction zone to the preheat zone is less than in a plane wave as gradients of temperature and concentration are lower. However, the amount of heat lost to the preheat zone by an element of mass in the reaction zone, is greater for a divergent wave than for a plane one. A mass element passing through the reaction zone of a plane wave loses an amount of heat to the preheat zone equal to that

which it had previously gained in the latter before entering the reaction zone. In divergent waves however, the heat lost exceeds the heat gained, resulting in a lowering of temperatures throughout the reaction zone. This produces a final temperature lower than the adiabatic flame temperature and reduces the burning velocity. It follows that there exists a critical wave divergence at which a heat balance between production in the reaction zone and loss to the preheat zone is only just established. At greater divergences than this the heat loss reduces the reaction zone temperatures to such levels that the reaction ceases and the flame is quenched by the ambient cold reactants.

A measure of the area increase or "stretch" that a divergent wave surface undergoes in propagating a certain distance was introduced by Karlovitz³⁷ and is known as the stretch factor or Karlovitz number, K . In order to define K meaningfully in terms of wave dimensions, the propagation distance over which the stretch is considered is defined as a length simply related to the width of the preheat zone. It can be shown² that this length is inversely proportional to the burning velocity and is easily calculable from measurable data, (values are required for thermal conductivity, specific heat, and gas density as well as burning velocity). Thus, K is defined as the fractional increase in surface area that a divergent wave undergoes in propagating a distance equal to its preheat zone thickness relative to the unburnt gas.

In the case of a spherical minimal flame it is therefore possible to calculate a critical value of the stretch factor K , provided the critical quenching diameter d_0 of the flame is known. Critical values of K have been calculated² for many different mixture compositions of various fuels

and are found to lie mostly between 0.5 and 1, even for mixtures of greatly differing burning velocities. Thus, it is possible, using the concept of the stretch factor K being a similarity constant, to obtain a substantial degree of correlation between experimentally measured values of the quenching distances, burning velocities, densities and specific heats of combustible mixtures. As the values of K agree only in their order of magnitude, the correlation is not perfect but is reasonable considering the uncertainties in experimental values and the nature of the concept itself.

It can be shown² that there exists a simple linear relationship between the critical value of K and the ratio H_{11}/H_1 . Thus, the concept of using either of these values as an approximate similarity constant for correlating critical diameters of minimal flames, implies that the structures of different combustion waves are so similar that it is necessary to specify only the burning velocity and the preheat zone thickness to completely characterize the wave. Since other wave structure characteristics do exist, this assumption can only be approximately correct.

1.3 Inhibitor Background

The suppression of ignition and extinction of combustion waves are obviously important factors in the field of safety. Flames can be extinguished and ignition can be suppressed by clouds of suspended particles and the extinction of flames by various incombustible dusts has been studied by various workers in order to place flame inhibiting materials in an

order of efficiency. Knowledge of the most effective extinguishing materials is needed in various fields for purposes such as fire fighting and the construction of sheathed explosives or their equivalent. In these explosives, which are designed to be used in flammable atmospheres without igniting the gas, an inhibiting safety material is applied as an annular sheath or incorporated in the explosive. After firing, the material mixes intimately with the explosion products and tends to suppress an ignition. A great deal of practical work has been done^{38,39} to determine the effectiveness of various sheathing materials and the most widely used chemical is sodium chloride (common salt) as it is both effective and cheap.

The fundamental study of inhibiting materials was first carried out by Jorissen who studied the effects of vapours on the explosion of gases⁴⁰ and the quenching effect of powders on methane-air explosions.⁴¹ Jorissen expressed the suppression efficiency of a material in terms of the concentration by weight required to extinguish a methane-air flame propagated in a glass tube. Dijkman⁴² showed that the particle size of the powders used was an important factor and that the extinction effect was roughly proportional to the surface area of the particle cloud. In further work Jorissen found the halides, particularly the alkyl halides, to be very efficient suppressants. Iodine has been shown to be a suppressant for reactions involving hydrogen and oxygen⁴³ and similar effects have been observed with bromine, chlorine, and organic halides.⁴⁴ The high efficiency of the alkyl halides has been attributed to a combination of low melting and boiling points and high latent heats of fusion and vaporization.

It is well established that the various powders of inhibiting materials, chemically different but of equal particle size, form two distinct groups - the more and the less efficient inhibitors. Work involving measurements of temperature and burning velocity has identified the latter as "thermal" inhibitors (e.g. alumina, silica etc.) acting mainly by means of a cooling effect which lowers the burning velocity, and the former as "chemical" inhibitors (e.g. potassium chromate, sodium chloride etc.) on the surface of which chain carriers of the reaction are destroyed by recombination.

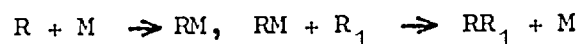
Dolan and Dempster⁴⁵ confirmed that the efficiency of finely divided solids in extinguishing flames is a function of the surface area of solid presented to the flame. This is to be expected for each possible participating mechanism (e.g. heat transfer, rate of vaporization, area of chemically active surface available etc.) provided that the particles are not so small that their vaporization time is small compared with their time of residence in the flame. Dolan and Dempster also first pointed out the fact that the inhibition of methane-air combustion by the alkyl halides cannot be explained in thermal terms alone. They found that the inhibiting efficiency of the solids continued to be dependent on particle size at sizes below that at which thermal equilibrium was reached between particle and flame. The mechanism suggested was that as the temperature to which the particles were raised was above the boiling point of the salt, at least partial vaporization had occurred, resulting not only in an increase in the effective heat capacity of the particles but also in ionic interference of the gaseous species in the combustion reaction. Such interference would tend to suppress the flame by breaking the chain of reactions leading to the expected products of combustion.

1.3.1 The Mechanism of Inhibition

Two mechanisms of inhibition resulting from the presence of small particles in a flame may be postulated:-

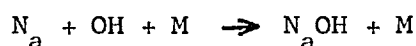
- (a) A heterogeneous mechanism such as radical recombination on a particle surface.
- (b) A homogeneous mechanism involving at least partial vaporization (and/or decomposition) of the small particles on entering the flame, producing some gaseous inhibiting species.

(a) Dewitt⁴⁶ et al. have not observed the release of any gaseous inhibiting species or inert diluting gases by solid particles either by vaporization, sublimation or decomposition. These authors suggest that there is no analogy between homogeneous and heterogeneous inhibition and that the latter is a surface phenomenon. Thermal inhibitors are assumed to act only by a cooling effect on the burning gas mixture which reduces the temperature to a value at which the flame cannot be self-sustaining. It is suggested that chemical inhibitors interact with the original reaction pattern by means of a heterogeneous chain termination reaction. It is supposed that the destruction of the chain carriers on the surface of the particles is due to a recombination mechanism such as



where R and R₁ are chain propagating radicals such as H and OH and M is a solid particle.

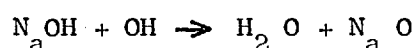
(b) Rosser et al.⁴⁷ have calculated that the residence time in a premixed flame is sufficient for substantial vaporization to occur for alkali metal salt particles less than 5 μm in diameter. This suggests a gaseous rather than a surface inhibiting mechanism. These authors also suggest the mechanism involves a succession of steps: heating of the particles by the hot flame gases; evaporation of the particles; decomposition or reaction of the vapour to produce metal atoms, and inhibition of the combustion process by the metal atoms. In the case of sodium salts, it was concluded that inhibition is associated with the sodium atom and that the effectiveness of the salt depends on its volatility and also on the availability of the atom after evaporation. The sodium atom was thought to remove chain propagating radicals by three-bodied reactions such as



where M is a third body, thereby reducing the supply of radicals in the flame zone. If the radical population in the flame is reduced below that which exists at equilibrium in the burnt gases, diffusion from the zone of hot products into the flame zone provides a new supply of radicals to promote the reaction. As this supply can only be eliminated by a large temperature reduction, it was concluded that the heat loss to the powder particles was also an important factor. The fact that the findings of Rosser et al. contradict those of Dewitte et al. may be due to a difference in the particle sizes used in each study.

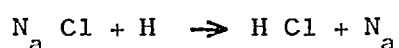
Friedman and Levy⁴⁸ studied the inhibiting effects of alkali metal vapours in order to eliminate the question of any effects of interactions

of gaseous species with surfaces of solid or liquid particles. They concluded that the inhibitory effects of alkali metal salts are not due to the alkali metal atoms but to some other species, and proposed that the effective species is the gaseous alkali metal hydroxide. The use of a vaporized alkali metal produced no observable inhibitory action in the experimental system used. This was attributed to the slow rate of conversion of the metal to its hydroxide. It was thought that the removal of radicals by metal atoms was not significant as such reactions involve a third body and probably do not occur early enough in the flame to affect propagation. Also, the competing two-body reactions of low activation energy, occur several orders of magnitude faster than three-body reactions. In conclusion, the removal of important chain carriers such as O, H and OH was thought to be due to the following types of reaction:-

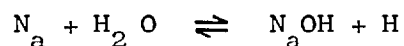


The suggestion that the effective inhibiting species is the metal hydroxide is consistent with the observations of numerous workers that oxygenated salts are more effective flame inhibitors than non-oxygenated salts.

In the case of sodium chloride, Dunderdale and Durie⁴⁹ concluded that inhibition can occur via the reaction



and that the reaction



is then responsible for the formation of N_aOH which can react with anion-forming entities such as CO_2 .

Birchall⁵⁰ has produced strong evidence supporting a homogeneous mechanism of inhibition and demonstrated vaporization of solids in flames by measuring flame conductivities. His results also suggest that for alkali metal salts the inhibiting species is the gaseous alkali hydroxide. The inhibiting mechanism proposed for substances such as alkali oxalates is one of initial decomposition to produce submicron particles which then vaporize and react in flames to produce the gaseous inhibiting species.

1.4 Previous Work

1.4.1 Electrical Spark Ignition

The study of minimum ignition energies of flammable gas mixtures has in the past usually involved the use of electric sparks as small sparks between closely spaced electrodes provide a close approach to point ignition.

The ability of a given spark to ignite a flammable gas mixture depends to some extent on its discharge characteristics. Since sparks have been used so extensively in ignition studies it is worthwhile considering briefly the way in which spark discharges are formed.

When a spark discharge occurs the gas in which it is formed changes very rapidly from an insulator to a good conductor. Experimental investigations⁵¹ have indicated that the main discharge current is always preceded by a small initial current and the mechanism by which these small currents are formed has previously received much attention.⁵² The initial formation of a spark depends on factors such as electrode material, spark gap width etc. However, the mechanism of spark generation appears to be similar for most spark discharges in gases.

A high voltage applied across two electrodes produces an electric field in the gas between them. Any charge carriers in the gas (e.g. ions or electrons) are accelerated towards the oppositely charged electrode by the electric field. A charged particle may undergo many elastic collisions with neutral gas molecules, but between collisions may acquire more kinetic energy from the field, until it has sufficient to undergo an inelastic collision with a neutral gas molecule. This results in ionization of the latter. Thus, each inelastic collision normally produces three charge carriers and for a number of such collisions the concentration of charge carriers increases exponentially. Additional charge multiplication processes can occur when the charge carriers reach the electrodes. Hence, a very small initial current is greatly increased by various mechanisms to form a large spark current whose final magnitude is limited by the characteristics of the electrical circuitry employed. The formation of the final spark takes a variable length of time from about one microsecond to a second depending on various factors, particularly the over-voltage applied to the spark gap. The breakdown voltage of the gap is defined as the voltage which will just induce breakdown in the gas if applied for an infinite time. Higher voltages will cause

breakdown to occur sooner and the ratio of the applied voltage to the breakdown voltage is termed the over-voltage.

Minimum ignition energies can be determined using electrical sparks only if the heat developed by the spark can be accurately calculated from experimentally determinable quantities. The measurement of spark energy falls into two parts: measurement of the amount of electrical energy fed to the spark gap, and determination of the fraction of the input energy that appears as heat in the spark.

The total electrical input energy can be calculated for capacitive or inductive sparks from the electrical circuit parameters. A more accurate measurement is obtained by measuring the spark current and spark gap voltage. Since these quantities vary with time, they must be traced using an oscilloscope. Certain early studies suggested that in a spark discharge most of the energy was retained by the electrodes and that only very little was imparted to the gas. However, experiments by Roth et al.⁵³, involving the use of a constant volume gas calorimeter, have shown that after discharge virtually all of the spark energy resides in the gas. Watson⁵⁴ showed that for powerful capacitive sparks in argon, a significant amount of energy is radiated away in the form of a shock wave. This effect is greatly reduced in spark ignition experiments by the fact that the sparks used are generally very much weaker. Nevertheless, slight shock wave losses do exist but were minimized by Rose and Priede⁵⁵ who increased the spark discharge duration and hence reduced the shock wave losses. It has also been established by others⁵⁶ that energy losses due to shock waves are very small for sparks used in ignition experiments.

Various experimental techniques have been used in the determination of minimum ignition energies by electric sparks but in general capacitive rather than inductive sparks are preferred. Differences in experimental technique, which may influence the results obtained, are usually associated with the way in which the spark discharge is initiated. The methods used have included the application of an over-voltage to the spark gap, the use of a trigger electrode, and the radiation of the spark gap with a radioactive source or ultra-violet light. These techniques obviate the necessity of using a switching device but leakage of charge, due to the high voltages used, still presents an experimental problem. However, Da Yu Cheng⁵⁸ has described a moving capacitor plate device which overcomes this problem. A detailed review of the various electrical techniques used in spark ignition experiments can be found elsewhere.⁵⁹

Apart from the electrical system employed, other factors which can affect experimental results include breakdown voltage, spark duration, energy distribution within the spark, electrode material and geometry, and spark gap width. The extent to which minimum ignition energies are affected by secondary factors such as gas velocity have also been investigated.⁶

The size and shape of the electrodes can critically affect the minimum ignition energy through their influence on heat losses from the incipient spark kernel to the electrodes. For minimum heat losses the spark gap width should be equal to the quenching distance. Below this the minimum ignition energy rises rapidly with increasing electrode diameter and decreasing separation. Pointed electrodes would be expected to give

minimum heat loss but are subject to rapid wear. Breakdown voltage is found to be roughly proportional to spark gap width and it can be shown⁶ that, for a spark of constant duration, energy release rises rapidly with gap width.

De Soete⁶⁰ has indicated that a point source of energy is twice as effective for the purpose of ignition as a line source. Hence, a glow type of discharge would seem preferable to an arc discharge since in the former, most of the energy release occurs close to the cathode in a small volume which may be regarded as a point source. Unfortunately, since this small region is close to the cathode, energy loss to the latter is high and for this reason arc discharges are generally preferred.

Energy losses to electrodes can be reduced by choosing an electrode material of low thermal conductivity. Also, the anode end of a discharge column can sometimes form a hot spot which vaporizes some of the electrode metal. The concentration of the vapour produced depends on the conductivity and vaporization properties of the material used. Thus, the thermal losses can be substantially reduced by using an electrode material of low thermal conductivity and low boiling point.

As previously mentioned, spark energy losses due to shock waves have been reduced by extending the time of discharge. However, it is advantageous, particularly in ignition studies concerned with flowing gases, to release the spark energy in the shortest possible time in order to prevent the heat from being dispersed throughout an excessively large volume of mixture. Swett⁶¹ found an optimum spark duration of 100 μ s for flowing propane-air mixtures while Ballal and Lefebvre⁶ found a

value of 60 μ s more suitable for flowing stoichiometric propane-air mixtures.

Energy losses to electrodes can also be reduced by shortening the spark duration. It has been observed that for discharge durations of 10 μ s or less, separations tend to develop between the sparks and the electrodes, particularly the anode. This reduces energy losses to electrodes resulting in lower experimentally measured values of minimum ignition energies. The separation mechanism is thought to be either an electric wind effect caused by residual voltage, or an effect due to an asymmetric temperature distribution along the spark column (i.e. hot spots near the electrodes). A study of the effects of spark discharge characteristics on minimum ignition energies was carried out by Ballal and Lefebvre⁶ as part of their work involving ignitions in flowing gas mixtures.

1.4.2 Laser Induced Ignition

Although the method of minimum ignition energy measurement using electric sparks has been brought to a high degree of accuracy there remain certain irreducible uncertainties. These include energy losses in the electrical system, and more particularly to the electrodes, both from the initiating plasma and from the subsequently expanding flame kernel. Such losses are inevitably associated with electrode spacings small enough to provide some semblance of point ignition.

In these respects the plasma formed by focussing a Q-switched laser pulse appears to offer considerable advantages as an ignition source. The energy release occurs within a very short time interval (of the order

of 10^{-8} - 10^{-7} s), within a very small volume, and is not associated with the proximity of electrode surfaces. There are no great difficulties associated with the ignition of a flammable gas mixture by means of a focussed laser beam when an excess of energy is used. However, when the energy dissipated in an initially transparent gas is to be minimized there are several problems to be studied, such as the difficulty in presetting the laser beam energy accurately, particularly when a passive Q-switch is used.

A preliminary investigation¹ into the use of focussed laser beams for minimum ignition energy studies was carried out by Weinberg and Wilson and revealed certain fundamental limitations when the radiation is focussed into a flammable gas mixture. It was found that the difficulties of the method are associated with the finite duration of the laser pulse. Initially the gas is transparent and, unless the power flux exceeds the threshold for breakdown (typically 10^{10} - 10^{11} W cm⁻²) it will remain so for the duration of the pulse and no energy will be absorbed. If the power flux is sufficient to generate an appreciable electron concentration at the peak of the pulse, the plasma front facing the incident beam absorbs incoming energy during the time between the onset of breakdown and the end of the pulse. This leads to the production of an extended and asymmetrical initiating source and an absorption threshold which has been shown to be already in excess of the minimum ignition energy for mixtures which are not either far from stoichiometric or at sub-atmospheric pressures. The finite time for which the energy is absorbed gives rise to the asymmetric nature of the initiating plasma kernel, if only because the latter grows by absorbing radiation from an incoming beam which converges to a focus from the finite aperture of a lens.

It was found that for methane-air mixtures well within the limits of flammability and at higher pressures, the minimum ignition energies measured were similar to those found by Lewis and von Elbe² using the conventional electric spark method. As the pressure was reduced however, or as the mixture approached the limits of flammability, the laser results fell well below those obtained for sparks between electrodes suggesting that the influence of the electrodes becomes more significant as the quenching distance increases. (Quenching distance is inversely proportional to pressure.)

This result is possibly due to the differences in the dimensions of the initial spark kernels of the two techniques. The dimensions of the laser spark depend to some extent on the focal length of the lens used and the duration of the pulse. The lens focal length can affect the elongation of the spark and the pulse duration obviously affects the time available for the plasma to expand whilst absorbing the incident radiation. As the laser spark energy can be varied by changing only the beam energy, it is possible to study various mixtures of different minimum ignition energy and quenching distance, using the same lens and pulse duration. In the case of electrical ignition, although the spark energy can be varied easily, it is necessary to change the spark gap width for each mixture used. This is done in order to minimize heat losses to the electrodes and obtain the lowest value of the minimum ignition energy for a given mixture. The optimum spark gap width can have a fairly extensive range of values over which the minimum ignition energy is virtually independent of electrode separation. Beyond this range, which commences at a separation equal to the quenching distance and proceeds to larger separations, the minimum ignition energy increases

with spark gap width. For electrode separations smaller than the quenching distance, decreasing separation also increases the minimum ignition energy. This increase is particularly rapid when large diameter electrodes are used. Thus, for electrical ignition, the spark gap width should be at least equal to the quenching distance of the mixture in use.

As the quenching distance increases, the necessarily elongated electric spark becomes progressively less of an approximation to a point source, in comparison with the laser spark. Therefore, it can be expected that any differences between laser and electrical minimum ignition energies will be most noticeable for mixtures of large quenching distance. For such mixtures, energy losses from an electric spark would be expected to be more significant, producing higher minimum ignition energy values than the laser sparks.

As previously mentioned, an energy absorption threshold prevented the study of gases at higher pressures and faster-reacting mixtures of smaller quenching distance. It was concluded that in order to remove this limitation it would be necessary to shorten the pulse duration and reduce the elongation of the laser spark.

1.5 Objectives and Purpose of Research

The main object of the present work was to investigate, using focussed laser pulses, to what extent the minimum ignition energies of flammable gas mixtures depend on the species carrying the plasma energy. Recent

theoretical considerations by Dixon-Lewis and Shepherd⁶² have suggested that the minimum ignition energy of a 60% hydrogen-air mixture depends on the form in which the energy is supplied. It was found that for a constant total energy, ignition was facilitated by increasing the proportion supplied as H atoms rather than as thermal energy. Also, studies of ignition by plasma jets⁶³ have shown that combustion rates in very lean methane-air mixtures can be considerably increased by the use of plasma ignition sources comprising radicals important in flame propagation, rather than conventional electric sparks.

The range of interest concerning various plasma constitutions includes inhibitors, e.g. sodium chloride which is commonly used in sheathed explosives for use in mines and flammable atmospheres. At the other extreme, it might be thought that some species - even possibly just moisture - would act as promoters by generating free radicals active in chain propagation within the plasma. Moreover, if the ignition energy did depend on plasma constitution it would be important to know the effect of inevitable contaminants such as copper or other electrode materials in electrical ignition. The results should therefore be relevant to a wide range of ignition phenomena.

The fundamental limitations which apply to ignition by laser beams focussed into gases were avoided by using minute targets in the form of wires or coated fibres of the order of 10^{-5} m in diameter placed at the focal spot. The use of minute targets not only offers a simpler alternative to reducing the pulse duration much below 40 ns but also enables the initial volume of the plasma, its chemical constitution and the amount of target material it carries to be varied, see Chapter 4.

In the preliminary investigation¹ plasma energies were deduced by subtracting the departing beam energy from the incident one, both of these being measured separately. However, in the present work the difference would not necessarily yield the plasma energy since reflection, scattering, heat absorption by unvaporised parts of the target, etc., may play a part. Since errors introduced by such effects would be expected to vary with the target material, it was considered essential to measure the plasma energy directly. To this end a microcalorimeter had to be developed which aspirates the plasma and measures its energy content, independent of its composition, see Chapter 3. This proved one of the most difficult parts of the investigation and the calorimeter design passed through several iterations and extensive calibration procedures.

Preliminary experiments were carried out using a 1 ms free-running pulse and an 8.6% (minimum quenching distance) methane-air mixture. The plasma constitution was varied by changing the target material, see Chapter 5.

The next step was to vary the plasma dimensions, mixture strength and pulse duration, see Chapter 6. The difference in the results obtained with free-running and Q-switched laser pulses was investigated using high speed laser schlieren cine photography.

The conclusions are contained in Chapter 7.

CHAPTER 2

DESCRIPTION OF APPARATUS

2.1 Ruby Laser

The laser used in the work to produce ignition was a Laser Associates 30J ruby. The laser head (Fig. 2.1) contains a silvered cavity of elliptical cross-section inside which the ruby rod and flash tube are situated along the two line focii. These components are both encased in quartz tubes and cooled by de-ionised water circulating in a closed system. The temperature of the water was not easy to control and this was found to be a shortcoming of the apparatus when the beam energy reproducibility was studied. Two adjustable quartz windows seal the ruby rod tube, the front window being the front laser cavity reflector. The rear reflector is a roof prism in front of which a dye cell Q-switch may be placed.

2.1.1 Alignment of Laser

Beam energy investigations later revealed the critical nature of alignment within the cavity and for maximum power and best reproducibility the following were observed:-

(a) The angular orientation of the optical axis of the ruby relative to the roof prism, was found to need occasional readjustment. The rod used was of the type cut with its axis at 60^0 to the ruby crystal optical axis to produce a plane-polarised output. This later enabled fine adjustments in the beam intensity to be made using a rotating polaroid device.

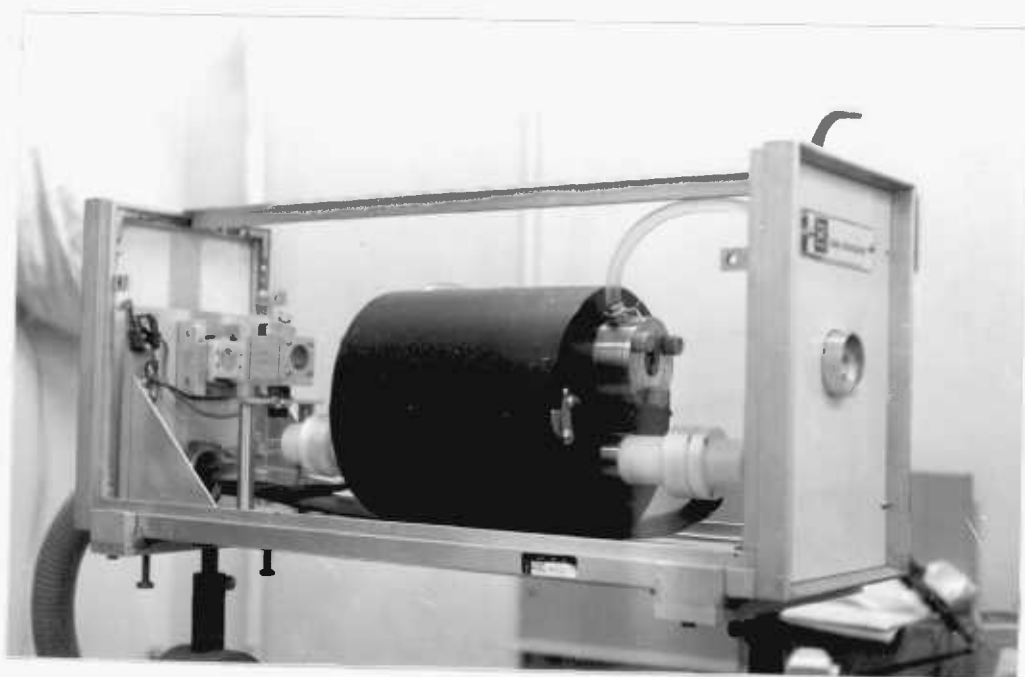


Fig. 2.1 Ruby laser head

(b) The centre of the roof prism was aligned with the rod axis by sighting down the ruby and moving the prism from side to side. During this adjustment a vertical needle was moved into the cavity between prism and ruby, indicating the correct prism position when the needle coincided with its own image at the centre of the rod.

(c) A point source of light was placed five metres from the laser on the axis of the rod. An autocollimator placed just in front of the laser was adjusted in position until an image was seen from every face. The prism was then aligned with the front window only, as it was found necessary to misalign slightly all other faces for maximum power. This adjustment was carried out with the dye cell in position when Q-switched pulses were required.

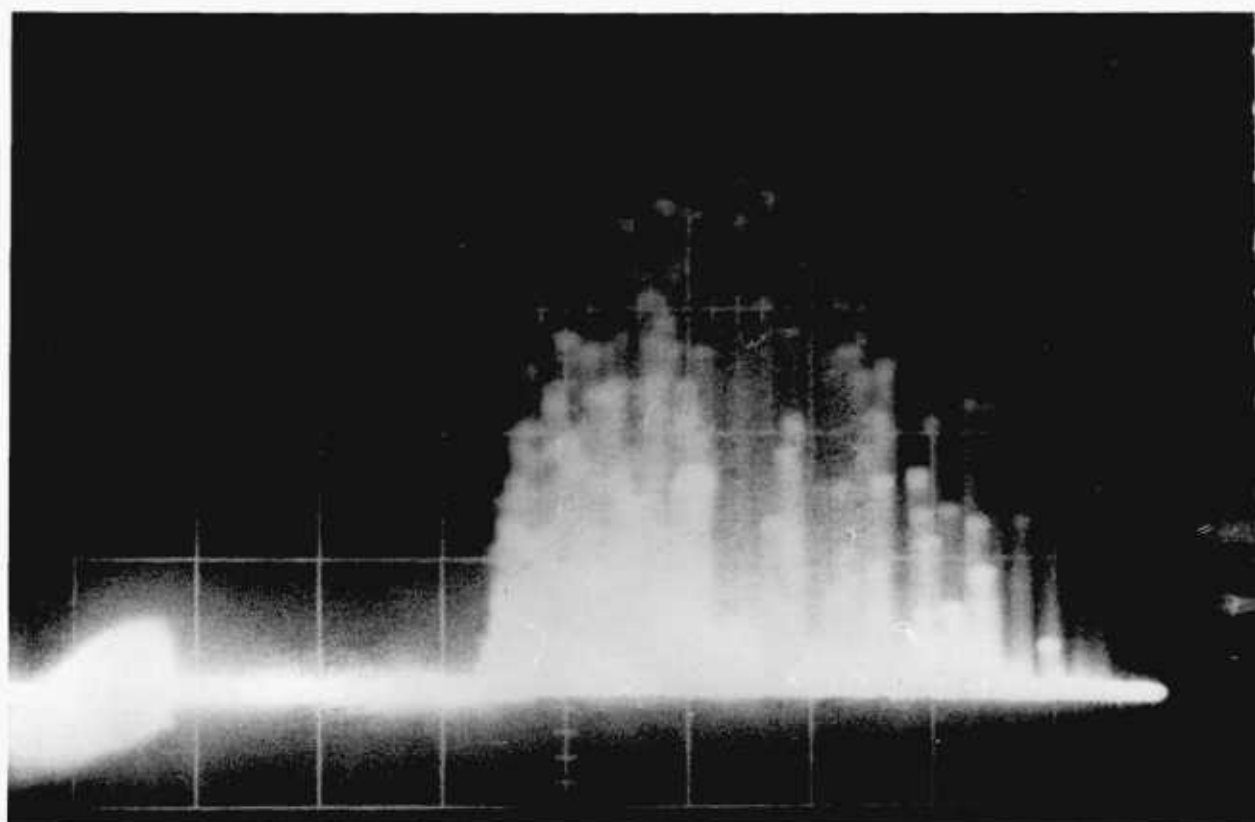
2.1.2 Outputs available

(a) Free-running

The free-running output was displayed on an oscilloscope screen using a suitable photodiode and photographed, see Fig. 2.2. It consisted of a 1 ms envelope beginning 0.5 ms after firing and comprised many short pulses of approximately 10^{-7} s duration separated by approximately 10^{-6} - 10^{-7} s. The beam energy, when measured, was found to have good reproducibility as shown in Fig. 2.3, and a maximum value of 30J. Figure 2.3 shows ten consecutive pulses with the calorimeter cooling curves curtailed.

(b) Q-switched

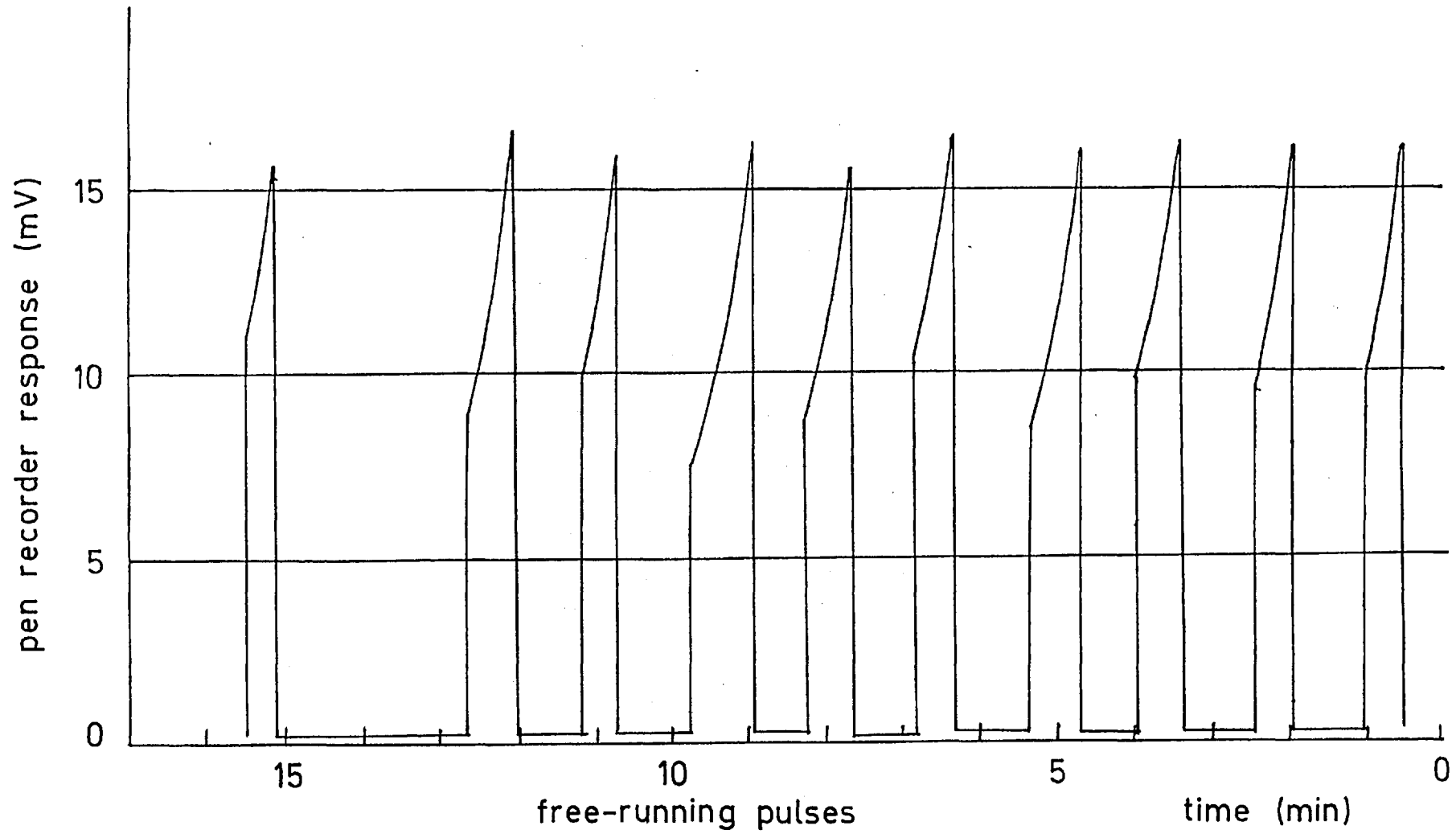
A dye cell Q-switch was used and the voltage was adjusted to produce a single spike which was displayed on the screen. It was not bright enough to photograph but could be seen to appear 1 ms after firing. An adjustable



(1 division = 0.2 ms $\rightarrow$)

Fig. 2.2 1 ms free-running pulse

Fig. 2.3 Pen recorder trace of free-running pulses



delay was introduced between the laser and oscilloscope triggers to permit expansion of the time scale whilst maintaining visibility of the spike, which was of 20 ns half-width and was later found to have a maximum energy of 2J. Two spikes were obtained by increasing the voltage and appeared 0.5 ms apart. The energy reproducibility of the Q-switched output was poor, the deviation being above $\pm 30\%$.

The experimental technique to be employed would involve focussing the laser beam onto small targets in the form of particles or fibres to produce small blobs of plasma. The targets would be surrounded by a standard mixture of methane and air and the beam energy adjusted to give an ignition threshold. The required value of the threshold plasma energy would then be measured by a special microcalorimeter in a separate experiment using an inert atmosphere. This measurement could not be made in the presence of methane due to the possibility of ignition. It was therefore essential to have good beam energy reproducibility to establish an accurate ignition threshold beam energy and subsequently to measure its corresponding plasma energy. The free-running pulses were already quite consistent but it was necessary to reduce considerably the energy deviation of the Q-switched output.

2.2 Construction of Reinforced Beam Energy Calorimeter

The beam energy calorimeter used throughout the work was a modified version of the totally absorbing spherical cavity specially developed in a previous study⁵ for absolute energy measurements. This was used to measure the laser beam energy directly when the reproducibility of the latter was studied and also in conjunction with a suitable beam splitter, to monitor the beam energy of every shot thereafter.

The calorimeter consists of a thin copper spherical shell into which the beam is focussed through a small aperture in the surface. Absorption of the radiation is by multiple reflection and very little escapes as the aperture area is a minute fraction of the surface area of the sphere. High sensitivity was required and to achieve this the thermal capacity and therefore the mass of the calorimeter had to be as small as possible consistent with high thermal conductivity. This means having a very thin shell which may be subject to damage if initial absorption of the radiation is by a small area of the calorimeter wall. The use of short focal length lenses increases the divergence of the beam entering the sphere, hence utilizing a larger area, but with Q-switched pulses the energy density at the focus may then be high enough for spark breakdown to occur, which could absorb a large fraction of the incident radiation. This was previously avoided by using the calorimeter in a cell at reduced pressure but it was found that any slight air leaks greatly affected the response characteristics. The matter was resolved by using a lens of focal length long enough to avoid breakdown and by constructing a calorimeter whose mass was low, for high sensitivity, but was concentrated on the back face where the radiation initially falls and where damage is most likely to occur.

The method of construction involved electroplating a suitable former such as a ping-pong ball which was first made conductive by coating with "conductivity paint". The ball was then totally immersed in acidified copper sulphate solution and made the cathode of an electrolytic cell. A copper anode completely surrounded the ball during the initial plating. The ball was then partially withdrawn from the electrolyte and the remaining mass required was deposited on a smaller area later to become the back face. It was found important that during electrolysis the current should never rise above 0.02A per cm² of surface being coated otherwise

rapid deposition of the copper produces an uneven and very fragile surface.

After plating, a small aperture (2 mm diameter) was drilled, and the sphere was filled with a suitable organic solvent to dissolve the celluloid. A quantity of small glass beads mixed with the solvent ensured removal of the paint by abrasive action.

In this way a 4 cm diameter copper sphere of mass 1 gm was produced with half the total mass contained in the rear 4 cm² of surface area. Copper-constantan thermocouples with 40 μ m diameter leads were attached with a negligible amount of solder. This thickness was chosen to minimize heat losses along the leads as a result of work done on the calibrating filament using thermocouples of varying thickness. Figure 2.4 shows the calorimeter in its polished metal cavity with the front of the housing removed.

Alignment was easily achieved using an auxiliary He-Ne laser which was set up so that the beam emerging from one of its ends passed along the axis of the ruby crystal and struck the roof prism centre. The beam from the opposite end hit a mark previously made by the ruby pulse on a sooted glass plate placed five metres in front of the laser. With the axes of both laser beams coincident, the calorimeter was aligned setting its aperture at the He-Ne beam focus produced by a suitable lens placed either in the direct beam, or that portion of it reflected from the beam splitter when setting up for monitoring.

The thermocouple outputs were amplified using a high gain Ancom 15C-3 differential D.C. chopper amplifier and displayed by a pen recorder. To compensate



Fig. 2.4 Beam energy calorimeter in polished metal cavity

for the temperature difference already existing between the calorimeter and its thermocouple ice junction, a small D.C. back-off supply was constructed and incorporated in the circuit to act as a zeroing device.

The calorimeter proved to be entirely satisfactory for both direct beam energy measurements of free-running and Q-switched pulses, and for monitoring purposes using an 18% reflecting titanium dioxide coated beam splitter in conjunction with a suitable condensing lens (Fig. 2.5), no damage being detected after 2 000 shots.

2.3 Calibration of Copper-constantan Thermocouples

Copper-constantan thermocouples were used for the beam and plasma energy calorimeters and for an investigation of the temperature along the length of the plasma calorimeter calibrating filament. As the lowest temperature differences to be detected would be a fraction of a degree - typically 0.1°C for the beam energy calorimeter monitoring a Q-switched pulse - it was considered essential to calibrate the thermocouples accurately around room temperature, at which they would be used. This was achieved using ice and water baths for the two junctions and by balancing the thermocouple voltage on a sensitive bridge accurate to less than $1\text{ }\mu\text{V}$. Readings were taken at 0.1°C intervals and the graph plotted (Fig. 2.6) was found to be linear between 20°C and 27°C giving a thermocouple response of $41.1\text{ }\mu\text{V} (\pm 1\%) \text{ per } ^{\circ}\text{C}$. The linearity enabled the temperature rises of both calorimeters to be calculated without knowledge of their initial temperatures.



Fig. 2.5 Beam splitter, condensing lens and beam energy calorimeter

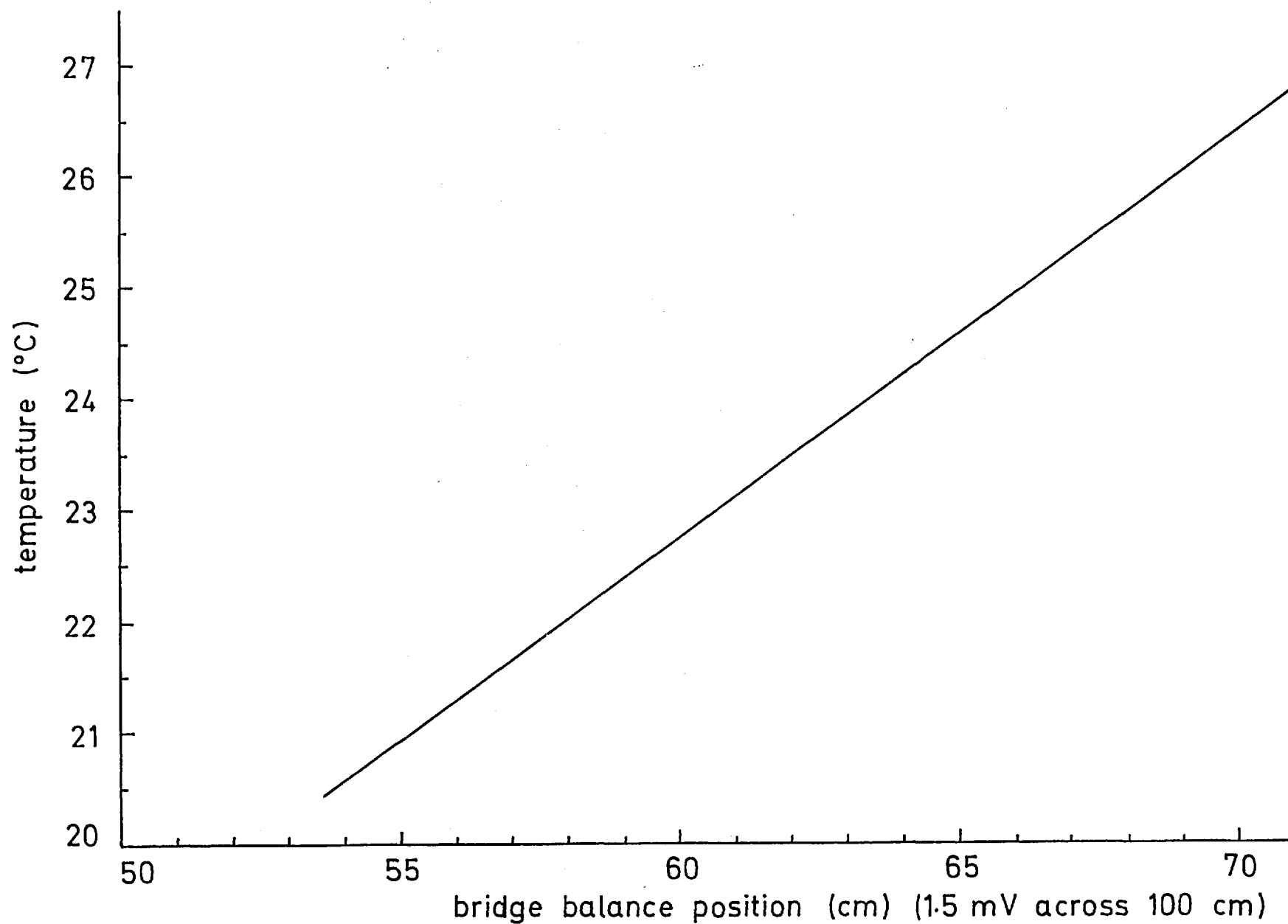


Fig. 2.6 Copper-constantan thermocouple calibration

2.4 Beam Energy Reproducibility and Number of Pulses in Q-switched Output.

For a study of beam energy reproducibility both with and without a Q-switch, the spherical calorimeter was set up for direct beam energy measurements.

The energies of free-running laser pulses - up to 30J for the system used - could be controlled only by varying the flash tube voltage. However, the reproducibility was found to be satisfactory, the variation being only 5%. For both modes of operation it was necessary to keep a careful check on the temperature of the circulating de-ionised water cooling the crystal and flash tube. This temperature, not being thermostatically controlled, was regulated using a heat exchanger with the mains water supply and slight changes significantly altered the beam energy.

The use of a passive dye cell Q-switch not only increased the beam divergence to 5 mrad but introduced a large beam energy variation due to the Q-switch dye bleaching at a slightly different instant for each pumping flash. For ignition work involving Q-switched pulses, it was necessary to improve the beam energy reproducibility considerably, as this would obviously directly affect the accuracy of the minimum ignition energies to be measured. This was done in conjunction with a study of the number of Q-switched spikes per pulse produced by various dye concentrations and flash tube voltages.

Various dyes tested included cryptocyanine in iso-propyl alcohol and diethyl dicarbo-cyanine in methanol, but the best reproducibility was obtained using a 10^{-4} molar solution of vanadyl phthalocyanine in nitrobenzene with an exhaustion indicator. Six drops of this solution

in a standard size cell containing the nitrobenzene solvent produced 1 - 3 spikes using a flash tube voltage of 1.8 kV. The number of spikes could be decreased by increasing the dye concentration or using a lower voltage. Hence, single spike operation could be achieved for any given voltage. The number of spikes per pulse was monitored for each shot using a Hewlett-Packard 4220 photodiode which was positioned to pick up a small amount of radiation reflected from the lens surface onto a white card. The output was recorded by either an oscilloscope or counting circuitry with digital display.

The laser was set for normal single spike operation and absolute beam energies measured were of the order of 1J but had a standard deviation of nearly 35%. The use of a Pockel's cell Q-switch was considered and would have been expected to reduce the deviation to 10%. However, the reproducibility was improved by a factor of 10 using the following procedure. Firstly, the front quartz window and rear reflector of the laser were aligned using an autocollimator, the ruby rod faces and all other surfaces within the cavity being misaligned by a small amount as this was found to increase power output. The laser was operated well above the lasing threshold, 2 kV being applied to the flash tube. To maintain a single spike output the dye was used at twice the normal concentration. For each fresh batch the initial shot was always erratic so the first six were discarded after which the dye was found to be more consistent. The cooling water was maintained at a steady temperature of 19°C as any changes directly affected beam energies. Intervals of two minutes were allowed between firings to enable the flash tube and ruby crystal to return to this temperature. In this way the beam energy deviation was reduced to an acceptable 4%.

Multi-spike Q-switched outputs were obtained simply by using higher voltages or less concentrated dye solutions and consistent outputs of between one and five spikes per pulse were obtained. It was not possible to vary independently the energy of any individual spike but the photodiode output displayed on an oscilloscope showed that for a double spike output the spikes, of 40 ns duration, were approximately equal in magnitude and spaced 0.5 ms apart.

2.5 Mixing System and Ignition Cell

An initial proposal was to perform the ignition experiments with the targets suspended above a suitable burner in a flowing stream of pre-mixed methane and air. A possible alternative considered was an ignition cell which would contain the target and could be filled with a mixture, the composition of which would be predetermined by partial pressures rather than flow metering.

The flow method, although more convenient to use, was rejected in favour of the ignition cell as determination of the mixture composition entailed calibration of the flow meters which was found to introduce an error of approximately $\pm 1\%$ in the composition, i.e. a 6% mixture would be $(6 \pm 0.06)\%$. Inspection of a typical curve from spark ignition studies showed this error to be unacceptably high for lean mixtures where minimum ignition energy changes rapidly with methane concentration. In comparison, the composition error using partial pressures was only $\pm 0.1\%$.

Other disadvantages of the flow system were:-

- (a) The uncertainty of mixture composition at the target due to possible entrainment of air.
- (b) Once ignition had occurred, it was found difficult to extinguish the flame quickly enough to avoid wasting further useable target surface

by completely destroying the thin fibres.

(c) The possible effect of the flow velocity on the minimum ignition energy.

Although this was considered an unlikely source of error, flow velocities have been shown to have some effect in spark ignition studies⁶.

The mixing system used is shown in Fig. 2.7 and included a large glass sphere in which the methane and air were mixed and stored, a quantity of mixture being transferred to the cell for each ignition by a plunger. It was not possible to fill the ignition cell directly using partial pressures as its volume, being small, was comparable with the total pipeline volume used. This made thorough mixing of the gases an impossible task. For this reason, a large quantity of standard mixture was prepared and mixed separately to be drawn upon many times. The manometer used contained dibutyl phthalate and the pressure heads were read to an accuracy of ± 0.5 mm.

The ignition cell is shown in Fig. 2.8 containing a target fibre held in a caliper suspended from its roof. To avoid any possible errors introduced by the presence of the caliper, the separation of its jaws was made much greater than the quenching distance of any mixture to be used. Ignitions were detected by an internal thermocouple sealed in a wall and the top pressure release valve prevented destruction of the windows when near-stoichiometric mixtures were used.

To prepare a mixture the methane line was first flushed with gas, the excess being led to a burner. The sphere was then flushed with air to remove any residual methane and the internal pressure was reduced, measured on manometer B and adjusted to a previously calculated value dependent on the mixture required and the measured atmospheric pressure. Methane was then gradually introduced into the sphere through tap A_1

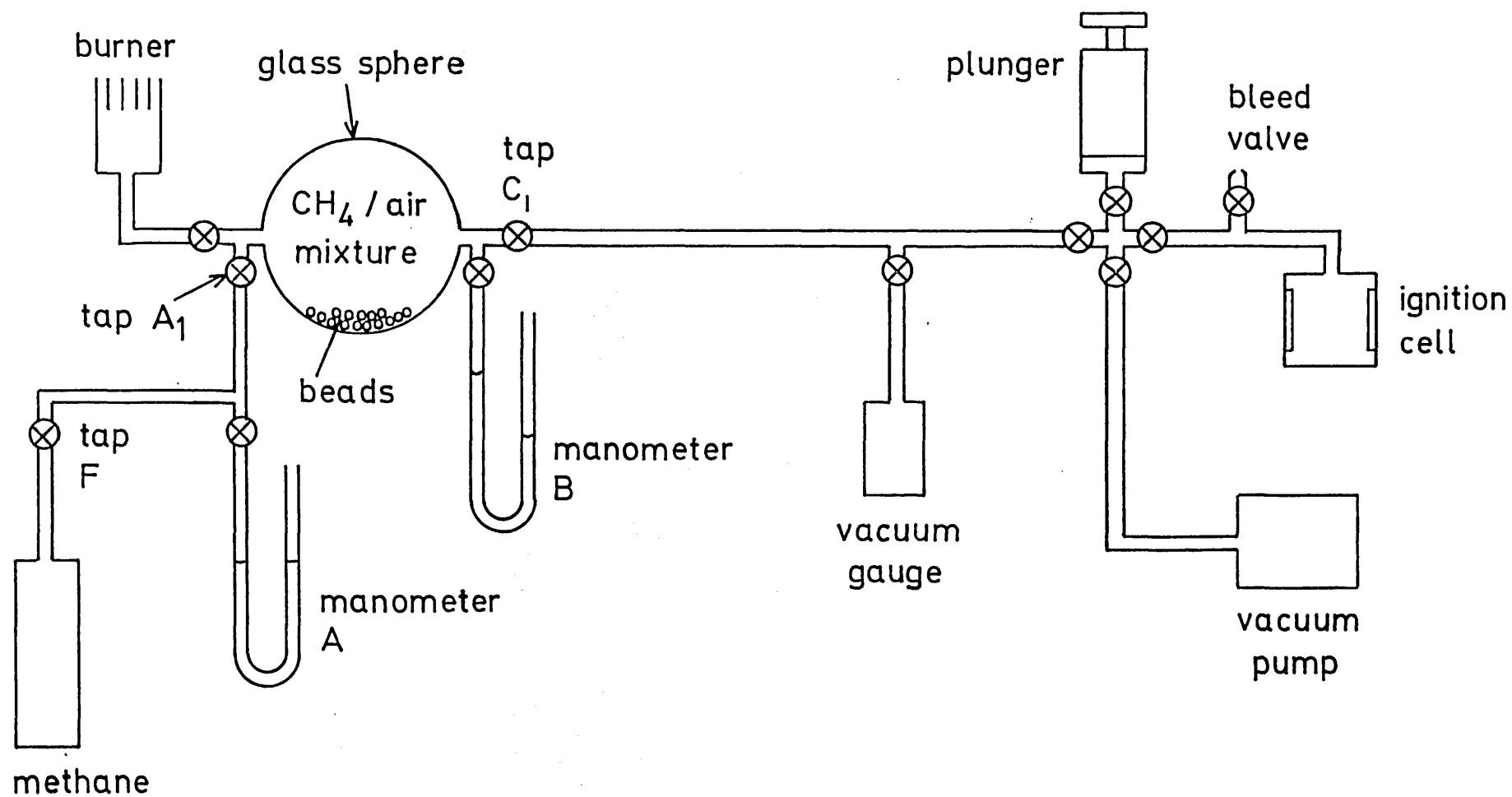


Fig. 2.7 Mixing system

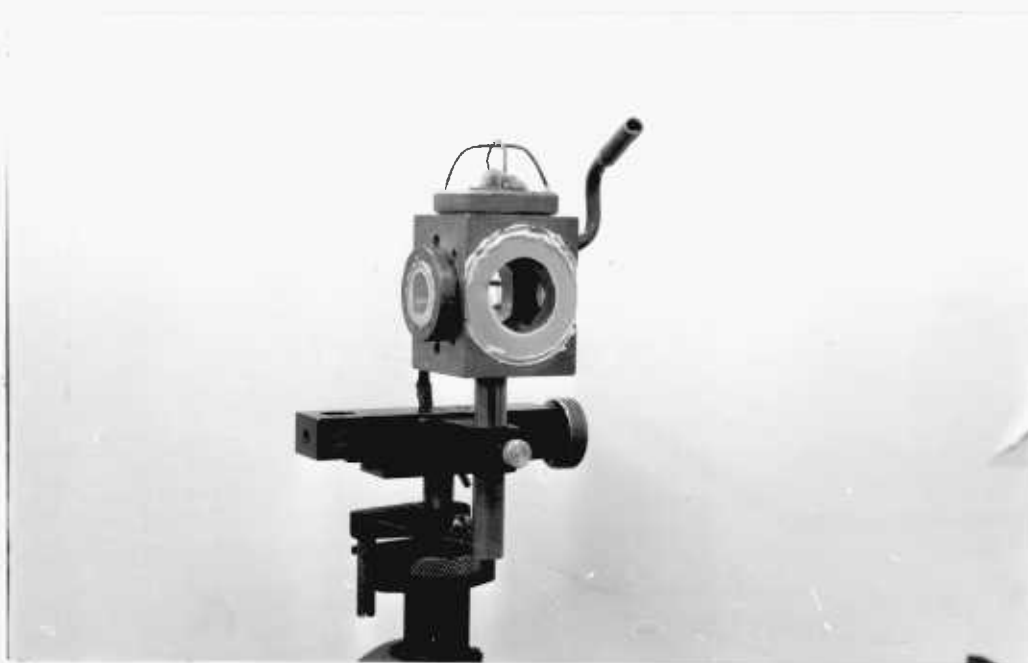


Fig. 2.8 Ignition cell (containing target)

until the pressure inside was atmospheric as shown by manometer A, tap F being used to isolate the methane supply. The sphere was then shaken enabling glass beads inside to mix the gases thoroughly.

After evacuating the ignition cell to a pressure of 0.1 Torr, the mixture was introduced through tap C₁. This left the pressure of the whole system below atmospheric but the cell pressure was increased using the plunger system and taps as a force pump to transfer more mixture. After allowing the temperature of the mixture to settle, any slight excess pressure was released from the cell through a bleed valve. In this way, the standard mixture stored in the sphere could be used for many ignitions.

2.5.1 Accuracy of Mixture Composition

Some of the initial ignition experiments were performed using single spike Q-switched outputs and methane-air mixtures which varied from 6% to 8.6%. The minimum ignition energies measured were found to be reproducible, with a deviation of about $\pm 10 - 15\%$ depending on the mixture. The error is due to a combination of fluctuations in the beam energy and the error in the plasma energy measurement.

As it was intended to test several different target materials, it was obvious that many batches of a given standard mixture would have to be prepared. It was therefore considered essential to keep any errors in the mixture composition to a minimum and to establish that any effects they might have on the minimum ignition energy being measured would form a negligible part of the overall experimental error. Day to day changes in the pressure, temperature and humidity of the air were also considered as results were required at room temperature and atmospheric pressure.

Factors to be considered affecting the mixture composition accuracy were:-

- (a) The purity of the methane used;
- (b) partial pressure errors due to the manometer reading error and the density error of the fluid used;
- (c) dilution of the mixture caused by residual air in the ignition cell.

(a) Methane purities used ranged from the commercial grade of 99.2% to an analytical grade of purity greater than 99.9%. For near-stoichiometric mixtures (8.6%) the commercial grade was found to be satisfactory. The composition error was calculated and by examining a typical curve relating methane concentration to minimum ignition energy any possible error in the latter was estimated to be approximately 1%. For leaner mixtures (6%) the corresponding value was 5% as here composition becomes more critical. Although still within the experimental error, analytical methane was used to make the effect negligible.

(b) The manometric fluid used was dibutyl phthalate and its density was measured to an accuracy of $\pm 0.05\%$. This was combined with the reading error of less than 0.5 mm to give a total error of $\pm 0.1\%$ in the composition. It was estimated that even for the leanest mixtures this would give rise to a maximum error of $\pm 1\%$ in the minimum ignition energy. In contrast, the composition error using flow meters was $\pm 1\%$ and for this reason the ignition cell was chosen, as mentioned above.

(c) Before introducing the mixture, the ignition cell was evacuated to a pressure of 0.1 Torr. The composition changes due to dilution of incoming mixture by residual air were calculated and led to an expected change in the minimum ignition energy of only 0.1% for a 6% mixture.

In addition to mixture composition, other relevant factors affecting the minimum ignition energy measured are the temperature, pressure and humidity of the air.

Theories of spark ignition and results of experimental work using temperature T and pressure P as variables have indicated that the minimum ignition energy E_i of a quiescent mixture can, within the limits of experimental error, be expressed as

$$E_i = A P^\alpha T^\beta$$

where A is a constant depending on the nature of the fuel. It has been found⁷⁻⁹ that, to a good approximation, $\alpha = -2.0$ and $\beta = -2.0$. This indicates that daily changes in atmospheric pressure and laboratory temperature, even if their effects were additive, would have little effect on the results, changing the minimum ignition energy by less than 3%.

It was necessary to consider humidity, as moisture, acting as a vitiant, can reduce the oxygen concentration of the combustion air. The laboratory humidity was measured daily and the resulting oxygen reduction in the air calculated. It has been shown⁴ that reducing the oxygen content of a methane-air mixture does raise its minimum ignition energy and, using results from work in this field, possible effects of laboratory humidity were calculated. It was found that the maximum effect, like that due to temperature and pressure variations, was much smaller than the experimental error, indicating that the drying of air was not necessary. This is in contrast with most electrical spark methods where moisture can produce significant effects by causing partial leakage of the capacitive charge.

It was expected that any effects of using inhibiting material in the experiments would be very large - inhibitors are known to have such effects in other fields of combustion - rendering the overall experimental error previously found of $\pm 10 - 15\%$, quite acceptable.

CHAPTER 3

DEVELOPMENT OF MICROCALORIMETER FOR PLASMA ENERGY MEASUREMENTS

3.1 Introduction

The preliminary investigation¹ into the use of focussed laser beams for minimum ignition energy studies involved the ignition of flammable gas mixtures due to breakdown produced in the gas at the beam focus. Plasma energies at the ignition threshold were deduced by subtracting the outgoing beam energy from the incoming one, both of these being measured separately by spherical beam energy calorimeters.

In the present work, igniting plasmas were produced by the vaporization of small solid targets onto which the beam was focussed. The required threshold plasma energies could not be deduced as before since amounts of reflection and scattering of the incident beam, heat absorption by unvaporized parts of the target etc. were unknown and may have been significant. Since errors introduced by such effects would be expected to vary with target material, even comparison of different test materials would be unreliable. It was therefore considered essential to measure the plasma energy directly.

Interferometric techniques were considered for this purpose but for directness of measurement it was decided to construct a special microcalorimeter which aspirates the plasma and measures its energy content, independent of its composition.

Due to the smallness of the calorimeter mass (a few mgm) and the temperature rises it would undergo (less than 1°C), heat losses had to be minimized to ensure high sensitivity. One possible cause of loss was conduction along the attached thermocouple wires. It was therefore necessary to investigate the possible effects of thermocouple thickness - which would directly affect the amount of heat lost by conduction - on the recorded temperature of such a small object taken through a slight temperature rise, in order to ascertain the thickness required to produce negligible loss from the calorimeter due to this cause. In addition, the thermocouples would need to be quick-responding in order to follow the transient temperature rise of the calorimeter closely.

This study was carried out in conjunction with the development of a suitable calibrating source for energies around 1 mJ. The calibration standard finally produced was a small, electrically heated filament of negligible thermal capacity, which also acted as the heated object in the thermocouple thickness investigation. The results of this also enabled any slight conductive losses from the standard itself to be accounted for by measuring the temperature gradient at the filament edges with sufficiently thin thermocouples.

The calorimeter and calibration source developments proceeded simultaneously as both involved several iterations. For clarity, these developments, along with the thermocouple study, are considered separately.

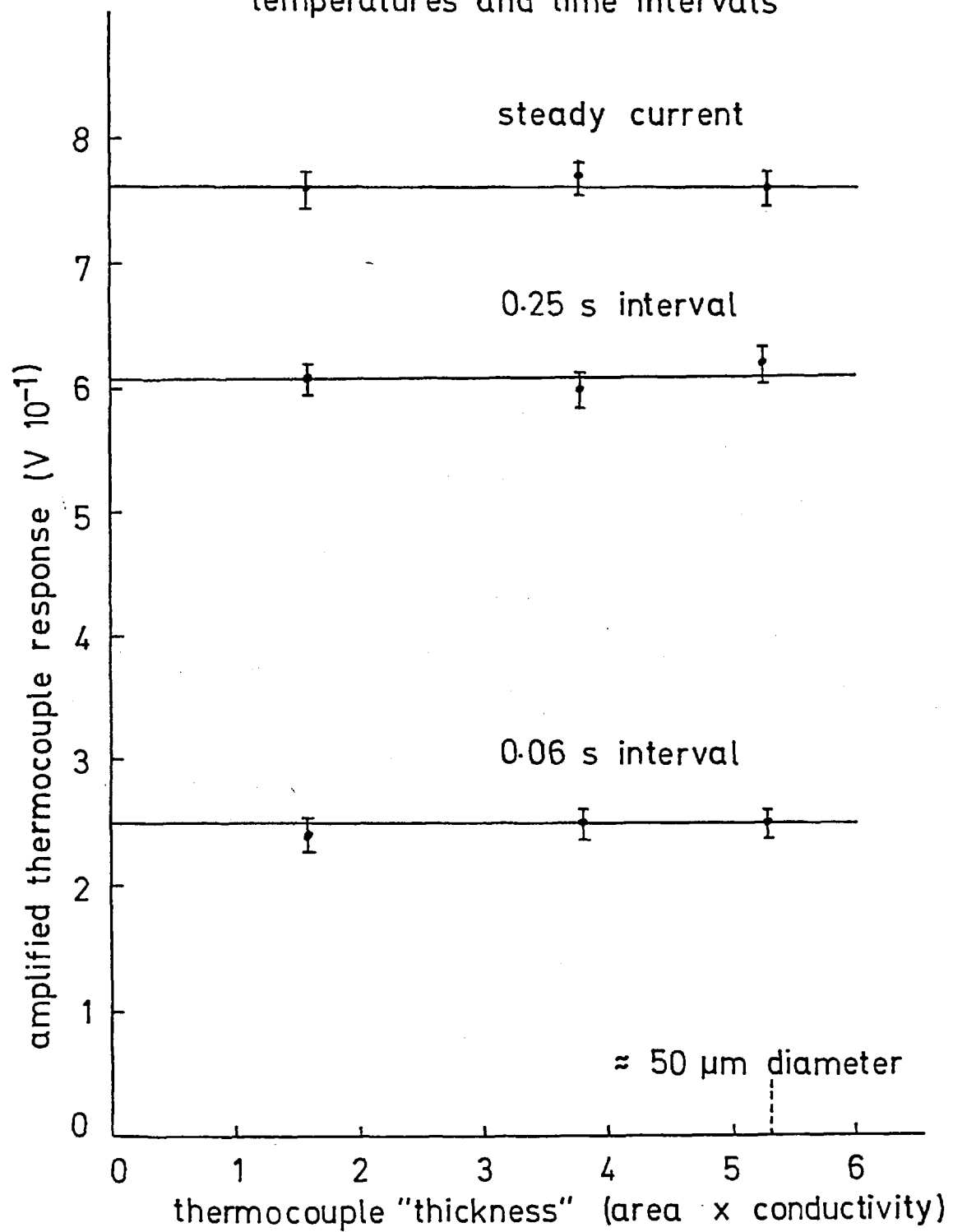
3.2 Thermocouple Thickness Investigation

Ten sets of thermocouple leads were constructed with diameters ranging from 200 μm to about 10 μm . These were tested by using each in turn to measure the temperature of the filament centre when a chosen current was passing. This was done for both steady and intermittent currents to test the thermocouple rise times.

Calibration of the calorimeter involving the delivery of a fixed amount of energy over different intervals had established that for delivery times below about 0.5s the response was close to the value obtained by extrapolating to zero time. To ensure that this effect was not thermocouple-limited, i.e. due in some way to slowness of thermocouple response, rise times were tested using currents flowing for various intervals down to 0.06s. The thickest thermocouples were found to respond slowly, some never quite reaching the temperatures recorded by the thinnest sets, even for steady currents.

Figure 3.1 shows results obtained using three thermocouples below about 50 μm in diameter. Three different temperatures were recorded and the time interval was changed for each. The highest temperature rises recorded were typically a few $^{\circ}\text{C}$ and the quantity plotted for thermocouple thickness is of arbitrary value but takes into account the cross-sectional areas of the thermocouple wires and their thermal conductivities. It was found that thermocouples of this thickness, or below, were equally responsive, all recording the same temperatures, even at the shortest intervals. The importance of this was the demonstration that these thermocouples were responsive for time intervals below the shortest needed

Fig. 3.1 Thin thermocouple responses for various temperatures and time intervals



in the calorimeter calibration. It was therefore unnecessary to construct even thinner thermocouples as these would offer no advantage both as regards speed of response and conductive heat loss.

Due to the extreme fragility of the thinnest wires, 40 μm was chosen as a suitable diameter. As a final check, thinner thermocouples were tested on the calorimeter itself during calibration but, as expected, no changes in response were observed.

For the calculation of any small conductive losses from the filament, it was expected that extrapolations to zero thermocouple thickness would be necessary in order to determine the temperature gradient at the filament edge. It transpired that this was unnecessary provided thin enough thermocouples were used for the measurements.

3.3 Construction of Calibration Source

Initial trials soon indicated that the early microcalorimeters could not be used for absolute measurements due to heat losses possibly caused by the mica support, convection, etc. It was therefore essential to construct a calibrating source for total energies around 1 mJ.

Direct illumination by He-Ne laser beams was considered for this role but was rejected due to some radiation being reflected out of the calorimeter and uncertainty as to the accuracy of the beam energy measuring apparatus.

The calibrating standard finally evolved consisted of a small, electrically heated filament of 30 μm diameter tungsten wire, held between two supporting prongs. The filament itself comprised a central coiled portion, 1 mm in length and 0.2 mm in diameter, connected to the prongs

by straight leads each about 1 mm long. Good electrical contact with the prongs, which was found difficult to achieve at first, was ensured by applying a small amount of "conductivity paint" to each joint.

For calculation of the various heating currents to be used, accurate determination of the filament resistance was required. This was achieved by subtracting resistances measured on a bridge, before and after applying a dead short across the prongs. The small temperature rises involved when the filament was in use produced a negligible effect on the resistance.

The filament mass, being so small, was difficult to measure accurately but a sample filament was found to weigh 0.1 mgm or less demonstrating its negligible thermal capacity.

In order to calculate the resistance of the central coiled portion, which alone was to be used as the heat source, it was necessary to measure the wire length in each of the filament sections. This was carried out by using a microscope to measure directly the lengths of the straight leads and the dimensions of the central helix from which its wire length was calculated. Determination of the total wire length also enabled the mass and resistance measurements to be checked independently by calculations, using the density and resistivity of tungsten respectively. Good agreement was found.

Before calibration of the calorimeter, it was necessary to account for any conductive losses which might occur from the filament itself. Using thin thermocouples with both steady and intermittent currents, temperature measurements were taken at various positions along the filament length. It was found that the temperature was approximately uniform over

the coiled portion and that temperature gradients existed mainly in the leads, close to the supporting prongs. It was decided that only the central coiled portion would be used as the calibration source, enabling heat loss from the leads to the prongs to be disregarded. In any case, this was desirable in order to give a greater semblance of a point source as the leads were each 1 mm in length and together dissipated 30% of the total filament energy. They were lagged with cement bonded silk fibres to ensure that hot gases were produced only from the coiled portion.

Calibration entailed the delivery of a chosen amount of energy over several different intervals. This was done initially by simply allowing the required current to flow for the period concerned, the hot gases being aspirated into the calorimeter.

In order to eliminate any remaining losses from the coil, another method was tried using the current flowing continuously with the calorimeter aspirating as before. This time an auxiliary air flow from a small nozzle was used which, either by blowing or sucking, prevented any hot gas from reaching the calorimeter. This flow was interrupted electrically using solenoid valves, allowing the calorimeter to aspirate hot gas for that interval concerned. With the current flowing continuously, time had been allowed for the prongs and leads to heat up and, if not reach, at least approach temperature equilibrium with the coil, thereby reducing any temperature gradients present. Heating of the prongs was confirmed by thermocouple measurements. Thus it was expected that, over the interval considered, conductive heat loss from the coil would be less than when the current flowed periodically, the prongs being cold in the latter case.

It was found that both methods gave similar calorimeter responses showing coil heat losses to be small. Due to the inconvenient nature of the auxiliary flow apparatus, it was decided to use only intermittent currents and account for the small losses by taking thermocouple measurements at the coil edge. This was done for each mode of calibration and the losses were found never to exceed a few %. This was also found to be the overall accuracy of the standard and included errors in the currents, time intervals, and heat losses themselves. The calibration standard is shown during construction in Fig. 3.3 and schematically in Fig. 3.2.

3.4 Development of Microcalorimeter

The first aspiration calorimeter built consisted of a small tube of mass 40 mgm, 2 cm long and 2 mm in diameter, made from copper foil 8 μ m thick. With thermocouples attached, this was mounted in a mica support which covered the mouth of a glass tube connected to a suction pump, rotameter and flow control system.

Using the filament as energy source, the calorimeter was tested and found to have low sensitivity, being unable to detect energies much below a few mJ. Also, the efficiency was only 10%, i.e. the temperature rise was only 10% of that expected assuming total heat transfer. To improve sensitivity, a second calorimeter of reduced dimensions (13 mm x 1 mm) weighing only 6 mgm was constructed. This detected 1 mJ but there was no great improvement in efficiency. Of course, if standard lean mixtures of about 6% methane in air were used for the ignition work their minimum ignition energies of over 1 mJ would be measurable. However, a disadvantage of using such mixtures is that their ignition energies vary greatly with composition making accuracy in the latter essential. This was, in fact, achieved with the mixing system chosen but,

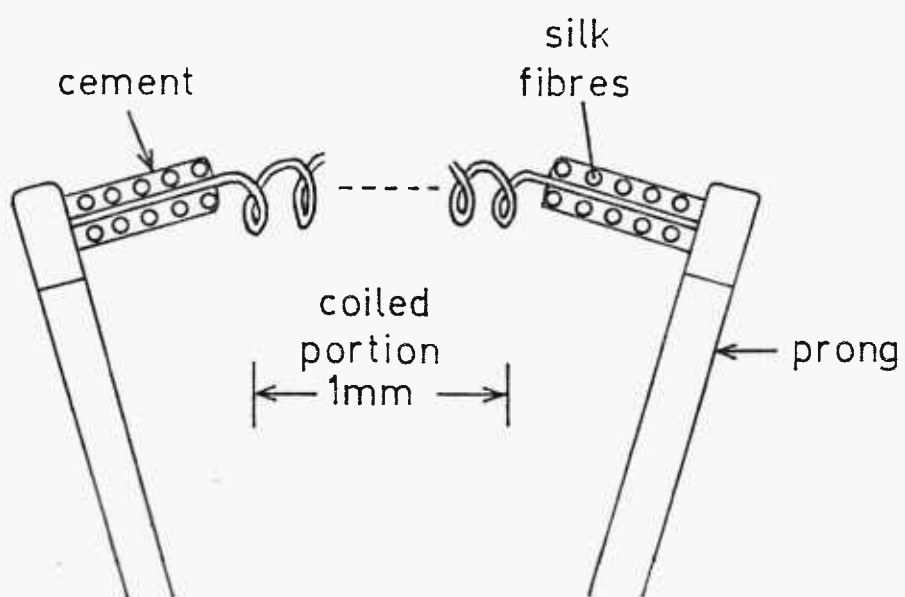


Fig. 3.2 Calibration source

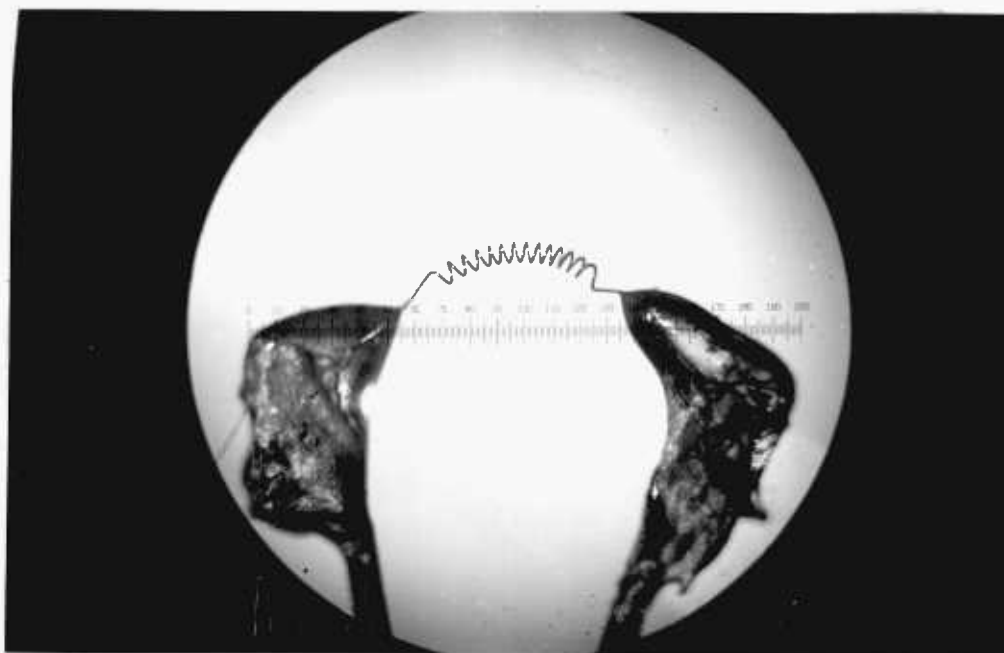


Fig. 3.3 Calibration source during construction

in order to remove the limitation of mixture choice, calorimeter development was continued to produce greater sensitivity.

The problem of low efficiency was thought to be due to heat loss in the mica support, or by convection, or by low heat transfer to the walls caused by the gas flow being laminar over such small distances. As the first two seemed unavoidable, the third was investigated by building calorimeters with baffles introduced to disturb the air flow. Another calorimeter design tried was in the form of a spiral for greater surface area and heat transfer, see Fig. 3.4. In this way efficiencies over 30% were achieved. Thinner foil 4 μm thick was tried and masses down to 2 mgm were used, though these calorimeters proved to be unnecessarily small and fragile. After several more generations, the design finally evolved and used throughout the work is shown in Figs. 3.5 and 3.6. The sensitivity required to measure plasma energies well below 1 mJ and hence make possible the study of even the most readily ignitable methane-air mixtures, was achieved by filling the calorimeter with a few mgm of copper "wool" to which the heat was transferred from the aspirated gas.

Initial experiments revealed that, due to this filling, the calorimeter picked up a small amount of energy radiated directly from the plasma. Some of the previous hollow and less sensitive designs had allowed this radiation to pass straight through. The radiation effect was made small by constructing the calorimeter in the form of a truncated cone, the smallest aperture (about 0.5 mm) being designed to face the plasma. A radiation shield (Fig. 3.7) protected the outer walls. Any remaining contribution was accounted for simply by deducting from the overall calorimeter response the radiation component measured in a duplicate experiment using zero aspiration rate. This procedure is valid provided

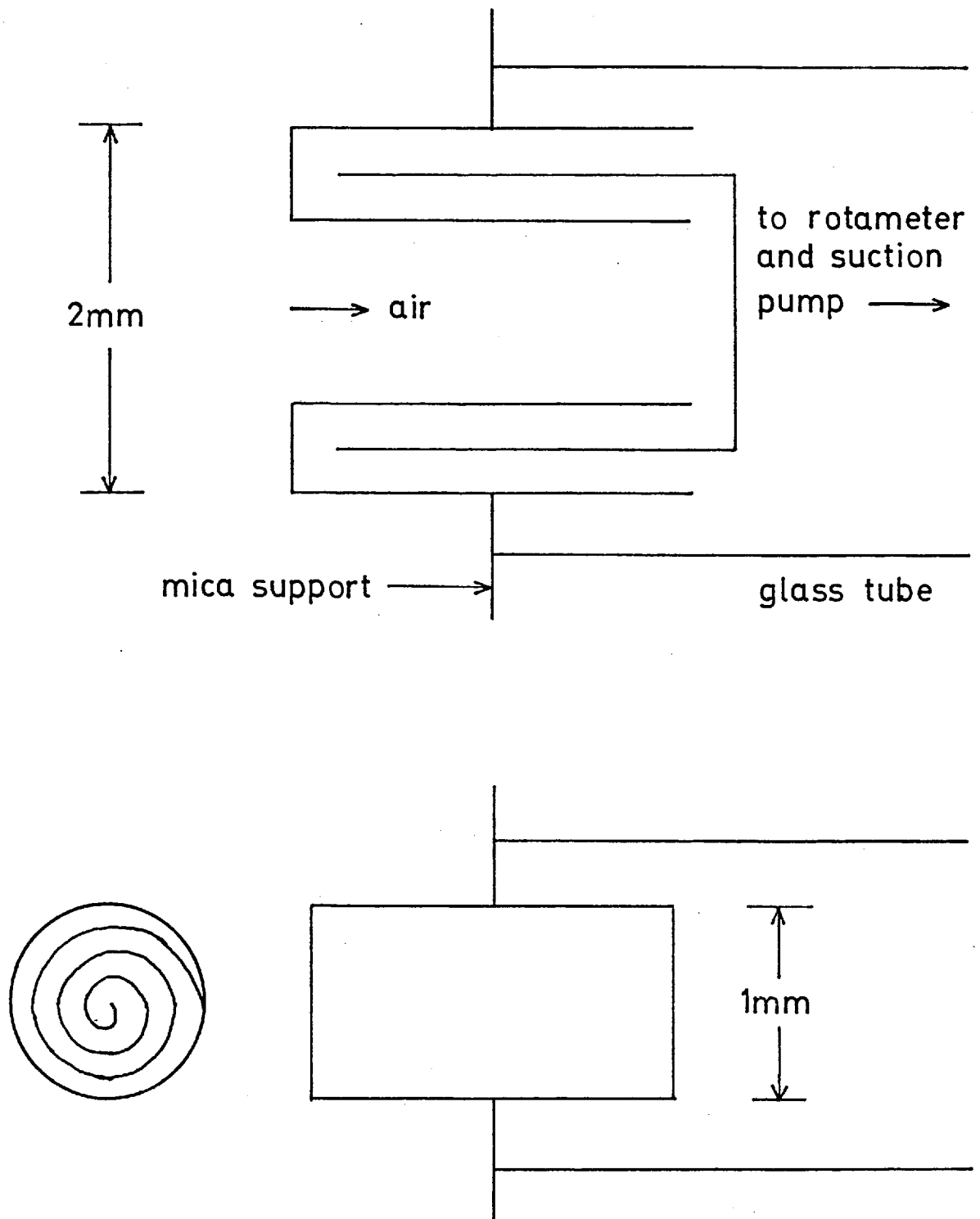


Fig. 3.4 Microcalorimeter designs

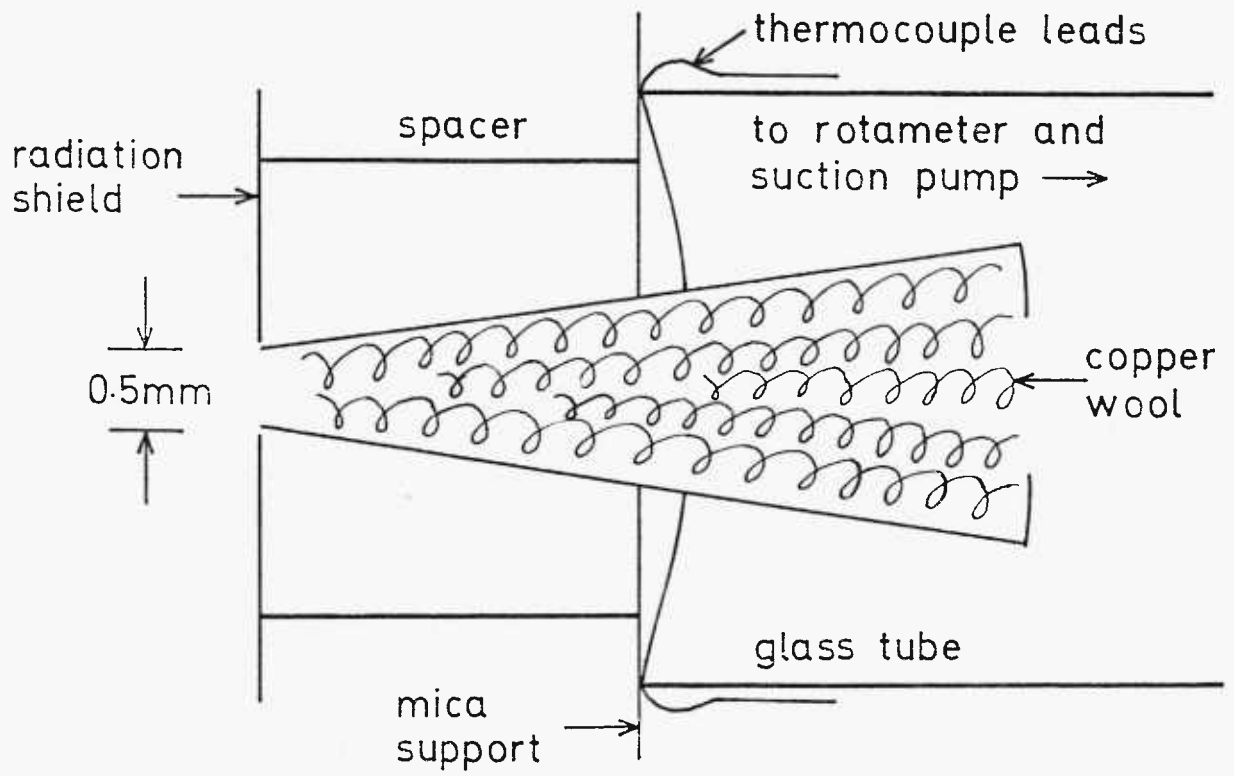


Fig. 3.5 Final microcalorimeter design

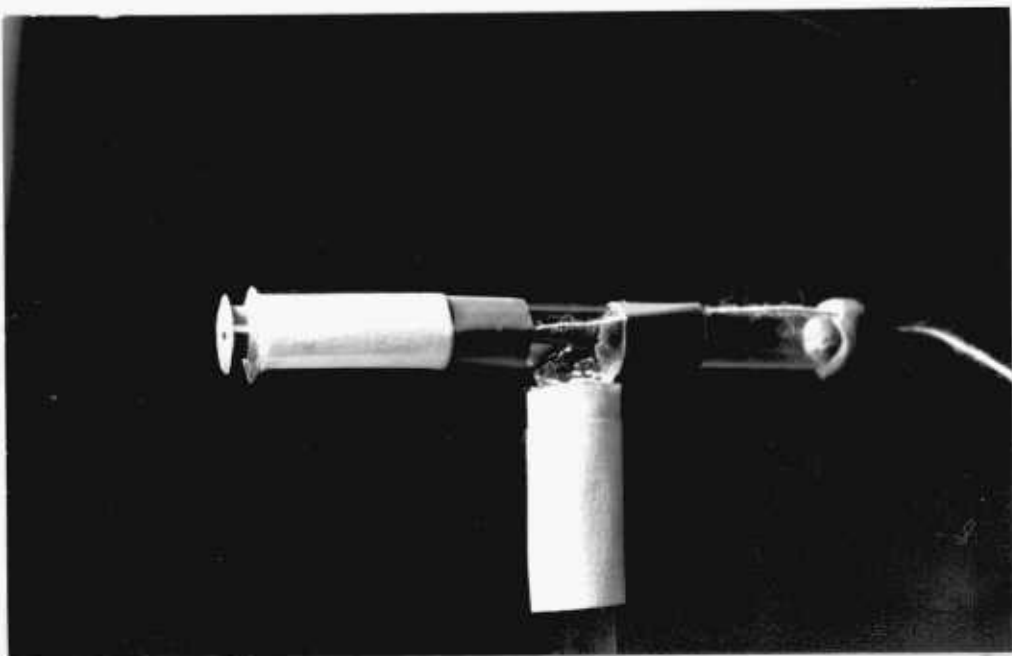


Fig. 3.6 Assembled microcalorimeter



Fig. 3.7 Radiation shield

the entrance aperture was far enough away for the hot gas not to reach the calorimeter in the absence of suction. The latter requirement was checked either by placing a microscope cover slip of low reflectivity between the aperture and plasma, or by using an auxiliary air flow to remove the hot gases completely.

Construction of the calorimeter cone involved the use of a suitably shaped former - heat insulating for soldering purposes - such as a tapered matchstick. In practice, it was found easiest to prepare a paper template, which when unwrapped, enabled the 8 μm copper foil to be cut accurately to shape when laid flat. The edges were tinned and then sealed together after mounting on the former. Likewise the thin thermocouples were attached using a negligible quantity of solder. After drilling the mica support, the cone was inserted. Due to its necessary orientation, i.e. with the smallest aperture foremost, a seal, causing minimum heat loss, was required to prevent the calorimeter from being dislodged later by the aspirated air flow. This was achieved using a needlepoint to place a few minute traces of resin on the join. The assembly was then heated in a steam bath for twenty minutes causing the resin to become much less viscous and flow around the seam before hardening. This produced a strong, airtight seal of negligible thickness. The nest of copper "wool", woven of 12 μm diameter wire, was shaped, inserted and held in position by copper fingers bent inwards from small cuts previously made in the larger aperture rim. The mica support was cemented over the glass tube mouth and construction was completed by attaching the radiation shield using a spacer to ensure that no part of it touched the calorimeter, see Fig. 3.8. The total calorimeter mass was about 8 mgm and, as with the beam energy calorimeter, a small D.C. back-off supply was incorporated with high gain amplifiers, the output being displayed on an oscilloscope.

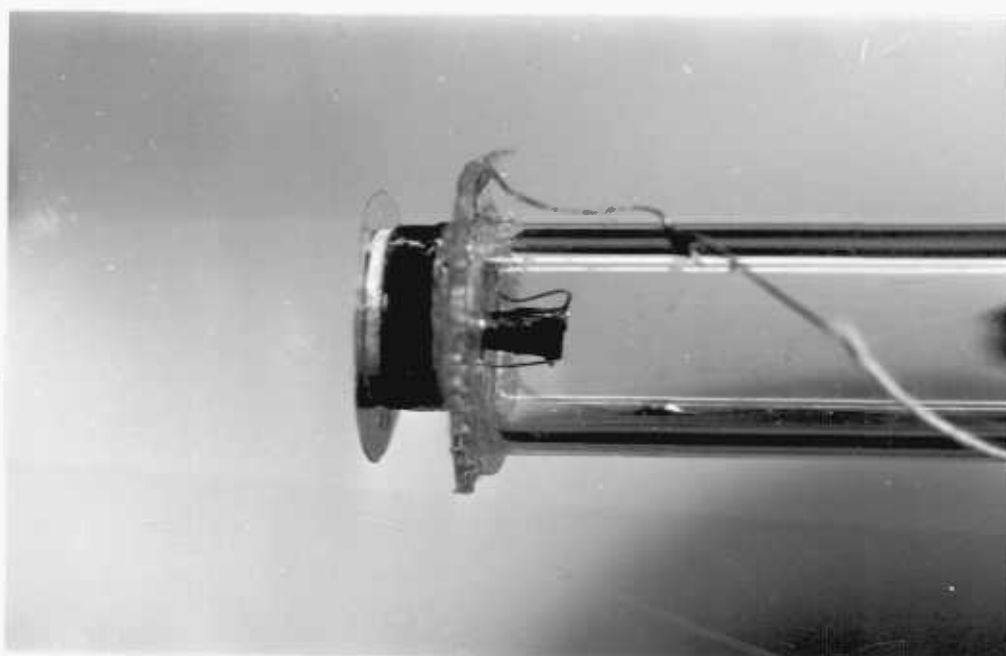


Fig. 3.8 Microcalorimeter during construction

3.5 Calibration of Microcalorimeter

3.5.1 Variation of Aspiration Rate

Calibration of the microcalorimeter, made necessary by the inherent heat losses, was first carried out varying the aspiration rate since this was necessary to ensure complete plasma capture and would affect the amount of extraneous cold gas inducted with the sample. The calibrating filament supplied 1 mJ of energy over short intervals, as described earlier. As expected, it was found that the calorimeter reading at first increased with aspiration rate and then became independent of it (until very high flows were reached) once a certain threshold was exceeded, demonstrating complete capture of the hot gas, see Fig. 3.9. For a typical separation between source and calorimeter used in the plasma energy measurements, this occurred at about 4 cc s^{-1} . This indicated that even during intervals (about 0.2 s or below), which when later used for 1 mJ energy delivery periods, produced little increase in calorimeter response with decreasing duration, the volume of gas aspirated greatly exceeded any expected plasma volume of a few mm^3 . It was necessary to establish this as the calibration would have been invalid for plasma energy measurements if the plasmas were produced over large volumes, albeit almost instantly, requiring much higher aspiration rates for capture.

This was, of course, no proof of complete plasma capture but a demonstration of its possibility. As an independent check of complete capture and of the minimum flow rate required to effect it, identical plasma energies were therefore measured varying the aspiration rate as with the

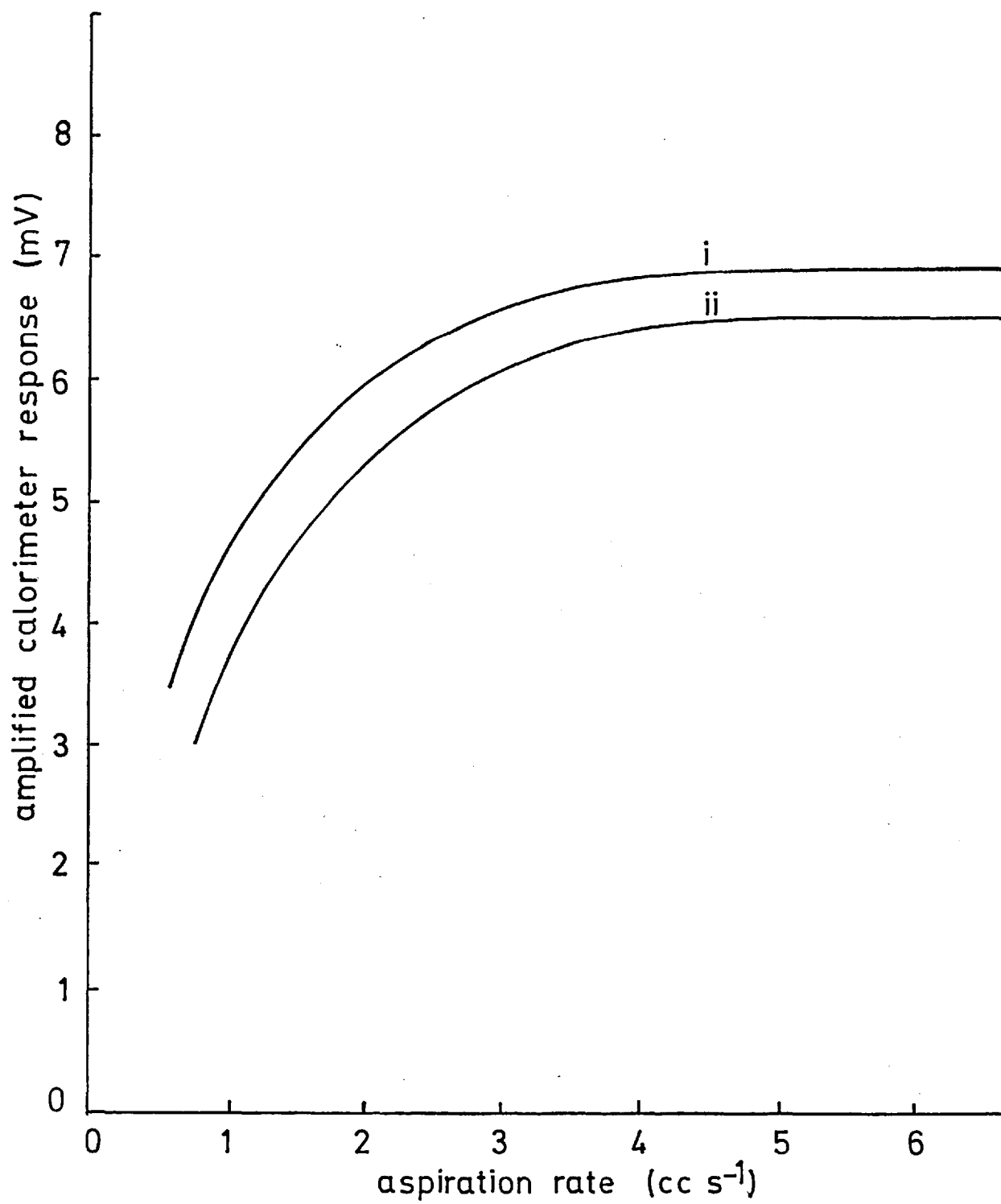


Fig. 3.9 Effect of aspiration rate
Microcalorimeter separations: (i), 1.3 mm;
(ii), 1.8 mm.

filament. This produced a curve similar in every way to that of the calibration (except for a difference in the maximum response value, as the standard 1 mJ was not used).

The separation of plasma and calorimeter was considered because of the radiation picked up by the latter. Although this component was measured separately and deducted as described, its minimization, using increased separation, was desirable. Experiments measuring plasma energies revealed that a convenient separation was typically about 1 mm, which was large enough to keep the radiation contribution small but not so large as to require excessive aspiration rates in order to exceed the capture threshold.

Complete capture was ensured using the calorimeter at its optimum flow rate, as indicated by the response being independent of flow beyond the threshold. However, the calorimeter's sampling volume was tested to demonstrate the absence of any possible calibration error due to some of the filament - itself of dimensions similar to those of the entrance aperture - not being on the calorimeter axis. This was done by moving the filament to and fro along the axis and also completely off axis by over 1 mm which changed the reading by an insignificant amount, showing the whole filament to be well within the region sampled. This also allowed energy measurements to be made for extended plasmas of about the same dimensions, which were later used in the Q-switched mode.

3.5.2 Variation of Energy Release Rate

Calibration for different energy release rates was necessary as it was not possible to deliver 1 mJ over the very short laser pulse duration. With aspiration at its optimum rate, various intervals ranging from 1s to less than 0.1s were used to deliver 1 mJ and the readings were extrapolated to zero time to give a calibration valid for the interval - deemed to be negligible - over which plasma production occurs, see Fig. 3.10. The longest intervals did produce lower responses, presumably because heat loss from the calorimeter had become significant before the completion of energy delivery. Shorter intervals apparently did not allow this to happen and the effect virtually disappeared. In fact, even for a release time as long as 0.5s, the response was less than 30% below the extrapolated value, the error in which was estimated to be negligible.

3.5.3 Linearity of Calibration

The linearity of the calibration relationship, under the optimum conditions established, was demonstrated using a suitable short interval to deliver various energies around 1 mJ, see Fig. 3.11. This made it relatively easy to measure the energy content of any of the plasmas produced. A threshold ignition probability of 0.5 was first obtained with the relevant mixture and target, after which the plasma energy was measured separately in an inert atmosphere. For convenience, air was used for this in most cases though with free-running pulses, nitrogen was also used for oxidizable materials as these gave different results in the presence of oxygen.

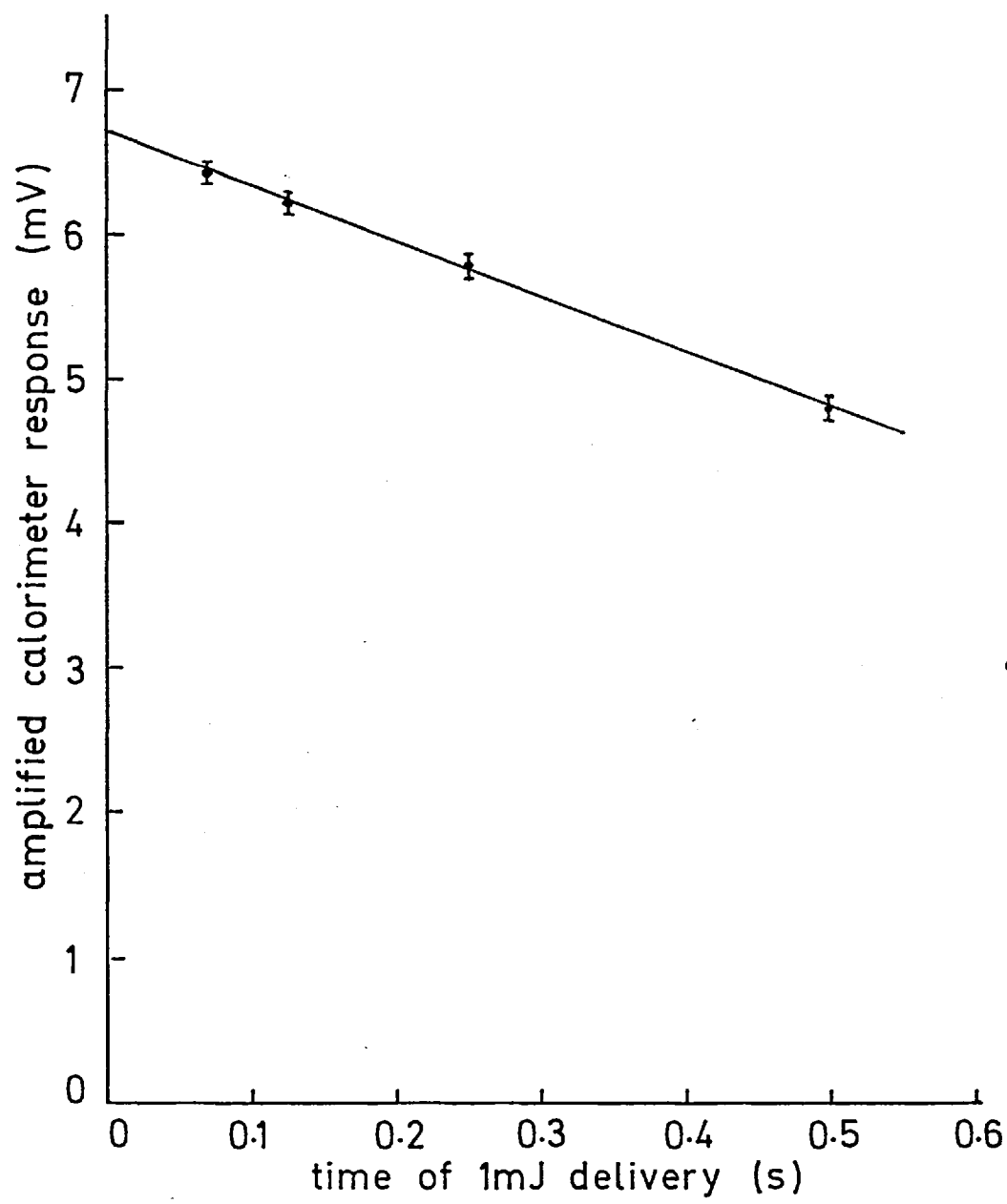


Fig. 3.10 Effect of energy release rate

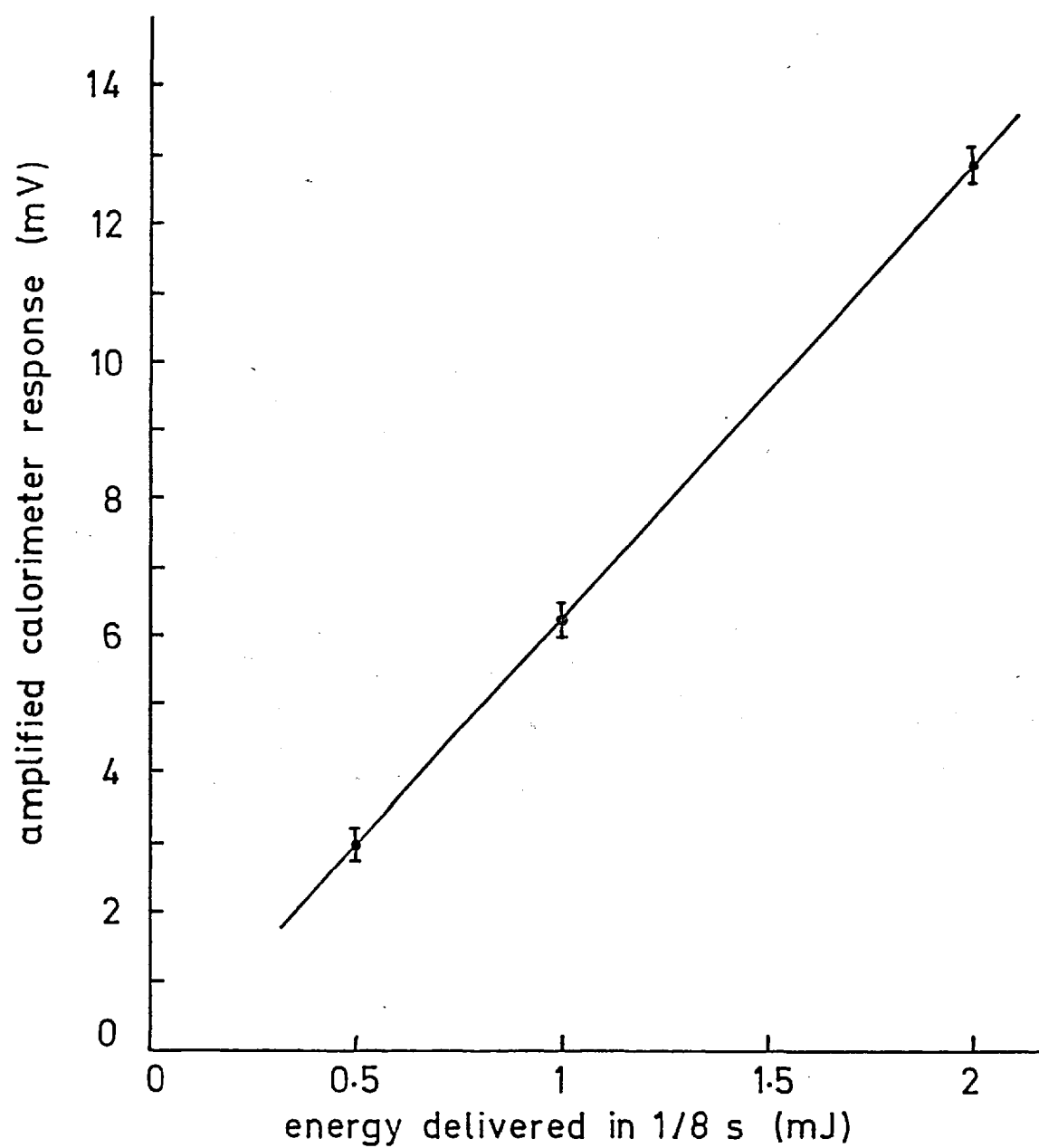


Fig. 3.11 Linearity of microcalorimeter calibration

For the comparison of minimum plasma ignition energies of various materials for a given mixture, the total error introduced by calibration was irrelevant. However, as this error was small, its combination with other uncertainties in beam energy, ignition probability, etc. yielded an overall experimental error of only 15% in the absolute determination of these plasma energies. As previously mentioned in Chapter 2, any effects of using targets of inhibiting material in the experiments were expected to be very large, rendering this error quite acceptable.

CHAPTER 4

PRODUCTION AND USE OF SMALL LASER TARGETS

4.1 Introduction

The production of suitable targets of various materials was an essential part of the work. The use of targets not only removes the absorption threshold previously found¹ when ignitions were produced by causing breakdown in an initially transparent gas, but makes available a range of other degrees of freedom. The mass of target material in the plasma, its chemical constitution and its initial volume, can all be varied by changing the target size, the material of which it is made and its position in the beam relative to the focal spot, respectively.

Plasma plumes may be produced from plane surfaces but the large thermal inertia and conductive heat losses associated with the use of such targets, would nullify an inherent advantage of laser produced ignition, namely, the absence of energy losses to an inevitable heat sink in close proximity, from both the initiating plasma and the subsequently expanding flame kernel. Furthermore, ignition may be caused by hot material or catalytic reactions around the focal spot and not by the plasma itself.

Instead, small targets in the form of wires, fibres and particles, were considered. Preliminary calculations showed that for energies of a few mJ, initial plasma volumes and target masses required would both be very small. In addition to the smallness of the target size, its good reproducibility, as with the beam energy, was an important factor since many readings would be required for the ignition experiments and plasma energy measurements.

It was concluded that sufficiently thin wires and fibres would make ideal targets, being uniform and, unlike particles, easy to suspend tautly and hence position accurately.

The fibres used - diameters ranged from 12 μm to about 80 μm - traversed the focal spot, which could be made very small (less than 100 μm). Thus the initiating plasma was acceptable for minimum ignition energy measurements as its dimensions could be kept well below the quenching distance of any mixture used - this being a necessary requirement for point ignition.

The mass of target material in the plasma could be increased simply by placing several fibres side by side in the same focal spot. Extended plasmas approaching the quenching boundary were easily produced when required, by moving the target to a defocussed position where the beam was wider. The use of fibres enabled this increase in volume to be made without introducing the effects of increased conductive heat loss, etc., which may have occurred with particle targets massive enough to produce such extended plasmas.

4.2 Production of Targets

The range of interest concerning target materials included metals such as copper, which are used as electrodes in conventional spark production and are available in thin wire form, and also non-ductile materials, e.g. inhibitors such as sodium chloride.

Sodium chloride was first tested by placing at the focal spot, single crystals stuck onto the side of a supporting quartz fibre which remained untouched by the beam. Apart from being difficult to reproduce and unusable for producing extended plasmas, such targets were unsatisfactory as the crystals were easily dislodged. It was decided to produce the uniform targets required by coating an inert quartz substrate with sodium chloride. In order to obtain the quartz fibres needed for this, mechanical pulling methods were tried with heated quartz rods, but it was found difficult to produce fibres less than 30 μm in diameter. Although those obtained would have been sufficiently thin, they were uniform over small distances only.

A technique was therefore devised by means of which long uniform fibres were produced by passing those mechanically pulled along the axis of an oxygen-enriched gas flame. The material expelled in molten form was drawn into finer fibres by the gas flow. After rising by convection, the fibres were caught whilst slowly descending. Uniform fibres several feet long and only 8 μm in diameter were produced in this way. This diameter could be varied by changing that of the original fibre and the flame temperature used.

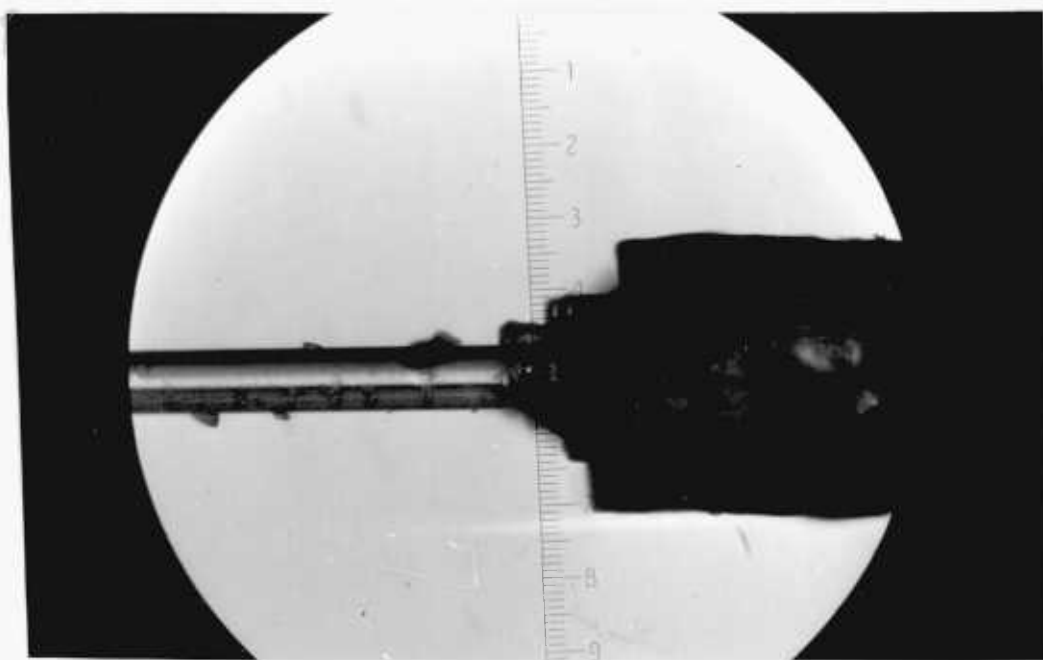
Coating of the fibres was first attempted using sodium chloride solution, but simple immersion was unsuccessful due to surface tension effects. Atomizer sprays producing small uniform droplets were used, but on the fibre these droplets coalesced and evaporated, leaving an irregular coating of many crystals. Sputtering techniques were considered but the method finally devised involved dipping the fibres in molten sodium chloride.

The salt was melted in a nickel crucible heated by a Méker burner and, as with the aqueous solution, it was not possible to "wet" the fibres by immersion. However, it was found that when the heat source was removed, after about thirty seconds - it was necessary to time this interval precisely - a thin layer of minute crystals rapidly formed over the surface. Coating was achieved by immersing the fibres just below the molten surface and quickly withdrawing them a few seconds before this crystal layer was due to appear. It soon became easy to coat with any required thickness by varying the speed and precise time of withdrawal. The extreme uniformity of the coating is shown in Fig. 4.1, which also shows a quartz substrate approximately 80 μm in diameter. This was one of the more massive targets used in preliminary experiments to demonstrate that, using free-running pulses, ignitions could not be obtained in the presence of sodium chloride, even with full laser power.

4.3 Use of Targets

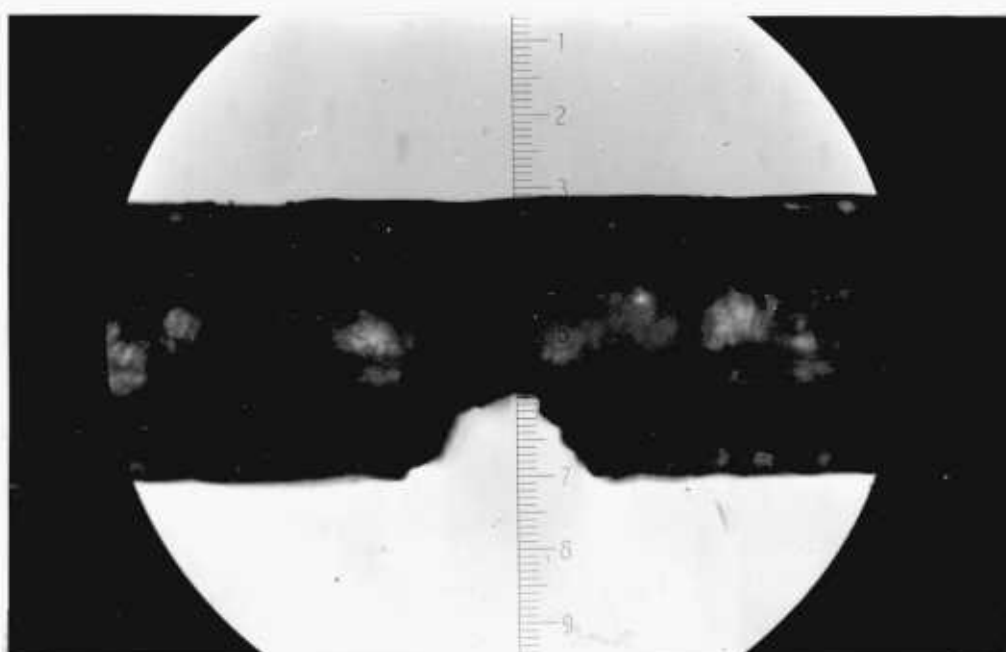
When coated fibres were used, it was originally intended to deduce the component of any plasma energy carried by the coating material, by subtracting from the total plasma energy, that, measured under identical conditions, carried by the quartz substrate alone. This would at least have allowed the comparison of various materials with regard to the effects of their plasmas on the minimum ignition energy concerned.

In practice, it always proved possible to measure the relevant plasma energy directly. For point ignition studies, the coating thickness chosen enabled the fibre to be placed slightly to one side of the focal spot centre. This permitted vaporization of the coating alone, the substrate being untouched by the beam, see Fig. 4.2. The thickness for extended plasma production was such that the removal of coating material never



(1 subdivision $\approx 9 \mu\text{m}$)

Fig. 4.1 Quartz fibre ($80 \mu\text{m}$ diameter)
coated with NaCl



(1 subdivision $\approx 9 \mu\text{m}$)

Fig. 4.2 NaCl-coated fibre used as target

uncovered and therefore never vaporized any of the quartz below.

Whenever fibres were not completely vaporized by the beam the mass of material in the plasma could be calculated to an accuracy of about 10% from the measured dimensions of the craters produced, these measurements being made with a powerful microscope, as discussed later. For Q-switched pulses at the ignition threshold, these masses were as low as 2.3×10^{-8} gm for fast reacting mixtures (8.6% methane-air).

CHAPTER 5

RESULTS: VARIATION OF IGNITING PLASMA COMPOSITION

5.1 Experimental System and Technique

The general layout of the experimental system is shown in Fig. 5.1.

The photodiode and beam splitter were positioned several metres from the laser so as to monitor the beam before it reached any other component.

The dye cell Q-switch was used for most of the experiments and, as this caused an increase in beam divergence, an iris was used to limit the beam width since it was found difficult to obtain a focal spot less than 1 mm in diameter without a circular stop. Coarse adjustments in the beam energy were made using neutral density filters. The finer control needed to establish the ignition threshold was obtained using a polaroid sheet mounted in a rotatable holder graduated in degrees and, as expected, the energy transmitted was approximately a sine function of the setting.

A variable length cell containing copper sulphate solution was also used for beam attenuation in early experiments, but was found less convenient. A lens of focal length 35 mm was used in most of the experiments but 100 mm was used to produce some of the extended plasmas.

The target fibres or wires were positioned in the ignition cell 5m from the laser, their position with respect to the beam being monitored by a sighting microscope. This microscope, along with the other components (Fig. 5.2), had previously been aligned with the auxiliary He-Ne laser set up to position the beam energy calorimeter for monitoring. The position of the beam focus could be accurately determined by sliding the microscope

Fig. 5.1 Layout of Experimental System

A, ruby laser; B, pulse counter; C, beam energy calorimeter; D, amplifier; E, pen recorder; F, neutral density filters; G, rotatable polaroid; H, iris; I, target; J, ignition cell; K, sighting microscope; L, He-Ne laser; M, schlieren stop; N, high speed cine camera.

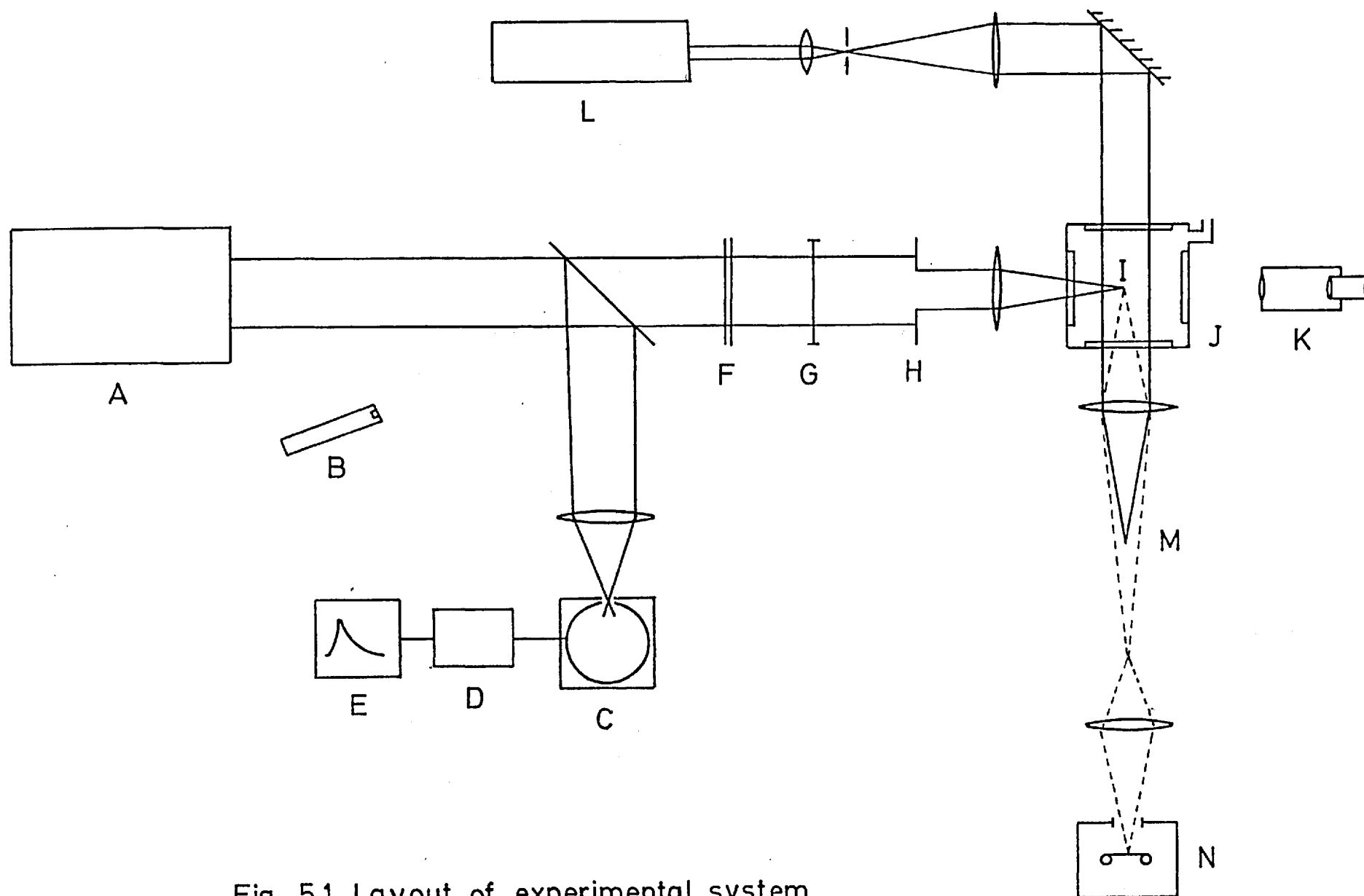


Fig. 5.1 Layout of experimental system

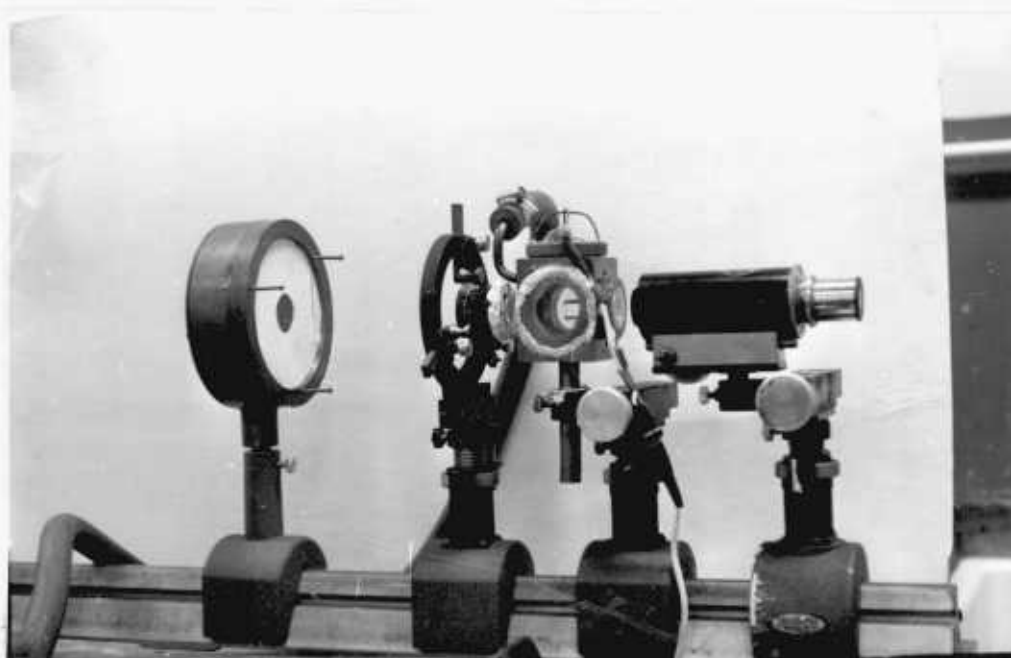


Fig. 5.2 Rotatable polaroid, iris and lens assembly, ignition cell containing target, and sighting microscope

along the beam axis until the eyepiece graticule image coincided with that of the ruby crystal under diffuse illumination, seen through the microscope. The crystal was effectively an object at infinity for the short focal length lens used, making its image coincident with the principal focus where the targets were to be placed. The microscope was also used to position the microcalorimeter relative to the targets when plasma energies were measured.

The He-Ne laser and schlieren system (Fig. 5.3) was used with a high speed Hitachi cine camera (Fig. 5.4) to photograph expanding plasmas produced by free-running pulses.

The first stage of the experiments was to determine an ignition threshold at which the plasma energy would be measured. An ignition of any mixture was indicated by a large response from the internal cell thermocouple and complete combustion of the gas was confirmed by the fact that subsequent pulses, even of high energy, produced zero response when focussed onto the remaining target. The beam energy was adjusted to give a threshold where the ignition probability was about 0.5, as indicated by many firings. The suction microcalorimeter was then used to measure the threshold plasma energy, a suitable glass plate being positioned upbeam of the target to compensate for the cell front window.

5.2 Preliminary Investigations

The basic premises were established in preliminary experiments. It was demonstrated that in the presence of any of the small targets no plasma energy threshold exists for any type of laser output, i.e. if there are beam energies so small that they would be completely absorbed or reflected by such targets, they must be negligible in comparison with minimum

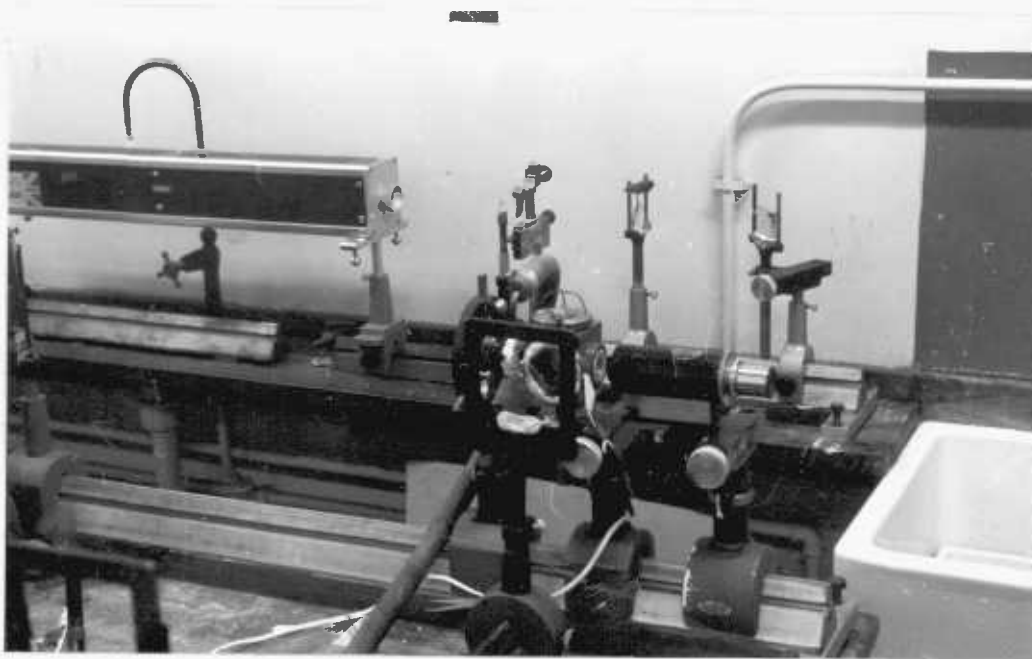


Fig. 5.3 He-Ne laser and schlieren system

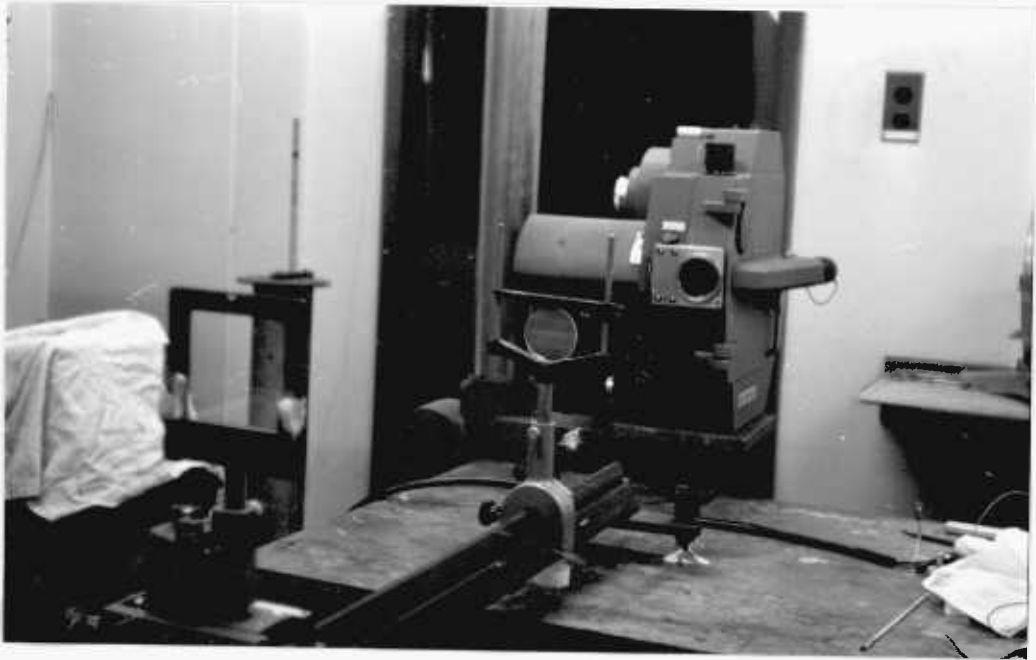


Fig. 5.4 Hitachi high speed cine camera

ignition energies. This was shown to be so by reducing the beam energy well below its ignition threshold value and measuring the energy of the plasma produced, which was found to be far less than its minimum ignition value.

Such a plasma energy threshold would have been analogous to that previously found without targets when Q-switched pulses were used¹. This latter threshold was due to the finite duration of the Q-switched pulse and the absorption, after the onset of breakdown, of its remaining energy. It had been shown¹ that this absorption threshold already exceeds the minimum ignition energy for mixtures which are not either far from stoichiometric or at sub-atmospheric pressures. In addition, the blast wave produced by the expanding plasma front absorbing the incoming radiation was shown to be powerful enough to initiate detonations rather than deflagrations in mixtures approaching atmospheric pressure.

The mixtures used in the present work included those close to stoichiometric and were all at atmospheric pressure. Also, the target was very small, even in comparison with the focal spot. It was therefore necessary to show that all ignitions occurring were due to the presence of the target alone and that the plasmas produced were not due, even in part, to any simultaneous breakdown in the adjacent gas. This was demonstrated by observing no ignitions and detecting no plasma production using the suction microcalorimeter, in the absence of the target, both of these experiments being conducted with the beam energy above its former ignition threshold value but evidently still insufficient to cause breakdown.

The preliminary ignition experiments were carried out without using the Q-switch. Instead, the free-running output was used. This was a 1 ms pulse comprising many short spikes. This output was chosen since it was

that of longest duration and it was thought that any possible effects of target material on minimum ignition energies would be most noticeable if the parent plasma were formed over an extended period and had the longest available time to reach the quenching boundary, i.e. to expand an amount equal to the quenching distance.

The mixture initially used was 8.6% methane in air as this corresponds to the minimum quenching distance of approximately 2 mm and would give the plasma the shortest possible distance to travel before reaching this boundary. Copper was chosen as the first target material as it is often used in electrical contacts where sparks may occur and has been used for electrodes in previous measurements of minimum ignition energies.

The first target was a single strand of 12 μm diameter copper wire suspended across a focal spot approximately 80 μm in diameter. It was found that even very low beam energies were sufficient to vaporize this target completely without producing ignitions. In an attempt to produce plasmas of greater energy the beam energy was raised, but even high values produced no ignitions. In order to raise the plasma density, which might increase the amount of incoming radiation absorbed, the target mass was increased by using thicker wires. A 50 μm diameter copper wire was also completely vaporized by the beam, but this time the mixture was readily ignited showing that the more massive targets of these dimensions provide ample target material for ignitions.

To investigate any possible effects of plasma composition the target material was changed and steel wire and sodium chloride targets of the same diameter were also used, the latter material being chosen as it is a known inhibitor. Ignition thresholds were obtained for both metals and

it was found, from the beam attenuator settings, that the beam energies required to produce ignitions indeed differed greatly for the two targets, the value for copper being over twice that for iron. In the case of sodium chloride the entire maximum laser output (nominally 30J) was insufficient to produce ignitions, even after the target diameter had been further increased to 80 μm (Fig. 4.2) and completely covered the focal spot.

Although the ignition threshold beam energies for copper and iron were very different, little importance was attached to them as it was thought that plasmas of different materials would absorb and reflect different proportions of the incident energy and possibly react with the oxygen of the atmosphere, making the plasma energy itself the relevant quantity to be measured.

Using the suction calorimeter, the threshold plasma energies for iron and copper were measured and found to be very similar - of the order of 2 mJ - showing clearly the important difference between the incident beam energies and those contained by the plasmas they produce. The plasma energy for iron was 1.8 ± 0.2 mJ whilst the value for copper was just 2.1 mJ even though over twice the beam energy had been used to produce it. The reason for this difference is that the iron plasma releases heat in an exothermic reaction with the oxygen of air. This energy forms part of the total amount detected by the suction calorimeter and means that much less incident beam energy is required to produce an ignition. This was confirmed by repeating the experiment using the same threshold beam energy but with the steel target and suction calorimeter inside a cell filled with nitrogen. A greatly reduced plasma energy was recorded (0.6 mJ), demonstrating the effect of oxygen.

Since no ignition threshold was established with sodium chloride, plasma energy measurements would have been meaningless. However, in order to establish that energy was truly getting into the gas and that the non-ignitions were not due to some unaccounted for phenomenon such as the target shattering instead of being vaporized etc., measurements were made with the laser working at full power. The energies involved were so far in excess of those for which the calorimeter was designed that damage did occur periodically and accuracy was difficult to achieve. Nevertheless, it was established that for sodium chloride targets the plasma energies produced were orders of magnitude above those for other targets.

5.3 Use of Q-switched Output

Having demonstrated the possible effects of target material on ignition energies using a free-running pulse, the next step was to approach as closely as possible the ideal of instantaneous point ignition. To this end the dye cell Q-switch was used to produce a single 40 ns pulse and the target size was decreased, the original 12 μm copper wire being used again with the 80 μm diameter focal spot. The mixture chosen for initial experiments was 6% methane in air as its higher minimum ignition energy - over 1 mJ - was measurable with early calorimeters. In contradistinction from the free-running pulse, the Q-switched output was found to produce ignitions easily and without completely vaporizing the 12 μm copper target. The ignition threshold was obtained and the minimum igniting plasma energy was measured to be 1.5 mJ.

It was decided to further the investigation into the effects of plasma composition on minimum ignition energies by changing both the amount of material in the plasma and as before, the target material itself.

5.3.1 Variation of Target Mass

Firstly, the mass of copper in the plasma was increased by using a larger target consisting of two adjacent copper wires suspended in the focal spot. In this way twice the copper surface area was presented to the beam, and it was expected that this would cause approximately twice the amount of copper to be vaporized for a given beam energy. On determining the ignition threshold for this target, it was found from the polaroid and filter beam attenuation values that the threshold beam energy was exactly the same as that for a single target. It might be expected that twice the mass of copper vaporized by a given beam energy would produce approximately twice the plasma energy, but subsequent measurements of the latter yielded the same value as that obtained using the single target.

From this result it appeared that the minimum ignition energy of a 6% mixture was independent of the mass of copper contained in the igniting plasma. However, a possible explanation considered was that the leading edge of the pulse vaporizes just sufficient copper to produce a plasma which covers the focal spot, thereby shielding the target from the remainder of the pulse. In this way the mass of copper contained in the plasma would be the same for both targets, the only difference being that for a double target half the mass would be removed from each wire. In order to resolve the matter it was necessary to determine the masses of copper used in each case.

This was achieved using a powerful microscope to observe the craters produced in each wire, see Fig. 5.5. The microscope measurements were used



(1 subdivision $\approx 2 \mu\text{m}$)

Fig. 5.5 Copper wire ($12 \mu\text{m}$ diameter)
used as target

to construct 3-dimensional scale models of the craters which, after measuring the density of the plasticine used, enabled the masses vaporized to be calculated. It was found that using two wires did double the mass of copper in the plasma and that this mass, for a single wire target, was only 5×10^{-8} gm ($\pm 10\%$).

5.3.2 Variation of Target Material

The plasma composition was next changed by using a different material. Sodium chloride targets were used and the resulting threshold beam and plasma energies were found to be exactly equal to those for both copper targets.

This indicates that for a 6% mixture the minimum ignition energy is independent of the igniting plasma composition when 40 ns pulses are used. The constancy of the beam and plasma energies for the copper targets also confirmed, as expected, that any conductive heat losses from the plasma, which would have been expected to vary with numbers of fibres, were negligible for targets of this size.

5.3.3 Discussion

In addition to the independence of minimum ignition energy of plasma composition, the fact that a given beam energy produces a plasma energy independent of the mass vaporized was thought to be due to the plasma produced expanding, covering the focal spot and absorbing most of the pulse remaining, making the beam energy the only important factor.

Thus, for a double copper target the incoming leading edge vaporizes copper from each fibre "not knowing" the other is present. Equal amounts are removed as the plasma cloud expands to capture the remaining incoming beam energy.

This expansion occurs at no less a rate for a single fibre as both targets, single and double, are very small in comparison with the expanded plasma dimensions. That is, the double target cannot be regarded as an extended plasma source which thereby accelerates plasma expansion - as one fibre is a tiny source so, therefore, are two adjacent ones. In this way, vaporization by the leading edge of a pulse of given energy occurs at the same rate, and for the same period, for both targets. Hence the mass removed is doubled in the case of two fibres yet the plasma energy, being determined by the beam energy, remains the same.

Similar pulse absorption was noted in the previous study¹ when, after the occurrence of breakdown at the beam focus, the plasma front facing the incident radiation was observed to expand towards the origin of the beam as it absorbed the incoming energy. This led to a pear-shaped, asymmetrical plasma kernel, the absence of the symmetrical lobe demonstrating that most of the incident radiation was absorbed by the expanding plasma. To check this in the present work, the beam energy calorimeter was used to measure directly the threshold beam energy incident upon the target.

This was found to be close to the plasma energy measured, showing that a large part of the pulse is absorbed by the plasma, and that the beam energy is indeed the important quantity in the determination of plasma energies.

The target masses vaporized by Q-switched pulses were very small and, as the quenching distance for a 6% mixture is rather large (4 mm), it was thought that at the critical stage, when the incipient flame kernel reaches the quenching boundary, so little target material was present that it had no effect on the minimum ignition energy. This suggested that attempts to circumvent this restriction should form the next stage of the work.

CHAPTER 6

RESULTS: VARIATIONS OF PLASMA DIMENSIONS, MIXTURE STRENGTH AND PULSE DURATION.

6.1 Variations of Plasma Dimensions and Mixture Strength

In order to establish any conditions under which the target material would affect the minimum ignition energy for the very short pulses, it was decided to produce extended plasmas which might approach quenching distance dimensions and promote the chances of the target material reaching the critical quenching boundary. To encourage this further the mixture was changed to nearer stoichiometric so as to decrease the quenching distance, various values being used to see whether the result was affected. These experiments were performed without increasing the time of energy release, the 40 ns Q-switched pulse being used, as before.

6.1.1 Plasma Extension

Extended plasmas were produced by placing the targets in defocussed beam positions of various diameters. A 6% mixture was tried first with the 12 μm copper wire traversing a beam width of 0.5 mm. To produce ignitions it was necessary to raise the beam energy as its density at the target was now considerably reduced. Since the beam width was now much larger than the target diameter, much of this increased radiation by-passed the target and was brought to a focus behind it. To avoid the possibility of breakdown there, the lens being used was changed for one

of greater focal length (10 cm) and greater focal volume.

After determination of the ignition threshold the plasma energy measured was found to be approximately equal to the previous value, showing no significant change between focal spot and extended plasma energies at the ignition thresholds, see Fig. 6.1. This may have been due to the extension still being small relative to the quenching distance (4 mm) of the 6% mixture, but there was no point in extending the plasma further with this mixture as the sensitive calorimeters available enabled any mixture to be studied, including those of much smaller minimum ignition energy and quenching distance.

6.1.2 Variation of Mixture Strength

The 8.6% mixture was used and this time the plasma dimension - up to 1 mm - formed a much larger portion of the quenching distance (2 mm) than for the previous mixture, producing, as expected, a quite significant increase in the minimum ignition energy to 1.1 mJ for a plasma dimension of 1 mm, see Fig. 6.1.

To test the effect of target material, sodium chloride targets were used at the same dimensions and in every case the plasma energy measured at the ignition threshold was found to be equal to that for copper.

The sodium chloride targets were easy to use in the ignition experiments and the ignition thresholds were easily determined. However, accurate plasma energy measurements at the larger extensions were more difficult

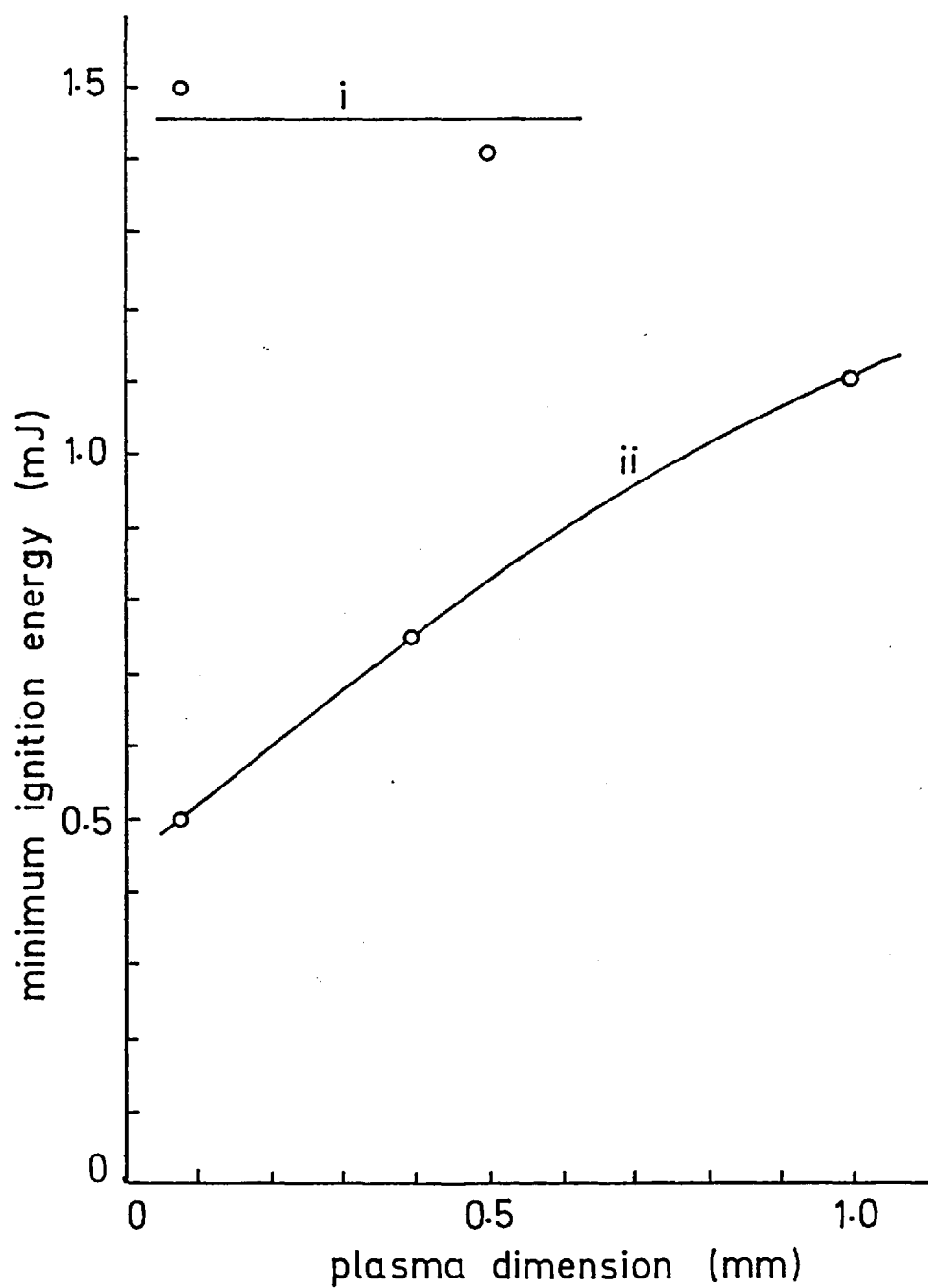


Fig. 6.1 Effect of extent of plasma
(i) 6% CH₄, quenching distance 4 mm.
(ii) 8.6% CH₄, quenching distance 2 mm.

for these targets as occasionally, small pieces of unvaporized sodium chloride flew off in various directions and some entered the calorimeter causing damage which necessitated repair and recalibration. As extended plasma energies were easier to measure accurately for copper targets, it was decided to test these targets using the sodium chloride threshold beam energy of a given extension. The plasma energy was measured and was found to be approximately equal to both the value obtained for a sodium chloride target and also that obtained for a copper target using its own threshold beam energy for the same extension.

As plasma energy depends on beam energy for a given target, it follows that, for extended plasmas, the threshold beam and plasma energies for copper and sodium chloride are equal. This had previously been found to be so for targets at the focal spot, see Chapter 5. The difference is that for an 8.6% mixture, the minimum ignition energy for a plasma dimension of 1 mm is over twice the minimum value of 0.5 mJ obtained with the focal spot. The important factor is that the target material again had no effect on minimum ignition energy, the expected increase at 1 mm possibly being due to energy losses associated with the asymmetric dimensions of the plasma in relation to the quenching volume.

Extrapolation of minimum ignition energies to zero plasma dimension for this mixture shows that, as expected, the focal spot value represents true point ignition to well within the experimental error. This must also apply to all other mixtures as they have greater quenching distances, which would be expected to reduce even further any possible differences between the extrapolated values of the minimum ignition energies and those obtained with a focal spot of finite size.

In order to compare results with those from other work using point ignition, various mixtures between 6% and 8.6% were studied, the 12 μm copper target being used in the focal spot position. Rich mixtures beyond stoichiometric were not used for this as they were not required for further ignition experiments and would have cumulatively contaminated the ignition cell windows with soot particles, introducing beam energy errors. The minimum ignition energies obtained (Fig. 6.2, curve 5) were found to be reasonably close to those from certain other studies^{2,3,4} using electrical spark ignition though it is clear that results from these latter studies can differ quite noticeably according to the experimental systems and techniques used. For example, curves 2 and 4, which represent ignition probabilities of 0.01 and 0.8 respectively^{2,4}, both lie distinctly below curve 3 even though this was for that circuit inductance yielding the lowest ignition energies and was drawn³ so that no ignitions ever occurred below it.

However, in general, the absence of heat losses to massive electrodes did not appear to make the laser minimum ignition energies appreciably smaller. This contrasts with previous results¹ obtained using mixtures either near the limits of flammability or at sub-atmospheric pressures. Here large quenching distances (over 1 cm) were involved and the laser results fell well below those for electrical ignition suggesting that the influence of the electrodes becomes more significant as the quenching distance increases, see Chapter 1.

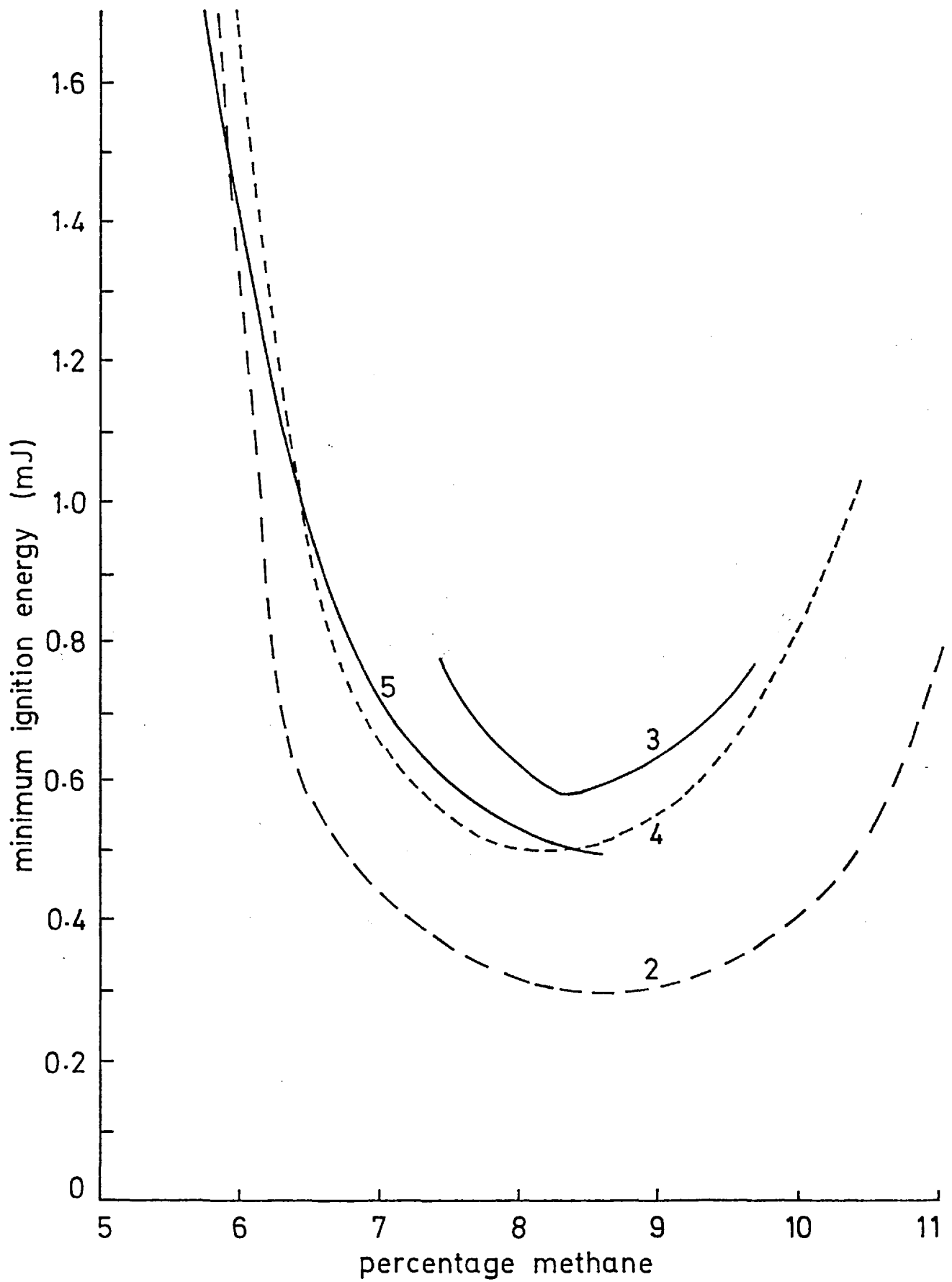


Fig. 6.2 Comparison of laser results with electrical spark minimum ignition energies - see ref. 2-4.

6.1.3 Discussion

Summarizing the work with single Q-switched pulses, the important factor to emerge from the results is clearly the independence of the minimum ignition energy of the nature of the target used. In this particular experimental system, no matter what variable was imposed, the minimum ignition energy proved to be *totally independent of the plasma constitution, with regard to both different materials and different amounts of the same material within the plasma.*

For "instantaneous point" ignition (i.e. 40 ns duration and 80 μm diameter) by focussed laser pulses we therefore have here an independent verification of the propagation-limited theory of point ignition discussed in Chapter 1. Since the material of which the initiating plasma is made has no effect on the minimum ignition energy, no significant amount of it can be present when and where the crucial stage, which decides whether or not the incipient flame kernel will propagate unaided, is reached. Therefore, it must be necessary for the reaction wave to propagate a certain fundamental distance before reaching the decisive stage, by which time the parent plasma must have been left far behind. In the case of Q-switched initiation the incipient flame kernel evidently attains its crucial quenching diameter before any of the plasma material reaches the reaction front.

Having already established the fact that this conclusion remains unaffected by changes in the plasma dimensions, the next step was to explore the variation in which the plasma constitution was known to be of major importance - see Chapter 5 - i.e., to investigate the effects of changes in the duration of the energy deposition.

6.2 Variation of Pulse Duration

Preliminary experiments had already shown the large effects of target material when 1 ms free-running pulses were used. The critical energy delivery period for plasma constitution to affect minimum ignition energy is thus shorter than 1 ms but longer than 4×10^{-8} s. To investigate how much beyond this the period of plasma formation needed to be extended before some effect was observed, the multi-pulsed Q-switched output was used, consisting of 40 ns pulses at about 0.5 ms intervals.

Early experiments using single Q-switched pulses and a 12 μ m diameter copper target with the 6% mixture, had indicated that it was not necessary to vaporize the whole target in order to produce ignitions but merely to remove some of the copper. However, using a twin pulse output, it was found possible to completely vaporize the target without producing ignitions. An ignition threshold was obtained for a double pulse output, and the plasma energy measured was found to be significantly higher than that for the single pulse threshold.

Since the suction calorimeter measures the total plasma energy for the whole output, this result indicates that plasmas formed at 0.5 ms intervals are independent and that ignition will not occur unless the energy of one of them exceeds the minimum ignition energy, even if the total plasma energy does. In practice, this implied the first pulse only, since the energy of the second could not be varied with respect to that of the first. Clearly, a larger mass of copper was used in the double pulse case as the target was completely vaporized. Mass measurements

using a microscope confirmed this and indicated that only two pulses were required to vaporize a target of this size, about half the copper being removed by each pulse. The experiment was repeated using up to five pulses in the output and the threshold plasma energy was found to be the same as for a two pulse output. This indicates that once the target has been vaporized by the first two pulses, those which may follow, which form no plasma as no target remains, have no effect on the plasma energy measured.

6.2.1 Discussion

The results of this investigation may be summarized by saying that the two plasmas acted as quite separate igniters. They do not "reinforce" one another and although the total plasma energy, unlike the single pulse case, depends on the total mass vaporized, ignition will only occur if one of the plasma energies, each being dependent upon its respective pulse energy, exceeds the minimum ignition energy.

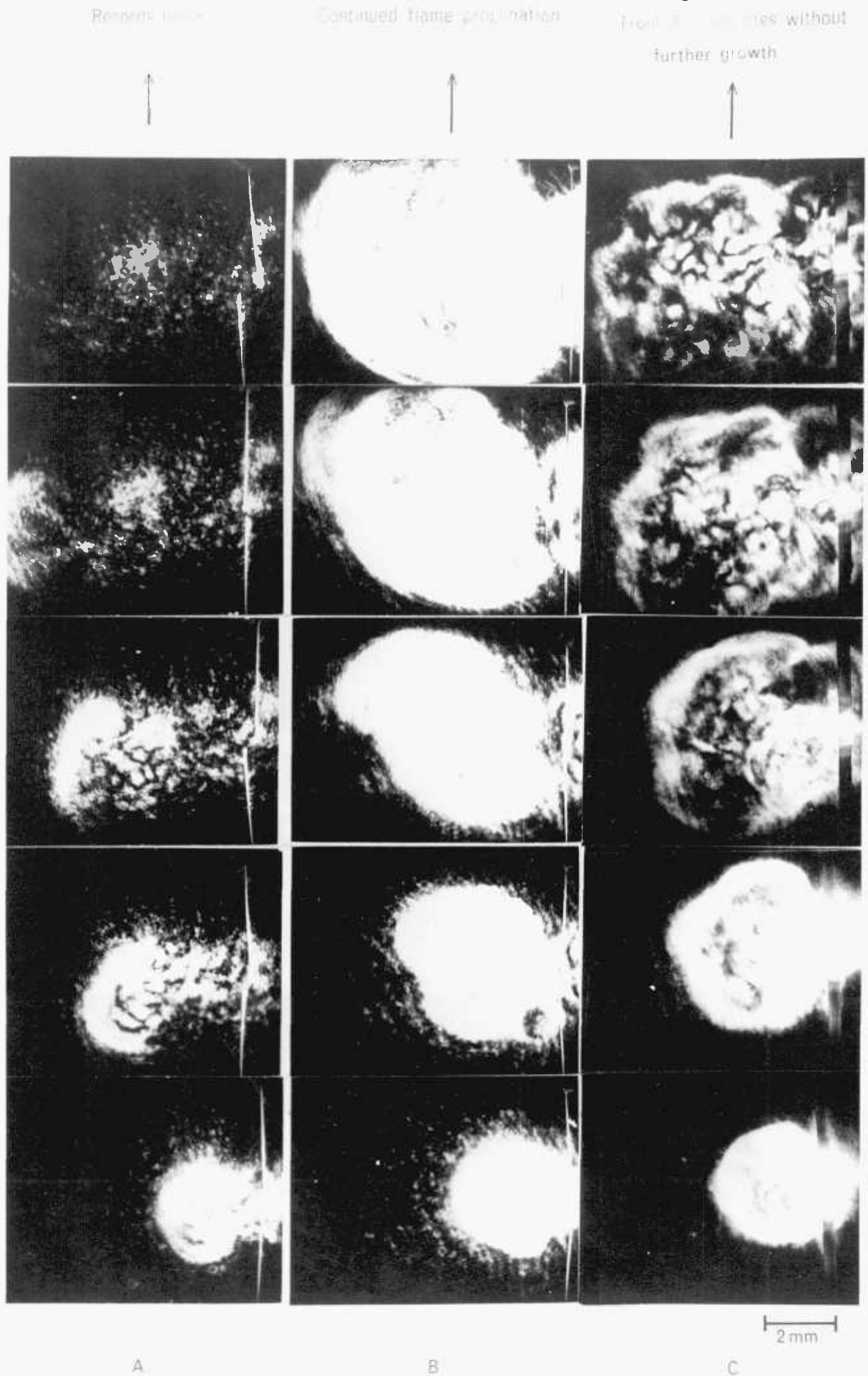
These results are, to some extent, duplicates of those obtained with single pulses, plasma constitution again playing no part. Clearly, the extra pulses of the multi-pulsed output have no effect on ignition and simply give both the monitored beam energies and plasma energies unnecessarily high values. Once the target has been vaporized by the leading pulses, the fact that following pulses have no effect on the energies of plasmas previously produced, indicates that the 0.5 ms interval is sufficient to allow plasmas to become so diffuse that they are unable to absorb any appreciable amount of energy from the following pulses.

A 1 ms free-running pulse however, contains many sharp spikes very much closer together (10^{-6} - 10^{-7} s apart). This output had been shown - see Chapter 5 - to enable the plasma constitution to greatly affect the minimum ignition energies. It was decided to investigate the reason why this type of plasma behaved in a different way using high speed cine photography.

6.3 High Speed Cine Photography

The Hitachi high speed cine camera, incorporated in an auxiliary He-Ne laser schlieren system (Fig. 5.3), was set up to photograph the expanding fronts. An 8.6% mixture was used with the 50 μm diameter copper wire and sodium chloride targets at the focal spot. The camera was used near its maximum speed of 10^4 frames s^{-1} . The alternate frames in Figure 6.3 are approximately 0.2 ms apart, the total of five in each sequence representing the duration of the 1 ms pulse.

Sequence (B) shows an ignition using the copper target at its ignition threshold, whilst (A) shows a non-ignition using the same beam energy, but with the target in air. The sodium chloride target, with which no fully developed deflagration resulted even at full laser power, is shown in (C). It will be seen that in this instance the initially smooth reaction wave breaks up later during the pulse as turbules appear and extinguish the flame. This indicates that if energy is continuously fed to the target, then provided enough material is present, the plasma produced is dense enough to be able to absorb energy and expand rapidly, eventually becoming turbulent as it catches the flame front and breaks through it locally, causing extinction when inhibiting materials are used.



(A) Plasma expanding without ignition. (B) Ignition. (C) NaCl-coated target.

6.3.1 Discussion

As was found in preliminary experiments, sufficient target material must be present to produce ignitions. The spikes contained within the free-running envelope each contain much less energy than a single Q-switched pulse. Ignition is not due to any one spike alone, as obviously each is unable to produce a plasma whose energy exceeds the minimum ignition energy. In the closely spaced train, each spike removes some target material to form a plasma. If the target is small enough to be completely vaporized before allowing the plasma cloud density to grow sufficiently, then not enough of the remaining incoming energy is absorbed to produce an ignition. Hence the amount of target material supplied must be at least enough to produce a plasma sufficiently dense to absorb an amount of energy adequate for ignition.

Absorption of the continuing energy supply also enables the plasma to expand rapidly and overtake the flame front, producing the expected effect - extinction, in the case of inhibitors, as already seen. In this way, continued flame propagation was never obtained with sodium chloride targets using free-running laser pulses. A 12 μm diameter copper target produced no ignitions due to lack of material. It was completely vaporized at low beam energies, but, even high values failed to produce ignition indicating that the plasma was not dense enough to absorb an appreciable amount of energy from the closely spaced spikes. A 50 μm diameter copper target however, also being completely vaporized by the beam, enabled the 8.6% mixture to ignite for a total plasma energy of 2.1 mJ. This value obviously depends on the nature of the target and the duration of the energy delivery. It is, of course, not equal to the true minimum ignition energy obtained using Q-switched pulses as it does not represent instantaneous ignition and there must inevitably be energy losses associated with the extended period of energy delivery.

CHAPTER 7

CONCLUSIONS

Preliminary experiments in the study of the effect of plasma constitution on the minimum ignition energies of flammable gas mixtures established certain basic premises. It was demonstrated that with minute targets no plasma energy threshold exists for any type of laser output. Using free-running laser pulses of 1 ms duration it was found that pulses of high energy produced no ignitions in 8.6% (minimum quenching distance) methane-air mixtures with very small targets of 12 μm diameter copper wire, even though pulses of low energy were sufficient to completely vaporize targets of this size. Larger targets of 50 μm diameter were also completely vaporized by the beam but produced ignitions readily, indicating that these more massive targets were needed to supply the amount of target material necessary for ignition to occur. The laser beam energies required to produce ignition were found to differ greatly for copper and steel wire and for sodium chloride coated quartz fibres, all of about 50 μm diameter. The value for copper was over twice that for iron, whilst the entire maximum laser output (nominally 30 J) was insufficient to produce ignition in the presence of sodium chloride.

As the relevant quantity to be measured in each case was the energy of the plasma produced, a suction microcalorimeter was developed which aspirates the plasma and measures its energy content, independent of its composition.

Use of this suction microcalorimeter revealed that even though the ignition threshold beam energies for iron and copper were so different, the

corresponding plasma energies were very similar (of the order of 2 mJ). For the iron target in nitrogen, the same incident beam energy yielded a greatly reduced plasma energy showing that the iron plasma releases heat by reacting with the oxygen of air - this being the reason for the smaller beam energy required for ignition as compared with copper.

In order to approach the ideal of instantaneous point ignition as closely as possible, the laser was next passively Q-switched and the target size decreased - giving a pulse duration of approximately 40 ns and an initial target diameter of approximately 12 μm . Measurements of minimum ignition plasma energy were carried out for targets of various materials, for various amounts of the same target material (several strands side by side in the focal spot) and for very lean (6%) and near stoichiometric (8.6%) methane-air mixtures, to vary the quenching distance which might affect the result. The minimum ignition energies of the two compositions were found to be 1.5 and 0.5 mJ respectively, in each case independent of plasma constitution both as regards different substances and different amounts of the same substance within the plasma. Moreover, the particular values of minimum ignition energy compare very well with those previously published for electrical spark ignition.²

These results establish an independent verification of the theory of point ignition: the criterion is propagation-limited and the decisive stage is reached when the incipient flame kernel has grown to a critical diameter. For "instantaneous" (i.e. 40 ns duration) initiation, the propagating reaction wave evidently attains this quenching distance before any of the plasma material reaches it.

The next step was to establish how this conclusion would be affected by changes in the plasma dimensions with the time of energy release remaining at 40 ns. The extent of the plasma was varied by placing the targets in a slightly defocussed area of the beam. The minimum ignition energies increased, as expected, but the phenomenon of the ignition wave outstripping and "forgetting the constitution" of its parent plasma remained - the minimum ignition energies were once again independent of the target material or amount of it in the plasma.

Double Q-switched pulses and high speed laser schlieren cine photography applied to the free-running events were used to investigate the difference between Q-switched and free-running pulses. The high speed photography of expanding fronts showed clearly how the two modes of behaviour are interrelated. It transpires that if energy continues to be fed to the target then the expanding plasma is able to catch up with the flame. The rapidly expanding plasma cloud eventually becomes turbulent as it overtakes the flame front, breaking through it locally and extinguishing it - if it contains inhibiting material. For this sequence to go to completion, sufficient target material must be provided. A 12 μm diameter copper target used at the focus of a free-running beam will vaporize completely at very low beam energies; thereafter no ignitions can be obtained even with high beam energies in the 8.6% mixtures. A 50 μm diameter copper wire however, allows ignition to occur for an input of 2.1 ± 0.2 mJ. Sodium chloride coated targets of the same dimensions will not produce ignition - or rather sustained flame propagation - even at full laser power.

The question of the effect of plasma constitution on minimum ignition energies thus appears to be independent of the plasma volume but dependent

on its duration. The initial laser pulse, whether it is on its own or followed by many others, is responsible for the expanding ignition front, the behaviour of which is independent of the constitution of the plasma, which is left far behind. However, so long as the plasma cloud remains dense enough, it continues to absorb energy for the duration of the incoming beam. This enables it to expand rapidly, eventually becoming turbulent and breaking through the flame front. This can result in suppression or promotion of propagation, depending on the constitution of the plasma. Thus, in the case of an inhibitor, the leading edge of an extended pulse is responsible for ignition, the trailing edge for extinction; short duration Q-switched pulses do not allow time for the latter.

The conclusion completely vindicates the propagation-limited theory of point ignition and validates previous experimental electrical spark-based measurements of minimum ignition energies, showing them to be independent of plasma constitution and hence electrode materials, so long as the discharge duration is short enough. At the same time it offers a practical means of suppressing ignition by use of inhibitors included in the ignition source (e.g. a sheathed explosive) by simply extending the duration of the energy supply. By the same token it suggests that promoters could be used similarly to improve ignition efficiency in practical systems by increasing the reaction rate on reaching the flame front under conditions when the flame might otherwise not have continued to propagate.

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LIST OF SYMBOLS

A	constant depending on nature of fuel
c_p	specific heat at constant pressure
d_o	quenching distance
E_i	minimum ignition energy
H_1	sensible heat in sphere of diameter d_o containing burnt combustion products at final temperature T_b
H_{11}	total conducted heat stored in minimal-flame wave of diameter d_o
h	total conducted heat stored per unit area in steady-state plane wave
K	Karlovitz number
k	thermal conductivity
M	third body (solid particle)
P	pressure
R, R_1	chain propagating radicals
S_u	burning velocity
T	temperature
T_b	final temperature of burnt combustion products
T_u	initial temperature of unburnt reactants
ρ_b	density of burnt combustion products at temperature T_b