

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH AND FIRE OFFICERS' COMMITTEE
JOINT FIRE RESEARCH ORGANIZATION

THE PERFORMANCE OF EXPLOSIOMETERS
PART I

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by

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SUMMARY ABSTRACT

This note reports the results of work being carried out, for the Factory Department of the Ministry of Labour and National Service on the development of a method of testing explosimeters.

One type of instrument was used in the investigation. This instrument measures the increase of temperature when the flammable atmosphere is burned on a heated platinum filament forming one arm of a Wheatstone's bridge circuit.

A comparison of six detector units supplied with two explosimeters and using pentane/air mixtures showed that the instrument readings obtained at first were close to or greater than the actual concentrations, the response being linear throughout the working range of concentrations.

Chemical ageing tests and other usages have shown that changes in the sensitivity of the detector unit occur, and readings obtained with the explosimeters appeared to be dependent to a certain extent upon the past history of the detector. Electrical heating of the detector appeared to have the effect of increasing the detector sensitivity.

In tests with various flammable mixtures the differences between the indicated and actual concentrations varied with the flammable constituent. Satisfactory indications of flammability were obtained with mixtures containing pentane, benzene, hexane, ethyl alcohol, diethyl ether and coal gas. Methyl ethyl ketone gave readings which were much lower than the actual concentrations tested, and no consistent results could be obtained with mixtures containing acetone or amyl acetate.

It is considered that the instrument provides a satisfactory warning of the existence of possibly flammable concentrations of a number of gases and vapours, but, because of the variation of the readings with different solvents it could not be used for precise measurement of the concentration of a vapour for which it had not been calibrated.

The instrument could not be used for acetone or amyl acetate.

It is suggested that the red warning band on the indicator dial be extended to cover a lower concentration than the existing 60 per cent of the lower flammable limit. This would provide a safeguard against inadequate sampling in compartments where pockets of higher concentrations might be missed, and also would cover the use of the instrument for vapours which give low readings.

It is also suggested that a label on the instrument should state the types of vapour for which it is suitable.

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THE STANDARDS OF PERFORMANCE
PART I

by

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INTRODUCTION

The use of flammable liquids and vapours requires that there should be a method of determining whether the concentrations are sufficiently high to cause a fire or explosion hazard. Instruments (explosimeters) have been designed therefore to measure the concentrations of these vapours, and to indicate whether the atmosphere is flammable. They do not, necessarily, indicate or measure the toxic hazard. The ideal instrument should give valid readings for a large number of gases and vapours, be portable, and suitable for use by unskilled operators. Some of the physical properties commonly chosen for measurement are:-

- (a) heat produced by combustion of the flammable vapour/air mixture,
- (b) change in volume of the mixture on combustion,
- (c) thermal conductivity,
- (d) refractive index,
- (e) velocity of sound in the mixture.

There are no existing standards of performance of these instruments and the only official tests made are for ensuring that they do not propagate flame to the atmosphere outside the instrument when used in flammable mixtures. In addition, there is only scanty information about the relative behaviour of different solvents with these instruments. For these reasons the Senior Chemical Inspector of the Factory Department of the Ministry of Labour and National Service asked the Joint Fire Research Organization to carry out work on explosimeters in order to find the limitations of the instruments and to provide information for use in advising users on the most suitable instrument for their particular requirements.

This report describes investigations on one type of explosimeter, which depends for its operation on the heat developed by actual combustion of the flammable constituent of the atmosphere (type (a) above).

The preliminary work has been:-

- (1) a comparison of two batches of detector units and two instruments to determine variations among them,
- (2) a study of the effects of repeated use in pentane mixtures and also of electrical heating of the filament,
- (3) a comparison of the behaviour of the instrument in atmospheres containing the vapour of one of several commonly used solvents and also low CO_2 ,
- (4) a study of the degree of solvent absorption by the sampling line of an explosimeter.

EXPERIMENTAL

SOLVENTS

Eight common organic solvents were used: an alcohol, an ester, an ether, two ketones, two saturated aliphatic hydrocarbons and an aromatic hydrocarbon. Table 1 below gives details of these solvents.

Table 1

Details of organic solvents used

(1) Solvent	(2) Manufacturer	(3) Boiling range °C	Physical constants				
			(4) Molecular weight	(5) Density of liquid g/cc	(6) Lower ^a flamma- bility limit per cent by volume	(7) Heat of combustion cal/g mol	(8) Heat developed in combu- tion of 100 litres lower flammable limit m ³ pure k cal
n-Pentane	May & Baker.	32-40	72	0.65	1.5	833	56
Benzene	" " "	79-82	78	0.88	1.4	782	49
n-Hexane	Capel, Cur- less and Leonard	-	86	0.66	1.2	990	53
Acetone	May & Baker.	*95% distills between 55.5-56.5	58	0.80	3.0	427	58
Ethyl alcohol	Distillers Co.	-	46	0.79	4.3	338	63
Amyl acetate	May & Baker.	*95% distills between 120-145	130	0.88	1.1	1043	52
Methyl ether	" " "	34.0-35.0	74	0.72	1.9	652	55
Methyl ethyl ketone	" " "	*95% distills between 79-81	72	0.81	1.8	582	47

^aThe values for the lower flammability limits were taken from Howard, H. F. and Jones, G. W. "Limits of Flammability of Gases and Vapours", Bulletin 503, Bureau of Mines.

The coal gas used in these tests was taken directly from the town supply. The results of a chemical analysis of this gas using a Bunsen and Wheeler gas analysis apparatus are given below in Table 2.

Table 2

Analysis of coal gas used

Constituent	Carbon dioxide	Saturated hydrocarbons	Oxygen	Carbon monoxide	Hydrogen	Saturated hydrocarbons	Nitrogen
Concentration % by volume	3.2	5.1	1.2	25.0	43.3	13.1	8.4

The lower and upper flammability limits of the gas for vertically upward flame propagation in dry, carbon dioxide free air, measured in the Howard and Jones standard apparatus, were 5.2 and 55.0 per cent by volume respectively.

EXPERIMENTAL

The instruments examined were two Model 2 explosimeters manufactured by the Fano Safety Appliances Co. Ltd., Glasgow. Each instrument was supplied with three detector units. The sample to be tested is drawn over a heated platinum filament (in the detector unit) which forms one arm of a balanced Wheatstone's bridge. Combustion occurs at the surface of the filament producing a rise in temperature with a consequent increase in the electrical resistance of the filament. The bridge is thereby unbalanced to an extent which is a measure of the concentration of flammable vapour in the atmosphere being tested. The resultant current is measured by a milliammeter. The milliammeter dial is calibrated to give the vapour concentration as a percentage of the lower flammable limit. To act as a warning device, the dial from 60 per cent upwards, is coloured red. Incorporated in the instrument are inlet and outlet flame arresters for preventing flame propagation from the detector unit; a rubber aspirator bulb draws the sample for test through the instrument at a rate controlled by a flow regulating orifice located in the aspirator bulb coupling. The filament is heated by an electric current drawn from dry batteries but in the present work two 2 v. 20 A.H. accumulators connected in parallel to a variable potentiometer were used in order to avoid complications due to battery deterioration. A diagram of the electrical circuit and flow system of the explosimeter are given in Figure 1.

The principle of operation of the instruments is that equal volumes of lower limit concentrations of a number of vapours produce similar quantities of heat on combustion (see Table 1 column 8), and therefore produce similar rises in temperature of a filament upon which the vapours are burnt.

The principal function of the instrument is to give a warning of the presence of dangerous concentrations of flammable vapours or gases, and measurement of the precise concentration is less important. It is, however, essential that the instrument should not indicate a concentration lower than the actual value. For accurate work it would be necessary to calibrate the instrument in the vapour in which it is to be used.

Mixtures of air and vapour were prepared by a batch method. It was simpler and easier to operate than continuous flow methods because of the small amounts of liquid required to be evaporated.

The apparatus used is shown in Figure 2. A 20 gallon (91 litre) open ended drum contained a framework supporting a sheet of absorbent paper and was sealed across the top by a thin sheet of either polythene, cellophane or aluminium foil (0.0015, 0.0010 and 0.0025 in. thicknesses respectively). This cover also provided a safety vent in the event of an explosion occurring if mixtures above the lower flammable limit were being examined. The aluminium foil was used for those vapours which attacked or permeated through the other covering materials. A measured quantity of solvent was dropped from a microburette through a tube in the side of the drum on to the absorbent paper. The volume of liquid to be evaporated could be measured to 0.01 ml which was always less than 1 per cent of the total volume required. The inlet tube was then plugged and the solvent evaporated either by rocking the drum and thereby causing the paper and supporting framework to swing from side to side inside the drum, or, as in later tests, by operating an electrically driven fan installed in the drum. After thorough mixing, the sampling line of the explosimeter was connected to the tube in the side of the drum, and samples for test were withdrawn by operation of the explosimeter aspirator bulb. Each test required the passage through the instrument of approximately 0.25 litre of the vapour mixture so that withdrawing samples for test had little effect on the pressure in the container, and consequently on the mass rate of flow through the explosimeter, because of the large volume of gas from which the samples were taken.

In the tests carried out with coal gas/air mixtures, the mixtures were prepared by water displacement of a measured volume of coal gas from an aspirator into the twenty gallon open ended drum used previously. The mixtures were mechanically stirred before samples were withdrawn for test.

METHODS

n-Pentane is used as the standard vapour by the makers for the calibration of M.S.A. explosimeters and was therefore used for this work.

PERFORMANCE OF NEW DETECTORS

Three detector units supplied with each of two Model 2 M.S.A. explosimeters were compared using pentane/air mixtures at four concentrations. For each detector unit three mixtures were prepared at each concentration, the mean of the explosimeter readings obtained are shown plotted against the actual concentrations in Figure 3. One detector unit (No. 2) was later tested in greater detail to establish whether there was a direct proportionality between the instrument readings and the actual concentrations throughout the working range. The results are given in Figure 4.

AGING OF DETECTORS

The effect of prolonged filament heating of a detector unit in air was studied by applying a potential difference of 0.69 volts corresponding to operation in an 80 per cent lower flammable limit pentane/air mixture. Periodically, the detector (No. 5) was connected to the explosimeter and the readings obtained with pentane mixtures of 79 per cent of the lower limit concentration were compared with those from an untreated detector (No. 1). This latter served as a measure of the effect of chemical ageing by pentane, since it was used for these measurements only. The results of both these investigations are shown in Figure 5.

PERFORMANCE WITH OTHER COMMON SOLVENTS AND COAL GAS

Concurrently with the ageing experiments, one detector unit (No. 2) was used for comparing the performance of the explosimeter with the solvents shown in Table 1, viz. benzene, hexane, acetone, ethyl alcohol, amyl acetate, diethyl ether and methyl ethyl ketone, and with coal gas. Tests were made with 106, 79, 53 and 26 per cent mixtures, in triplicate with pentane, hexane, benzene, industrial methylated spirits, in duplicate with coal gas, and single determinations with ether and methyl ethyl ketone. The results are given in Table 5 and Figure 6.

SOLVENT ABSORPTION BY SAMPLING LINE

Qualitative tests were made on the absorption of solvents by the explosimeter sampling line. Samples of 100 per cent lower limit concentration were drawn through the sampling line for two minutes, and the line was then flushed with air for half a minute. After leaving for a further two minutes the aspirator bulb was again operated and the maximum explosimeter reading noted. The results are given in Table 3.

Table 3

Absorption of vapour by sampling line

Material	Maximum reading (as per cent lower limit)	
	Pentane	Benzene
Soft rubber	10	28
Polythene	5	24
Ethanol (as supplied)	5	34

RESULTS AND DISCUSSION

In the comparison of the three detector units supplied with each of the two explosimeters using standard pentane/air mixtures, the readings obtained at first with the three detectors of one explosimeter agreed very closely with the actual concentrations of the mixtures, whereas the readings obtained at first with the second batch of detectors supplied with the second explosimeter were all high (see Table 4 below).

Table 4

The comparison of detector units

Explosimeter number	Detector number	Mean explosimeter readings in pentane/air mixtures (per cent of lower flammable limit)			
		At 106 per cent	At 79 per cent	At 53 per cent	At 26 per cent
1	1	104	79	53	25
	2	100	80	53	23
	3	112	79	55	26
2	4	>112	95	67	34
	5	>112	99	69	36
	6	>112	102	72	38

The results obtained by interchanging the detector units, instruments and aspirator bulbs confirmed that the differences in the readings were due to differences in the detector units.

About five squeezen of the aspirator corresponding to a total flow of about 250 ml, in about $\frac{1}{2}$ minute, produced a steady deflection of the indicator needle which was maintained by continued aspiration.

Prolonged electrical heating of a detector filament (No. 3) in air for 350 hours produced irregular changes in the sensitivity of the detector, giving instrument readings higher than the actual concentrations of the pentane/air mixtures tested (see Figure 6).

Changes in detector sensitivity were also observed with the detector (No. 1) which was repeatedly used for measuring pentane/air mixtures but which was not subjected to electrical heating in the intervening periods. The duration of each of the tests was a little under two minutes, inclusive of the time taken to set the zero of the instrument. Two tests were carried out at each concentration on separately prepared mixtures, several hours elapsed between each pair of tests. Initially there was a rise in sensitivity, after which there was a sudden fall and the sensitivity returned to around its initial value.

PERFORMANCE WITH OTHER COMMON SOLVENTS AND COAL GAS

Comparisons were made between a number of vapours and gases using detector No. 2. The results are given in Table 5.

During these tests it was found that the sensitivity of the detector filament changed irregularly when checked in pentane/air mixtures. In consequence, the sensitivity to pentane was checked regularly; the results of the check experiments are included in Table 4 together with the main results. The differences between actual and indicated concentrations expressed as percentages of the actual concentrations, were obtained from the curves of Figure 6.

Table 5

Solvent or gas	Mean explosimeter readings for actual concentrations. Per cent lower flammable limit				Average deviation of explosimeter readings per cent of actual concentration	Explosimeter reading for 79 per cent pentane/air mixture. Per cent lower flammable limit	
	106	79	53	26		Before use	After use
Benzene	>112	100	73	37	+32	-	88
Hexane	109	85	58	27	+6	87½	88
Industrial Methylated Spirits	101	80	54	19	-4	88	88½
Diethyl ether	110	81	50	24	0	92	88
Methyl ethyl Ketone	70	53	30	13	-36	86	86
Coal gas*	>112	94½	58½	31½	+22	80	83

*Actual concentrations of coal gas examined were 100, 75, 50, 25 per cent lower flammable limit.

With benzene/air mixtures the instrument readings were about 32 per cent high and with hexane/air mixtures the readings were about 6 per cent high.

The concentrations of the mixtures with industrial methylated spirits were calculated assuming the solvent to be pure ethyl alcohol. The readings were about 4 per cent low. Three tests were made with pure ethyl alcohol which showed no deviation. Industrial methylated spirits and ethyl alcohol are thus reasonably comparable. The results for coal gas/air mixtures were about 22 per cent high. Methyl ethyl ketone gave consistent readings about 36 per cent low.

Diethyl ether, acetone and amyl acetate affected the sensitivity of the filament. In the first series of tests made with ether, triplicate tests were made in mixtures of 106 and 79 per cent actual concentration, and the readings obtained were 104 and 76 per cent. At 53 per cent actual concentration two successive readings were 46 per cent, but the third and fourth tests gave readings of 67 per cent. The instrument was then checked against a 79 per cent pentane/air mixture and gave a reading of 96 per cent compared with 88 per cent at the commencement of the test. The figures in Table 4 were obtained from a set of single tests made in 106, 79, 53 and 26 per cent ether/air mixtures which gave readings of 110, 81, 50 and 24 per cent. The tests were alternated with tests on pentane/air mixtures to check changes in filament sensitivity. The change of sensitivity was small, the pentane mixture gave readings of 92 per cent at the start of the test and 88 per cent at the finish.

When acetone was tested every reading obtained with any mixture was always less than the preceding reading. The readings decreased with the number of readings and also with the time between successive tests when more than one reading was made from the same batch of mixture. It seemed possible that the vapour was leaking through the cover of the drum, whether polythene or cellophane, but a drop in the readings was found when two drums were used, cover to cover, to reduce leakage, and also when aluminium foil covers were used. It was therefore concluded that acetone vapour was reducing the sensitivity of the filament. When tested in pentane it gave a low reading, but after a few minutes use in pentane the original sensitivity was restored.

With amyl acetate, the highest reading obtained from a 106 per cent mixture was 15 per cent.

Tests showed that solvent absorption on the inside wall of the sampling line does occur (Table 3). This action was specific, for example it was found that benzene was absorbed more freely on the Ethical sampling line supplied than on a similar tube of polythene, whereas the reverse was obtained with pentane. It is therefore necessary to flush out the sampling line with air after making a test, and also it should be flushed before using the instrument.

SUMMARY AND CONCLUSIONS

Two instruments with two batches of three detector filaments in each have been examined. With one batch of filaments all the readings were higher than the actual concentration. Readings from the other batch differed by about 3 per cent from the actual concentration, in 4 tests out of 12 the readings were low, in 3 tests they were high and in 5 tests they were correct. There was thus a notable difference between the two batches of filaments. The error in this instance was in a favourable direction, but conceivably other batches could be in error in an unfavourable way.

The sensitivity of the detector filament changes with age. One filament of the first batch, heated in air, for 50 hours gave a very high reading of 106 per cent in a 79 per cent pentane/air mixture. After 100 hours the readings decreased slightly but after 350 hours the reading was still over 100 per cent. The changes were erratic.

Another detector was used only in pentane/air mixtures and was initially correct in a 79 per cent mixture. The readings increased irregularly with the number of determinations made and reached a maximum of 92 per cent after 40 determinations had been made, then fell, and after 60 determinations the readings were within about 6 per cent of the actual concentration.

Different vapours produced different readings. The highest positive deviation was shown by benzene (37 per cent high), coal gas was 22 per cent high and hexane was 6 per cent high. Readings with pentane, industrial methylated spirit and diethyl ether were close to the actual concentrations and methyl ethyl ketone gave readings about 36 per cent low. No consistent readings were obtained with acetone or amyl acetate.

Ether, acetone and amyl acetate all affected the filament. After using in acetone the sensitivity was restored by heating the filament in pentane vapour.

The majority of the readings obtained were thus near to or above the actual concentration and for all the vapours except acetone and amyl acetate the instrument could be used with confidence to indicate the presence of hazardous amounts of vapour. With regard to methyl ethyl ketone, the low readings obtained suggest that it would be advantageous to extend the red warning on the dial to a lower figure. Thirty per cent would include the 50 per cent concentration of methyl ethyl ketone. The extension of the red warning area would also be advantageous when sampling tanks or compartments where pockets of different concentration can exist as it would be a safeguard against inadequate sampling where possible pockets of higher concentration could be overlooked.

The principle of approximately equal quantities of heat being produced by lower limit concentrations is sufficiently valid to permit the instrument to be used as a warning device but it does not permit the instrument to be used universally for precise measurement of vapours for which it has not been calibrated.

It has been noticed that the Poole (1) instrument carries a warning label concerning its use in certain vapours and there is also a note in the instruction book stating that the calibration covers the petroleum group of hydrocarbons and correction curves are required for other vapours. The M.S.A. instrument carries no label and the instruction book warns only against its use for high boiling solvents in ovens where condensation could occur in the sampling tube. It is suggested that the instrument should carry a warning label stating the vapours for which it is suitable and also recommending the user to consult the manufacturer before using it in other vapours.

The poisoning of the filament by acetone and amyl acetate indicates that the combustion type of instrument may not be suitable for them and possibly a different type of instrument would be preferable.

ACKNOWLEDGEMENT

Miss J. S. Hall assisted with the experimental work.

REFERENCE

1. POOLE, R. J. Inst. Elect. Engrs (1943) 25 Part II 258.

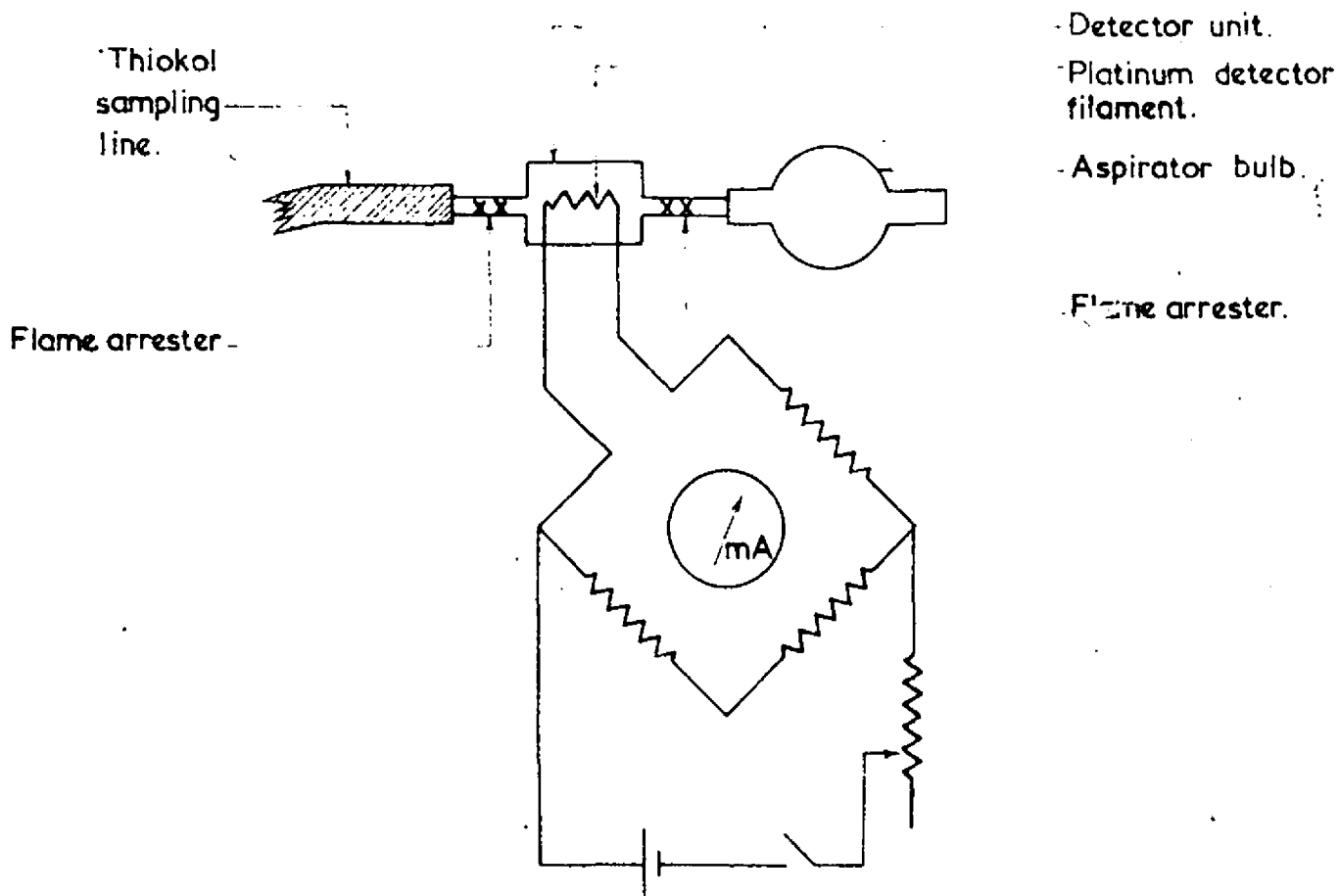


FIG. 1. DIAGRAM OF ELECTRICAL CIRCUIT AND FLOW SYSTEM OF EXPLOSIMETER.

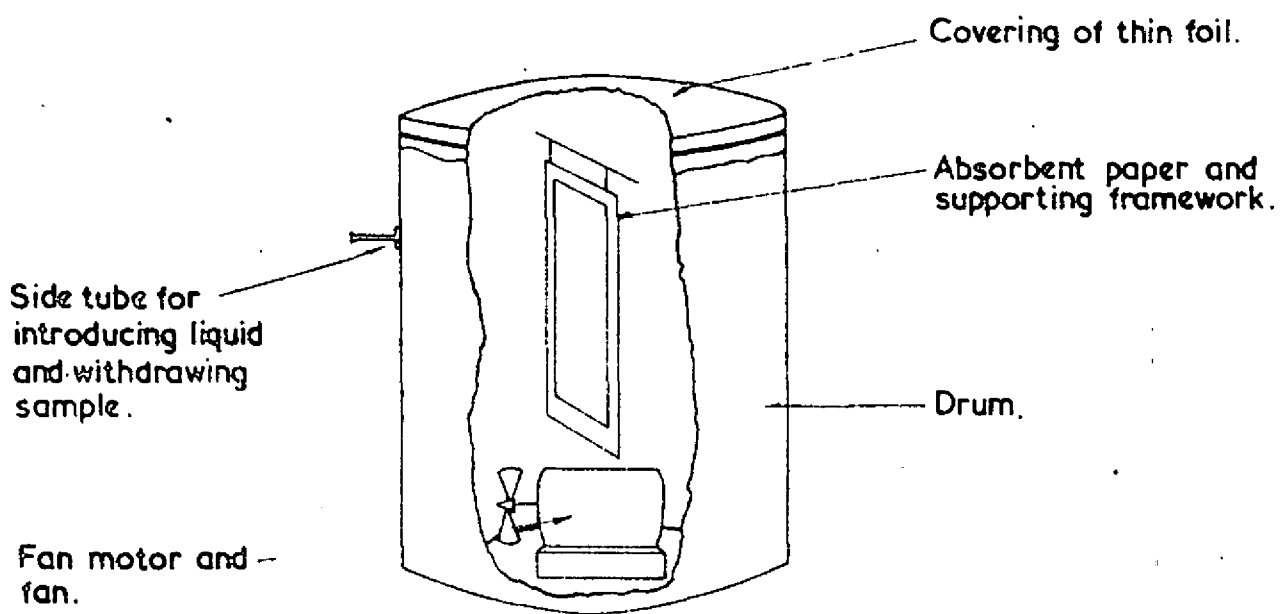
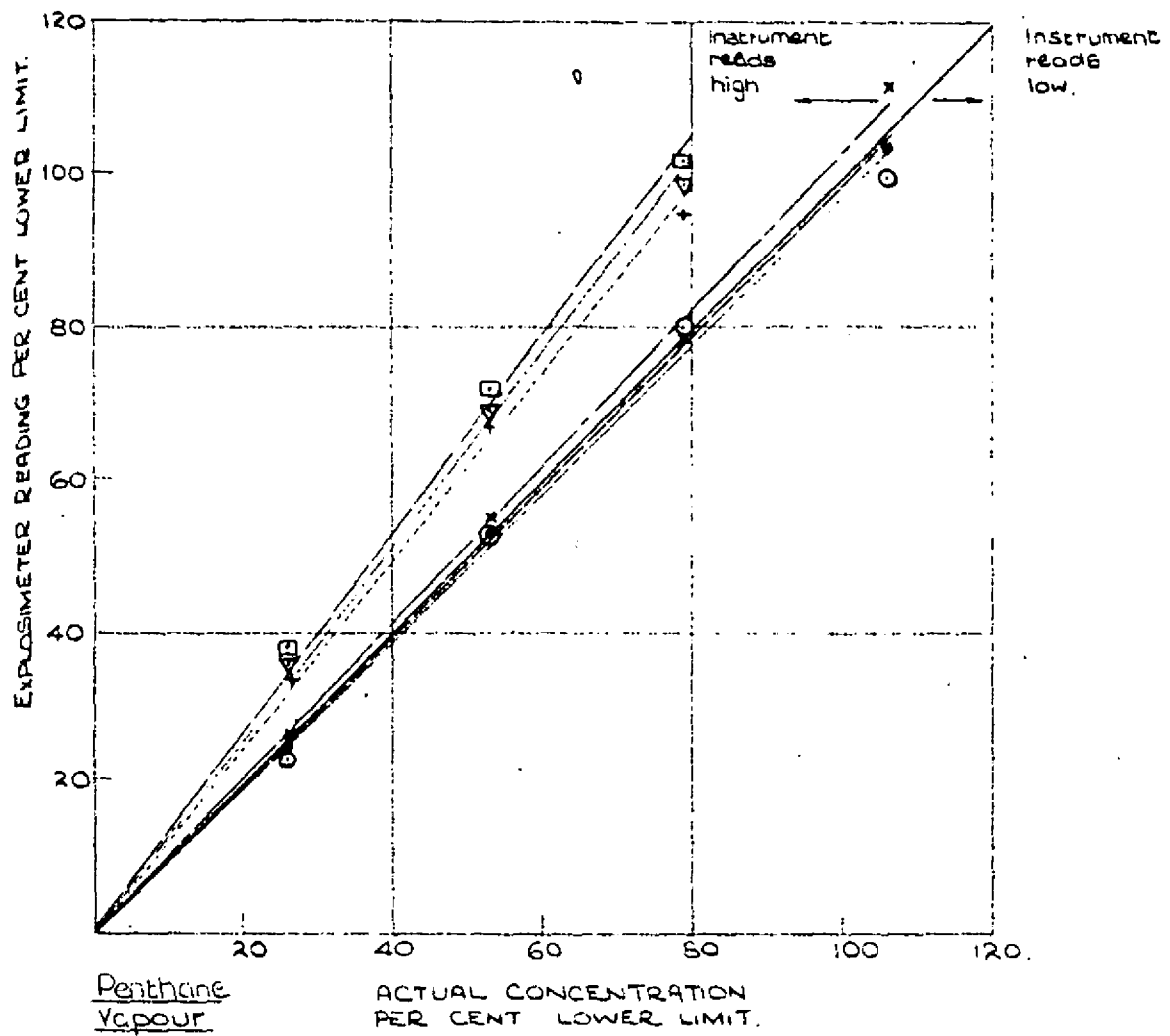


FIG. 2 APPARATUS FOR PREPARING VAPOUR / AIR MIXTURES.



- - Detector 1
 - - " 2
 - x - " 3
 - + - " 4
 - ▽ - " 5
 - - " 6
- } Batch 1.
- } Batch 2.

FIG. 3. COMPARISON OF NEW DETECTOR UNITS BEFORE AGEING OR OTHER TREATMENT.

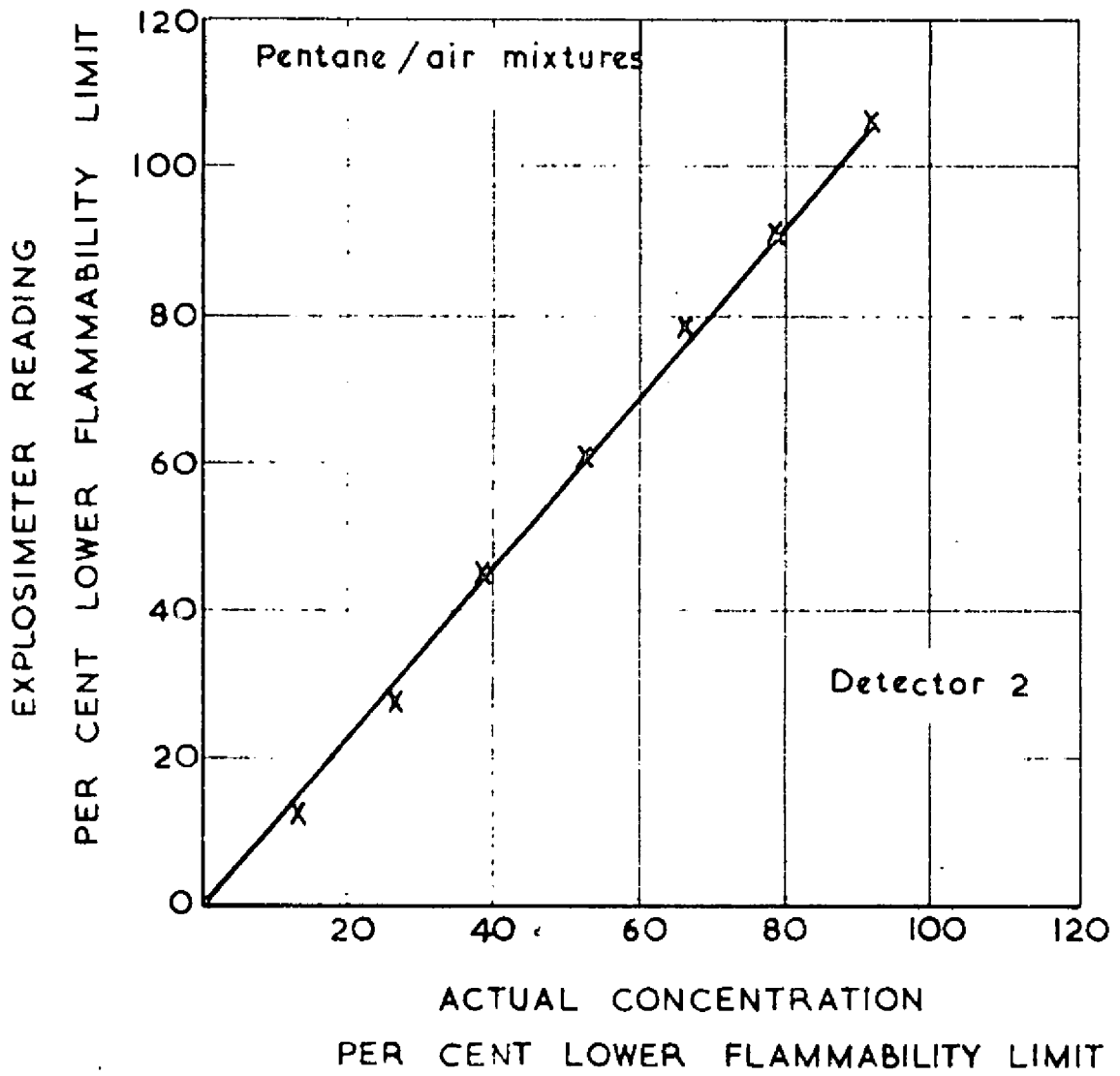


FIG.4. TEST FOR LINEARITY OF RESPONSE

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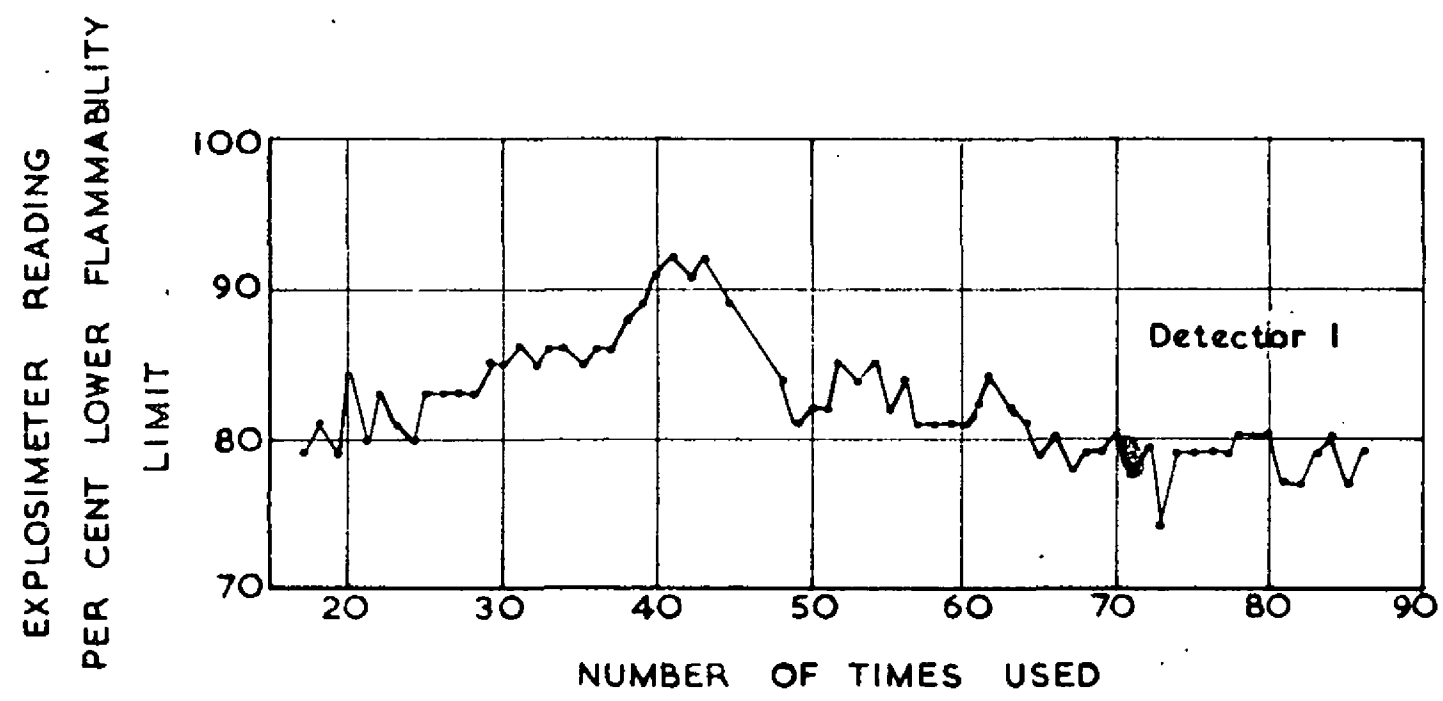
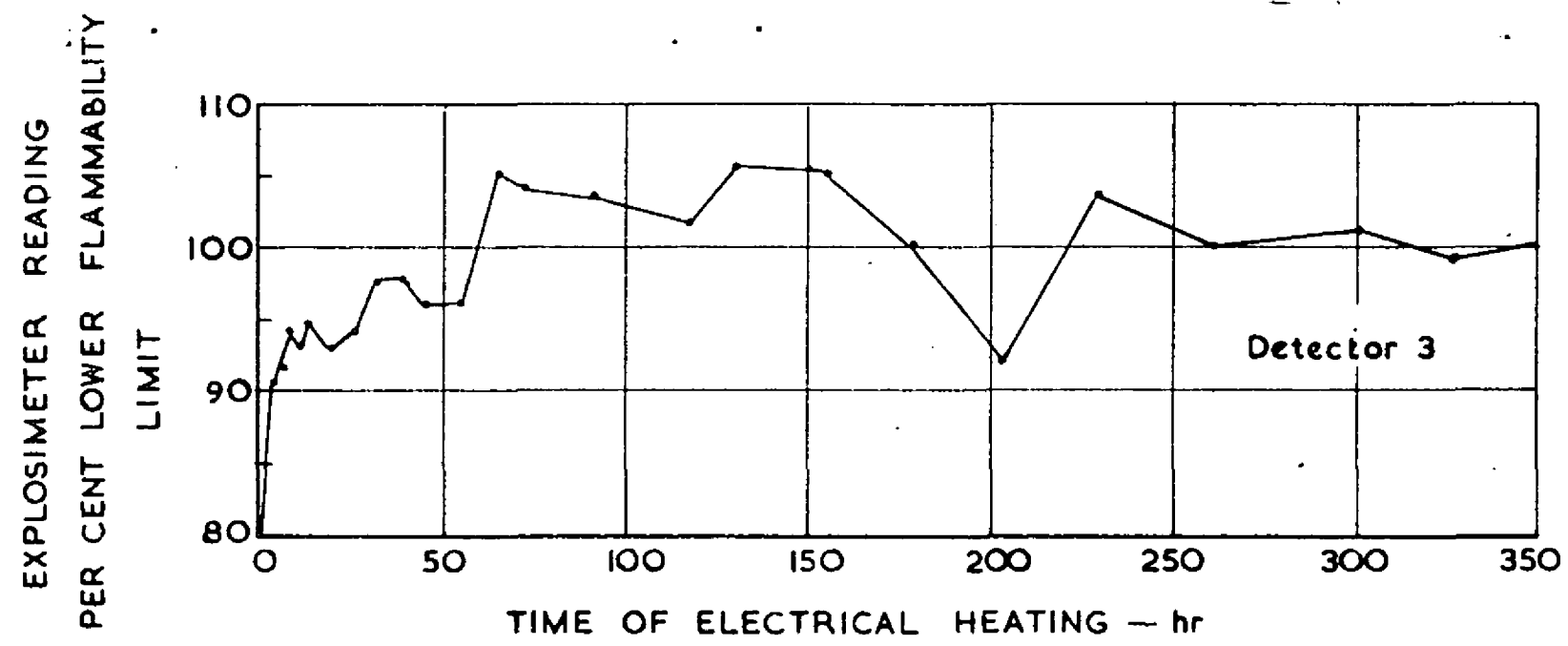


FIG.5. AGEING OF DETECTORS (CONCENTRATION OF TEST MIXTURE = 79 PER CENT LOWER LIMIT PENTANE/AIR)

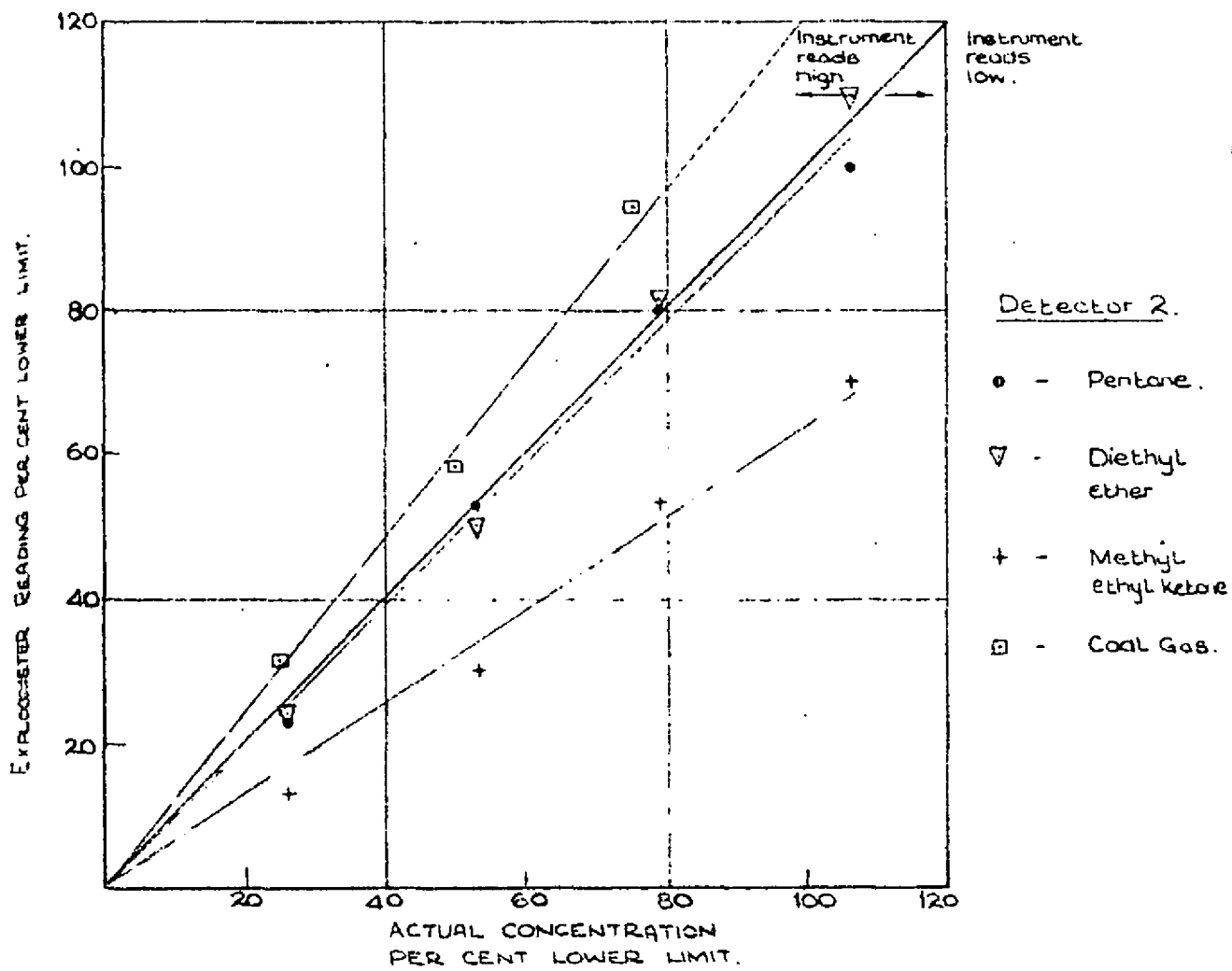
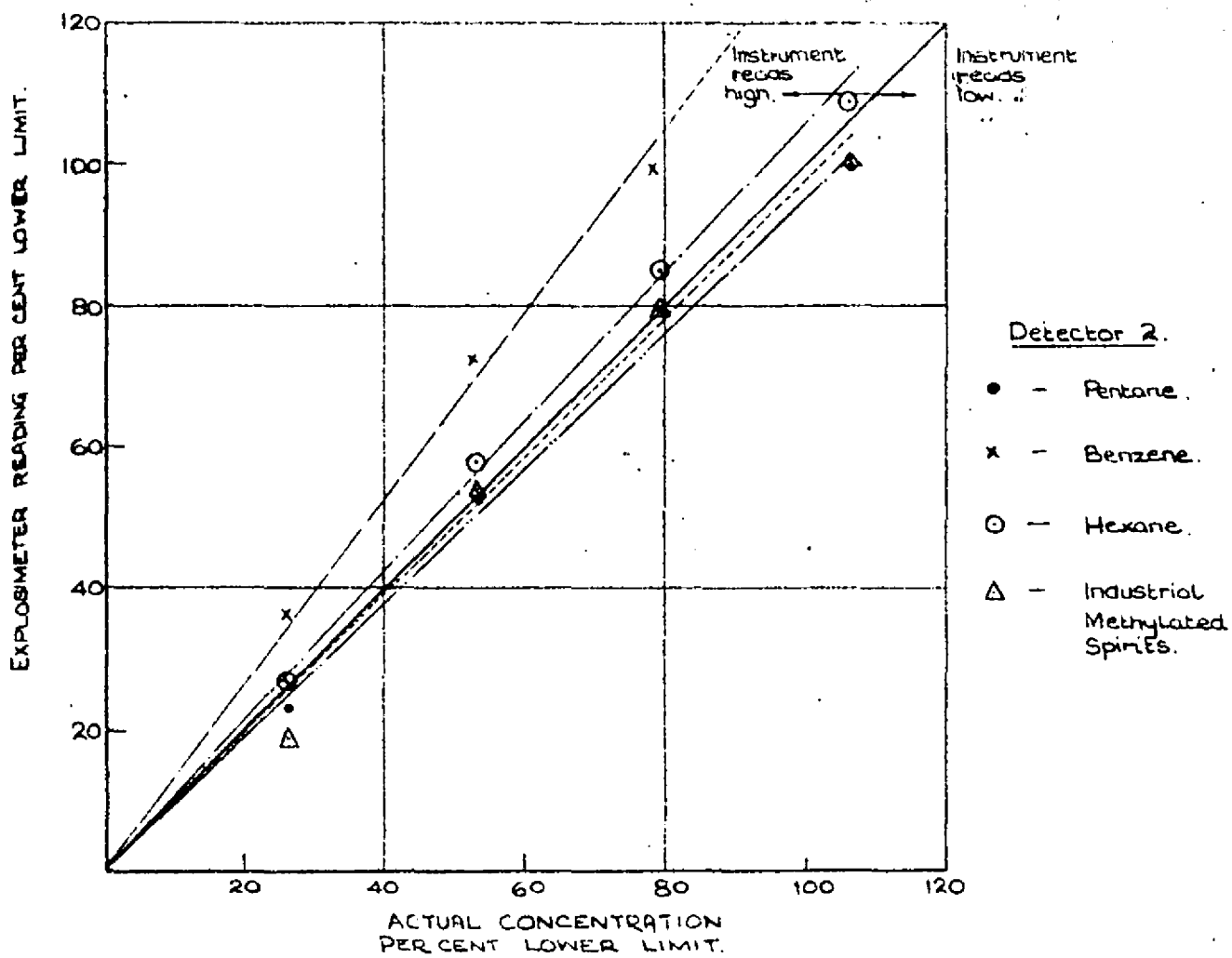


FIG 6 COMPARISON OF PERFORMANCE WITH VARIOUS SOLVENTS AND COAL GAS.