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Vehicle Emission Control Technology - A Correlation of Emissions in Relation to Source

by

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ABSTRACT

Vehicle emission control technology literature is reviewed and the conclusions are reached that the emissions control problem has been approached from too narrow a viewpoint. An "end of the pipeline" solution will not be economically feasible, and a new overall approach is needed to tackle the problem more realistically.

Various automotive air pollutants are monitored at three sites in England. A correlation study is performed to try to pinpoint the source of the pollutants. The results of the short-term sampling procedure are that no simple correlations of the various pollutants prove statistically significant and a "pinpointing" attempt fails.

A new method for determination of organic lead in air is tested out for its stability.

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PART I

Vehicle Emission Control Technology.

- A Review -

1. Introduction

1.1 General

The atmosphere is a thin cloak of air wrapped around the earth. Although it contains only one atom for every 200,000 atoms in the earth's interior, it is far more important to life than is the great interior mass of our planet. The atmosphere supplies oxygen (O_2) to breathe, carbon dioxide (CO_2) for photosynthesis, an ozone (O_3) screen against deadly ultraviolet light, rain to water the continents, and insulation from the cold of space.

The chief atoms of the atmosphere are: nitrogen (N), oxygen (O), hydrogen (H), carbon (C), and argon (Ar). These are non-metallic elements, and in the periodic table (see a chemistry textbook) are found predominantly in the upper right-hand region. This is the gas-forming region, and among the many atmospheric gases and vapours to which this region gives birth are the five major constituents of clean air. The constituents and their percentages of the atmosphere are as follows:

Gas	Molecular weight	Percentage by vol. mol fraction
Nitrogen	N_2 - 28.016	75,65
Oxygen	O_2 - 32.000	20,29
Water	H_2O - 18.016	3,12
Argon	Ar - 39.944	0,90
Carbon dioxide	CO_2 - 44.010	0,03

Other gases in the atmosphere constitute less than 0.003 percent, as given in the following table:

Gas	Molecular weight	Percentage as ppm (vol)
Neon	Ne - 20.183	17,4
Helium	He - 4.003	5,0
Methane	CH_4 - 16.04	1,16
Krypton	Kr - 83.8	0,97
Nitrous oxide	N_2O - 44.01	0,94
Hydrogen	H_2 - 2.016	0,49
Xenon	Xe - 131.3	0,08
Ozone	O_3 - 48.000	0,01
Radon	Rn - 222.	$0{,}06 \times 10^{-12}$

Minor constituents may also include dust, pollen, bacteria, spores, smoke particles, SO_2, H_2S, hydrocarbons, and larger amounts of CO_2 and ozone, depending on weather, volcanic activity, local industrial activity, and concentration of human, animal, and vehicle population. In certain enclosed spaces the minor constituents will wary considerably with industrial operations and with occupancy by humans, plants, or animals.

So far, man's activities have had little effect on the three abundant gases-nitrogen, oxygen, and argon. But nearly every other chemical constituent has been altered in local areas, and some throughout the world.

Enough carbon dioxide has been pumped into the air by fossil fuel combustion to raise its content in the atmosphere 10 percent in only one century-a trend that threatens worldwide changes in climate. The precence of particles in the air has also increased throughout the world, and could have similar repercussions. Worse, the atmosphere above many urban areas is now laden with toxic substances like carbon monoxide, sulphur dioxide, and ozone. These exist in amounts up to hundred times greater than are found in fresh air. In addition, exotic chemical substances that our ancestors never encountered are now common above cities.

Clearly, we cannot afford to ignore these changes in the chemical environment of our atmosphere, for each day we inhale- and thereby bathe our sensitive lung tissue in- about 20,000 liters of air. There is no other part of our chemical environment with which we are in such intimate and continuous contact.

Air pollution is the presence in the ambient air of one or more contaminants, which can be naturally occurring or man-made. The quantities, characteristics, and duration of these contaminants are, ormay tend to be, injurious to human, plant, and animal life or may interfere with the enjoyment of life or use of property.

1.2 Classification of air pollutants

Major classes	Subclasses	Typical members
Inorganic gases	Oxides of nitrogen (NO_x)	Nitrogen dioxide, nitric oxide
	Oxides of sulphur (SO_x)	Sulphur dioxide, sulphuric acid
	Other inorganics	Ammonia, carbon monoxide, chlorine, hydrogen fluoride, hydrogen sulphide, ozone

Organic gases	Hydrocarbons	Benzene, butadiene, butene, ethylene, isooctane, methane
	Aldehydes, ketones	Acetone,formaldehyde
	Other organics	Acids, alcohols, chlorinated hydrocarbons, peroxyacyl nitrates, polynuclear aromatics
Aerosols	Solid particulate matter	Dusts, smoke
	Liquid particulates	Fumes, oil mists, polymeric reaction-products

(Source of tables: Handbook of Environmental Control, vol. I, Air Pollution ; Chemical Rubber Co., 1972)

1.3 Relation of thesis to air pollution

Successful widespread use of catalysts to purify gases and vapours in manufacturing processes in the technological world is supported by extensive research competence in academic and industrial laboratories. This fact leads one to wonder why catalysts are not widely used to purify automotive exhaust. The major difficulty with past approaches to catalytic devices as a solution to the automotive exhaust problem has been philosophical. Most proposers and critics of catalytic devices earlier took the viewpoint that such devices should be capable of bearing either all or none of the burden of reducing emission levels (Haagen-Smit, A.J. 1964), (Heinen, C.M., 1968), (Ridgway, S.J. and J.C. Lair, 1960), (London, A.L., 1961), (Stern, A.C., 1962).

There were a few exceptions (De Rycke, D., 1963), (Innes, W.B. and K. Tsu, 1962). The earlier objective of a single catalytic device adaptable to any car and capable of purifying the exhaust of virtually any engine while meeting rigorous standards of cost, maintenance, and durability (see California Requirements for Device Certification as of 1965) has faded away.

Much has been said (Hurn, R.W., 1968), (U.S. Dept. of Comm., Dec., 1967), (Faith, W.L., 1960), (Innes, W.B. and K. Tsu, 1962) of the deactivation of exhaust catalysts by lead, sulphur and other chemical compounds. Basically, these can be viewed as economic problems rather than as technical difficulties which must be overcome. Indeed, the solutions to most of such problems are already on the market. Lead is being filtered out of petrol by catalytic mufflers, or alternatively vehicles run on lead-free petrol. Since 1966 in California, and all over the U.S. in 1968, engine modifications have reduced the amount of hydrocarbons emitted by the average new car to about one-third and carbon monoxide to about one-half the level exhausted by new cars in earlier years (Brubacher, M.L. and E.P. Grant, 1967). In a context of well-maintained engines modified for relatively low exhaust-emissions levels, disposable or refillable catalytic devices will perform satisfactorily. However, they will not perform well unless designed into specific power systems by car manufacturers.

Gasoline engines have been evolving steadily over the years in terms of performance and economy of operation. Drivers of cars have become conditioned to demanding and expecting good drivability, instantaneous power at their toe-tips, good mileage per gallon of fuel being especially important after the birth of the power crisis 1973/4, and minimum maintenance cost. In the majority of car purchasing decisions, cost, fuel economy, performance, and styling continue to be the major deciding factors. The value system of the driving public does not yet generally place enough premium on superior exhaust control systems or on a program of regular maintenance of their cars by highly skilled mechanics. Car advertising, heavily directed at styling and performance, may be taken as a sometimes fallible indicator of the driving public's priorities. The public's opinion of car maintenance is indicated by the relatively low estate of skilled garage mechanics and the relatively large amount of do-it-yourself car repair. Therefore, to control and to maintain control of automotive air pollution, enforced legislation is an absolute necessity. In the U.S., legislated standards for automotive exhaust are a reality, of which the most stringent ones of the state of California are an example, which many nations aim their standards towards. Of extreme importance is the fact that this program was laid out for making these standards progressively more stringent over a five year period. Car manufacturers have met these standards by making economic choices between feasible alternative methods. In the recent years, the main indication has been that most are going over to catalytic cleaning systems, although there are still problems connected with them to be solved.

A number of new types of engines with less severe emission problems than present internal combustion spark ignition engines have been publicized and discussed (Bolt, J.A., 1967), (Korth, M.V., and A.H. Rose, Jr., 1968), (Lienesch,J.H. and R.W. Wade, 1968). Among them are electrical motors energized by batteries or fuel cells, external combustion engines using water or some other working fluid, and gas turbine engines (Agnew, W.G., 1968). As a matter of necessity, car manufacturers have constructed prototypes and made cost-performance studies of such new power systems for at least two reasons. First, car manufacturers need to know if their competitive position might be underminable. Second, they need to know the cost differential available for further improving the internal combustion spark ignition engine. Thus far it appears that automobiles will be powered by present types of gasoline engines for at least the next decade (Bolt, J.A. 1967), (Ludwig, J.H., 1967), (Tsao, K.C. et al., 1974). More fundamental is the criticism of the present type type of automobile powered by any engine as a costly, hazardous, and inefficient means of transport (Ross, H.R., 1968). Development of an alternative to our present car-motorway system is likely to require several decades.

1.4 The role of Catalytic Devices

The proliferation and evolution of techniques for the control of air pollutants in automotive exhaust has been dramatically rapid over the past ten years and promises to be equally dramatic over the next few. There is a mountain of literature recording the data of the past and projecting possible paths of the future. To relate this welter of data and techniques to catalytic devices, a systems approach is needed. A catalytic device for exhaust treatment cannot be designed in isolation because it is only another significant variable in the particular power system of which it is a part. Other parts of the power system must be optimized to include the capabilities and limitations of the device. To be sure, a single overdesigned type of device could be built to handle the exhaust from the unmodified engines of well-maintained compact, sport, or luxury cars and some poorly maintained cars. Because of the large car population, the economic waste of such overdesign has been and will continue to be unacceptable to legislators and to the automobile manufacturers.

In terms of a systems approach, the power train of cars has been subjected to a new constraint. Carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxides (NO_x) in the exhaust must now not exceed certain limiting values. As frequently happens when a new, significant variable is introduced in a system, large blocks of earlier data become irrelevant or must be repeated with measurement of the new variable included. Most of the significant variables affecting exhaust-emission levels of CO, HC, and NO_x have been either identified or studied thoroughly within the past 20 years. For reasons already cited, car manufacturers cannot summarily sacrifice the performance optimization of engines to achieve minimal exhaust-emission levels. However, the mechanisms controlling emission levels of CO, HC, and NO_x have been sufficiently well clarified that car manufacturers have been able to meet the emission standards without impairing engine perfomance. In fact, car manufacturers have done rather well so far (Brubacher, M.L. and E.P. Grant, 1967), (McMichael, W.R et al., 1968), (Acres, G.J.K. and B.J. Cooper, 1972), (Cantwell et al., 1974), and one might well ask what factors will compel the use of catalytic devices as emissions standards approach closer to zero. Two factors come to mind. First, the car manufacturers have had to concentrate more on reducing CO and HC levels until 1971, when the law of reduced NO_x emissions came into force in the States. Up to that time, while reducing CO and HC levels, the only restrictions on NO_x was that it should not increase by more than 15 percent in the process. The point is that combustion conditions within the cylinders favoring low

CO and HC emissions also favor increased NO_x emissions.

The second factor that will compel the use of catalytic devices is somewhat more subtle. It concerns the way in which compliance legislated emissions standards is to be enforced. To comply with federal standards (U.S.), car manufacturers must obtain certification that the cars they produce for sale will on the average not exceed standard emission levels of CO, HC, and NO_x (Federal Register, 1968, 33, no. 108). Eventually, each state will have to enforce continued compliance to emission standards from the amorphous public. Such a situation virtually demands that each and every car periodically must pass an emissions test administered by the state. California and New Jersey were among the pioneers to studying exhaust analysers for the use in their state-operated car inspection stations (EST, 2,9,659 (1968)), (Pattison et al., 1968). Other states have followed. If we then consider the plight of the motorist whose car does not pass inspection because its HC emission level is somewhat high. Engine flaws or maladjustments causing relatively small increases in emission levels can be very elusive of diagnosis. Recycling through an inspection station time after time without passing is a frustrating experience. At such a juncture there would be much appeal to a snap-on type of catalytic device or "exhaust filter" similar to present air and oil filters with respect to maintenance and installation. Another aspect of the foregoing concerns quality control in car manufacture. Car manufacture is a mass production operation. Performance of cars produced will fall on the familiar Gaussian bell-shaped probability distribution curve. As emission standards are pushed toward zero, the curve will be compressed. Two papers on carburettor quality control (Bier, K.C. et al., 1969) and (Eberhardt J.E. and J.A. Beck, 1969) demonstrate the problem well. The cost of keeping the performance of all new engines within a very narrow quality control range may well begin to exceed the cost of designing a catalytic device into the power system. As regards older engines that still will have to comply with regulations, this solution seems to be even more favorable.

2. History of catalytic devices

There has been a steady stream of patents and publications on catalytic exhaust treatment for the past 50 years. At times the stream has slowed to a tricle but there have been three major surges. The first surge came in the late 1920's and early 1930's (see table on pre-1950 U.S. patents concerned with exhaust catalysts next page). Since the engines of the day were of low compression ratio and were richly carburetted, NO_x emissions were not a real problem. As a matter of fact, because of the low automobile population, there was not a real automotive exhaust problem at all in today's terms. Even so, the exhaust smoke was visible, the smell of unburned gasoline was apparent, the toxicity and presence of CO were well known, and tetraethyl lead was finding use as an antiknock additive for gasoline. Many scientists were genuinely concerned. Those who worked on the problem used the approach described in the first chapter, namely to devise a sort of "black box" to be attached to any engine. Improvements in car manufacture did reduce the visible manifestations of automobile exhaust (Agnew, W.G., 1968). There was no documentation that the invisible portion of automobile exhaust was directly or indirectly an air pollution problem. Therefore, there was no basis for legislation regulating automotive exhaust.

The second surge in effort expended on catalytic exhaust treatment started slowly in the 1950's, grew to enormous proportions in the early 1960's, and ended abruptly in 1964 (see tables of patents, these years). Conclusive documentation was then at hand demonstrating that the HC and NO_x in automotive exhaust were the major cause of photochemical smog in the Los

Angeles basin (Faith W.L., et al., 1957), (Faith W.L., 1957), Leighton, P.A., 1961),(Altshuller, A.P., Lonneman, W.A., Sutterfield, F.D. and S.L. Kopczynski, 1971). Much has been written about the triangular Los Angeles bowl with mountains for two of the walls and a very light sea breeze for the third wall. Thermal inversion layers of air put a lid on the bowl. The picture is completed by the bright California sun shining through the lid and irradiating the exhaust of about three million automobiles to make photochemical smog inside the covered bowl. Smog incidents regularly aroused public clamour that something should be done.

California's situation was almost desperate in the early 1960's. Most of the nonautomotive sources of air pollution had been or would soon be cleaned up. Photochemical smog had been publicly identified with automotive exhaust. The California Motor Vehicle Pollution Control Board (CMVPCB) had been established to do something about the problem. California had passed a law requiring that the concentration of HC and CO in exhaust gas be substantially reduced.

Automotive Pollutant Levels vs Standards in California 1960

	Approx. uncontrolled exhaust emission level per car	Maximum exhaust emission level required by law-if triggered
HC	900 ppm	275 ppm
CO	3.2 %	1.5 %
NO_x	1500 ppm	350 ppm

The law was inoperative until at least two devices that could reduce emission levels,as shown previously, had met the requirements detailed in the "California Requirements for Device Certification in 1964 "(Middleton,J.T., 1962). In other words, the CMVPCB was faced with public demand to do something about smog, knew that auto exhaust gas was the primary cause of smog, but had an inoperative law for remedial action (Middleton, J.T., 1961). Car manufacturers, collectively known as Detroit, were generating much valuable information (Heinen, C.M., 1968). However, at that time the likelyhood that Detroit would trigger the law seemed remote (Jensen, D.A., 1964), (Caplan, J.D., 1962).

At this juncture, various teams of catalyst manufacturers and muffler manufacturers (Faith, W.L., 1963) such as Walker Manufacturing Co. with American Cyanamid Co., W.R. Grace Co. with Norris-Thermador Co., and Arvin Co. with Universal Oil Products (UOP) began to run fleet tests to qualify catalytic mufflers or noncatalytic afterburners for HC and CO removal under the California law. These teams were later to be characterized as "unsung heroes" (Jensen, D.A., 1964). Again the approach was as described in the first chapter, the "black box" one. The test fleets were selected by the CMVPCB to be representative of the California car population. It was surprising and discouraging to discover what poor condition an engine could be in and still provide quite adequate transportation. In initial fleet tests, no catalytic devices were able to cope with the formidable emission levels of these badly worn and/or maladjusted engines. In subsequent fleet trials the teams were allowed an initial tune-up of the engines to manufacturer's specifications. A sufficient number of devices then passed fleet tests to trigger the law. At the same time Detroit announced a capability to meet California's standards with their own devices (Applied Science and Technology Index, 1964, p. 27). Detroit's devices relied primarily on lean carburetion with or without injection of air into the exhaust system for further combustion of HC and CO to meet standards (Beckman, E.W. et al., 1967), (Chandler, J.M. et al., 1967), (Steinhagen W.K. et al., 1967). In due course, Detroit's fleets also passed the requirements set by California in 1964. In 1965 the law was revised. The new requirements of California State included 50,000 mile device durability and a cost limitation of not more than $65 per car for the exhaust control system. The devices that triggered the law were decertified for not meeting the revised requirements. In retrospect, this outcome was best for the U.S. economy.

The third surge of effort on catalytic devices came in the late 1960's and is still going strong. For the first time a systems approach was used with Detroit and catalyst manufacturers are cooperating to optimize power systems including a catalytic device. One group consists of the Ford Motor Company and the American Cyanamid Company. Another group is the Inter Industry Emissions Control Group (IIECG) made up initially of Ford and the Mobile Oil Corporation, later joined by American Oil, Atlantic Richfield, Fiat S.p.A., Marathon Oil, Mitsubishi Heavy Industries Ltd., Nissan Motor Company (Datsun), Standard Oil of Ohio, Sun Oil, and Toyo Kogyo Co. Ltd. (Clewell, D.H., 1968). A third group made up of Esso and Chrysler were focussing mainly on fuel and engine technology without the use of catalytic devices. As can be seen from this, the main impetus in the catalyst devices technology has been in the U.S. in the early years of the "art", but has had widespread effects all over the world. In 1970, the U.S. standards were translated into grams per mile and simultaneously made more stringent. California added oxides of nitrogen to the list of pollutants brought under control in 1971, and with the 1973 cars, control of NO_x became mandatory throughout the country. The scheme read as follows:

Federal Exhaust Emissions Requirements,
1975 Test Procedure, g/mile.

	Prior to Control (1960)	1968	1970	1972	1973	1975-76
HC	15	6.3	4.1	3.0	-	0.41
CO	90	51	34	28	-	3.4
NO_x	5	-	-	-	3.1	0.4

As described before, the main research effort pre-1970 went into oxidation catalysts, whilst post-1970 research has been more concerned with the reduction of NO_x into molecular nitrogen. Up to 1975 (recently postponed to 1976), emission targets for CO and HCs could be achieved by engine modifications alone (in the case of new engines), and NO_x could be controlled by recirculating a proportion of the exhaust gas (EGR) into the induction manifold. Subsequently in 1976 (now postponed to 1977, at least), the permitted level for NO_x emissions would be substantially reduced to a value that could not be controlled by EGR. This gradual imposition of emission legislation has had a considerable influence on the developement of control methods including the use of and further research into catalysts.

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3. Catalyst Technology

Over the past 50 years engine and fuel technologies have made tremendous strides. Catalyst technology also has made great advances. An enormous catalysis literature has been built up. A large array of sophisticated empirical systems have been developed. There is still lacking, however, a quantitative theory explicitly describing the mechanism of heterogeneous catalysis. In the absence of predictive theory, a great deal of screen testing of different catalyst compositions must be performed. Catalyst compositions with excellent activity for exhaust gas purification have been found as a result of screen testing (see lists in chapter 2). Whether these catalysts are or are not adequate depends on the way minimum performance standards are set, as discussed previously.

Catalysts used in devices are composite materials usually in the form of free-flowing granules or honeycomb-type support for the active area. Individual granules are either cylindrical or spherical with the diameter of the circular cross-section about 1/16 to 1/4 in. Catalyst granules are usually built up from a porous refractory inorganic oxide, such as alumina, silica, silica-alumina mixtures, or calcined clays, called the catalyst support. Covering the surface of the pore walls is a thin layer, hopefully not more than a few molecules deep, of the active catalytic ingredient called the promoter. The promoter is usually one or more metals or metallic oxides. Promoters decrease the original pore volume of the support depending on the amount of promoter added. Porosity of catalysts for use in exhaust treatment ranges from about 0.2 cc/g, a dense catalyst, to over 1.0 cc/g, a light catalyst. For tolerance toward lead from leaded gasoline, high porosity is desirable. On the other hand, low porosity is desirable for good mechanical strength of the catalyst granules (see pat. 3,282,861). In practice, one compromises on intermediate porosities. The average diameter of the pores in an exhaust catalyst is measured in Ångströms (1×10^{-10}m) and is usually less than 100 Å. Internal surface area due to these small pores ranges from 100 to 300 m^2/g in fresh catalyst. In more mundane terms, a 10-lb bed of such catalyst has a pore wall surface area of roughly 100-300 acres. Because the thin film of active promoter is spread out over this surface it is of the utmost importance to avoid conditions which cause the pores to become blocked with inert material, cause the surface area to decrease by destruction of small pores, or cause the film of promoter to agglomerate into crystalline masses.

Considering first the thermal degradation of typical catalyst supports, alumina, silica, and clays begin to lose surface area rapidly in dry heat at elevated temperatures (Levy, R.M. et al., 1968). The effect of the loss of surface area on catalyst activity is cumulative, irreversible, and adverse. At high temperature there is migration of molecular moieties of silica or alumina in the support. As the smaller pores become filled, the remaining pores become larger. For relatively pure alumina there is not a net decrease in pore volume (Levy, 1968). There is a net decrease in pore volume for catalysts made from silica-alumina, which may also involve the promotors (see pat. 3,094,394), (Leak, R.J. et al., 1970), (Schlaffer, W.G., et al., 1965). A net decrease in pore volume simply means that the catalyst granules shrink in size as sintering progresses. Mobility of the molecular moieties of alumina or silica is enhanced by the presence of water vapour. Automobile exhaust contains about 15% by weight of water vapour. The table below illustrates the surface area decline of gamma alumina as a function of time and temperature:

Effect of thermal treatment on alumina surface area

	Surface area of gamma alumina after	
Temperature	5 hr in air	5 hr in 3:1 air-stream
Room temperature	278	
600°C (1112°F)	210	154
700°C (1292°F)	192	131
800°C (1472°F)	155	106
900°C (1652°F)	129	81

(From Levy, R.M., et al.,1966)

Large quantities of gamma alumina-based catalysts are used by the petrolum refining industry. Their operations with these catalysts are essentially steady-state continuous hydrogenations or dehydrogenations at temperatures ranging up to about 900°F. A carbon deposit called coke, although it contains some hydrogen, does accumulate in the catalyst pores. It is periodically burned off under carefully controlled conditions. Even so, the catalyst is exposed to transient temperatures of perhaps 1200-1300°F during coke burnoff. The life of such catalysts will range from one to eight years depending on the temperature histoy of the particular catalyst. Life of catalyst in exhaust devices can certainly be cut short thermally as evidenced by the initial fleet failures in California. However, in subsequent fleet tests, (Weaver, E.E., 1969), (Yarrington, R.M. and W.E. Bambrick, 1970), the primary cause of catalyst deactivation was deposition of lead on the catalyst rather than catalyst sintering. In these fleet tests there were high-temperature (above 1200°F) excursions but not prolonged high-temperature situations.

The three components of exhaust gas desired to be catalytically converted are CO, HC, and NO_x. Most catalytic device work prior to 1970 was directed at the oxidation of CO and HC to the innocuous products CO_2 and H_2O. Over the long term, CO_2 may not be innocuous (Stanford Res. Inst., Feb.,1968). Removal of NO_x will be considered later. Catalysts disclosed in the patent literature for HC and CO oxidation appear to include virtually all the metals of the Periodic Table single or in combination on about all of the known refractory porous inorganic oxide supports. The tables in the previous chapter list some but by no means all of the pertinent U.S. patents. Those listed are intended to illustrate the diversity of catalyst compositions and the diversity of people and organizations active in the area. There have also been publications on HC and CO oxidation catalysts containing chromium (Feenan, J.F., et al., 1964), cobalt (Schachner, H., 1960), vanadium (Innes, W.B. and R. Duffy, 1961), uranium (Bienstock, D. et al., 1963), copper (Kontsoukos, E., and Nobe, K., 1964), and other metals (Cannon, W.A.,and Welling, C.E., 1962), (Hoffer, L.J.E. et al., 1964), Reddi, M.M. and R.A. Baker, 1964). Filiform (Leak, R.J. et al., 1968) and honeycomb (Johnson, L.L. et al., 1961) catalyst structures have also been described, tested, and are now commercially available. Their catalytic action is much the same as described for the granular type. In sum, catalysts of excellent oxidation activity for HC and CO are known. The problem is rather to design specific catalysts for specific devices to serve specific engines.

Catalyst activity may be considered in terms of the Arrhenius rate equation:

$$r = A \cdot \exp(-E_{act}/RT)$$

where:

r = reaction rate,
A = pre-exponential term
E_{act} = energy of activation
R = gas constant
T = absolute temperature

For a reaction normally proceeding in the vapour phase the activation energy is lower when the reactants are adsorbed on a catalyst surface because of the energy of chemisorption. For first-order reactions this may be shown by writing the exponent term as $-(E_{act} - Q)/RT$ where Q is the energy of chemisorption. More generally, the numerator of the exponent is called the apparent activation energy. Catalytic oxidation of HC, CO, and H_2 in exhaust gas appears to follow first-order kinetics as long as there is an excess oxygen present (Innes, W.B., and K.Tsu, 1961) A catalyst not only effectively lowers activation energy requirements, it also substantially increases the pre-exponential term A (Thomas, J.M. and W.J. Thomas, 1967). In non-catalytic vapour phase reactions, A is presumed to be a measure of the number of effective collisions of reactant molecules per unit time. An effective collision is defined as one resulting in reaction. For catalytic reactions A is presumed to be a measure of the number of active sites on the catalyst surface. An active site may be defined as a place on the catalyst capable of inducing effective collisions between reactants, one or more of which is chemisorbed on the catalyst. There is usually an effective increase in concentration when a reactant goes from the vapour phase to the chemisorbed state. Because chemisorption lowers activation energy, a higher percentage of collisions is likely to be effective. Both the increase in concentration and the lower activation energy requirement will increase A and hence the reaction rate.

When exhaust gas containing O_2, CO, and HC is put through a catalyst bed at room temperature nothing much happens. As the exhaust gas temperature is raised a point will be reached, usually in the range of 300-700°F, where the temperature in the catalyst bed begins to exceed the temperature of the inlet exhaust. This is called the lightoff temperature for that particular catalyst.

Starting with a cold engine, the time elapsed until lightoff will depend on the temperature, composition, and rate of the exhaust gas flow and on the mass and heat capacity of all the hardware that can cool off the exhaust gas. Heat sinks during warmup are the exhaust manifolds, the exhaust pipe, any exhaust pretreating devices such as lead traps, the catalytic device, and the catalyst bed.

The lightoff temperature depends, other things being equal, on the promoters and the number of active sites or surface area of the catalyst. Different promoters form different chemisorbed species with the reactants, resulting in greater or lesser apparent activation energies for reaction to occur. While the number of active sites is obviously important, there are other factors. These can be seen when the sequence of steps in a catalyzed reaction is examined:

Diffusion of reactants into catalyst pores
Chemisorption of reactants
Formation of activated complex
Breakdown of activated complex
Desorption of reaction products
Diffusion of products out of catalyst pores

Promoters have differing rates for the sequence of chemisorption-reaction-desorption (Thomas & Thomas, 1967), i.e. they are able to handle greater or lesser amounts of reactants per unit of time per active site. Platinoid metal promoters usually provide for lower lightoff temperatures than base metals, probably not because of greater site density but more likely through combination of greater lowering of activation energy requirement and higher rates of processing reactants at active sites.

As the catalyst in a device loses surface area the lightoff temperature increases. For practical purposes, when the surface area of an exhaust catalyst reaches about 40 m^2/g, the lightoff temperature is usually well above 1000^{o}F and the catalyst is dead. In the previous chapter, a number of patents are listed, directed towards solving the lightoff problem. Proposed solutions range from use of an "igniter catalyst" to electrical heaters to injection of raw gasoline into the inlet exhaust.

The importance of early lightoff can be seen in the way HC and CO are determined for device certification. Vehicles are tested from a cold start on an appropriately loaded chassis dynamometer. The vehicle engine is put through a seven-mode cycle (idle, acceleration, cruise, and deceleration) four times for warmup and five times after it is hot. The HC and CO analyses from the four warmup cycles and from two of the hot cycles are used to calculate emission levels. Weighting factors reduce the influence of warmup more than the engine choke increases it. If a catalytic device does not achieve lightoff until the first hot cycle, the very best HC and CO conversions that could be expected from it would be less than 60%. It is worth noting that emission levels formerly expressed in parts per million or percent are now expressed in terms of grams per mile. The change was made to correlate emission standards with car size. There are tables available giving emission concentrations for HC and CO for several car sizes (usually expressed in weight terms).

The problem of lead deactivation of exhaust catalysts is well known (Innes, W.B. and K. Tsu, 1962), (Weaver, E.E., 1969), (Yarrington, R.M. and W.E. Bambrick, 1970). At present, leaded gasoline may not legally contain more than 4 ml of tetraethyl lead per gallon of gasoline and in practice averages about 2.5 ml/gallon. Scavengers must also be added, usually ethylene dichloride and dibromide, to prevent large deposits of lead oxides from building up in the engine cylinders. Volatile lead halide salts are formed via the scavengers. Gasoline also contains combined sulphur to the extent of about 0.05% by weight. This sulphur is oxidized to SO_2 when gasoline is burned. At the flame-front, where the temperature is very high in the cylinder (5000^oF) any SO_3 formed will dissociate back to SO_2 and O_2. The equilibrium constant shifts very much in favour of SO_3 formation at the temperature of the exhaust system, usually below 1200^oF. At these temperatures the reaction rate of SO_2 and O_2 is so low that very little SO_3 should be formed. However, almost any oxidation catalyst effective for CO and HC is also a good catalyst for SO_2 oxidation. So, linked up with the water vapour formed in the exhaust system, the formation of sulphuric acid is possible. In fact, a recent study has confirmed that catalytic converters will produce H_2SO_4 emissions. It was found that converter equipped cars give off 0.05 g H_2SO_4 per mile in a fine mist (Moran, J., 1974). Ford/Batelle found that SO_2 coming from the engine is converted to SO_3 in the catalytic device as compared with an engine without a converter by a concentration factor of 50 to 1. (SAE preprint 740287, 1974). The use of the converters will also involve the exposure of the general population to low levels of new polluting platinum and palladium compounds. Exposure to platinum compounds is likely to range from 1/100 to 1/10 of the threshold limit values for platinum salts (Oil & Gas J., 29 Oct. 1973). It has been predicted that this combination of H_2SO_4 and metal salts could become a health hazard in the urban U.S. in 2 years with the existing programme.

The dewpoint of the lead halide salts in undiluted exhaust gas ranges from about 650 to 850^{o}F (Yarrington & Bambrick, 1970). Diffusion of lead halide salts as liquid or vapour into the catalyst pores followed by reaction with SO_3, either in the vapour phase or just before desorption of SO_3 from the catalyst surface, undoubtedly accounts for the fact that lead deposits on exhaust catalysts are invariably mostly lead sulphate (Yarrington & Bambrick, 1970).

Nonvolatile lead salts block the pores of the catalyst and lower the diffusion rate of CO and HC to the interior of the catalyst support. An account is made of patents related to lead deactivation of catalysts in the previous chapter. Among them are

Among them are patents on the washing of lead from catalyst and on subjacting catalysts to impact to dislodge the lead salts and restore catalyst activity. Another indication that lead salts act by imposing a diffusion barrier rather than poisoning the promoter is that CO conversion falls of much less rapidly than HC conversion as lead deposits build up (Weaver,E.E.,1969). CO is a relatively small and light molecule with a higher diffusion coefficient than the average HC in exhaust gas.

Periodically, questions concerning the elimination of all lead from gasoline are raised. A U.S. report from 1967 by Lawson et al., issued by the API shows then that eliminating all lead from gasoline would involve a capital cost to the petroleum industry of about 4.25 billion dollars. Amortization and added operating cost would appear publicly as an increase of several cents per gallon in the selling price of gasoline. Another solution is the use of lead filters prior to the exhaust or thermal reactor type converters. Those are generally more expensive than the catalytic type, but can use leaded fuels and hence higher compression ratios can be used for the engine design resulting in a greater fuel economy. The selection, therefore, is purely a question of balancing out the economy of the alternatives. The use of the lead "muffler" filters alone would considerably cut down the existing emissions of lead in the atmosphere.

An important characteristic of catalysts is their selectivty in catalyzing some reactions more than others. Selectivity is related to the energy of chemisorption of reactants and to the activation energy needed for reaction to occur. Both of these factors can be measured for a given catalyst-reactant system.

There is, however, no known way to predict quantitatively how selectivity will change as the catalyst is changed. Generally, oxidation catalysts for exhaust gas tend to oxidize preferentially the more reactive hydrocarbons such as olefins, iso-paraffins, and cycloparaffins (Innes, W.B. and Duffy, R., 1961). Aromatics and acetylenes are oxidized more slowly. As might be expected, methane and ethane are the most difficult to oxidize. As reaction temperature is raised, the selectivty of catalysts in general decreases and ultimately disappears.

Total CO and hydrocarbon (H/C) emissions by the CVS test are greatly dependent on the cold-start activity of the oxidation catalysts, as said before. Therefore, in the most recent years, development of satisfactory catalysts has been concentrated primarily toward improving their low temperature activity (Carlson, D.W., Chu, P. and F.G. Dwyer, 1973), (Lloyd, W.G. and D.R. Rowe, 1973), (Wedding, B. and Farranto, R.J., 1974), and (Acres, G.J.K., 1974).

A wide variety of laboratory screening tests have been devised for CO/HC oxidation catalysts. The test of Innes and Duffy (1961) was described before. Acres and Cooper (1972) used both synthetic gas mixtures and exhaust from a single-cylinder engine to measure the activity and durability of oxidation catalysts and the effects of various catalyst poisons. Similar studies have been undertaken by Barnes and Klimisch (1973), Bauerle and Nobe (1973), (1974), Liederman et al. (1973) and Voorhoeve et al. (1972). Others have described these systems mathematically (Harned, J.L., 1972), (Hawthorn, R.D., 1974) and Kuo et al., who also did some work on the oxidation kinetics.

As mentioned before, poisoning of catalysts by lead in gasoline has caused designers a lot of trouble, resulting in the remedy of using lead-free fuels. Lead can, however, not be completely removed. The lead in "unleaded" fuel comes from contamination by leaded fuel as a result of sharing pipelines, tank trucks, and other fuel distribution facilities.

The effects of sulphur combustion products on particulate base metal vehicle emission control catalysts can be even more severe than those of lead. Sulphur alters the chemical composition of these catalysts, so low levels of sulphur accumulation on the catalyst are more detrimental to catalyst performance than small accumulations of lead or phosphorus (Fishel, 1974). The exact poisoning mechanisms of these elements on the catalyst are currently not well understood, but significant research effort is being undertaken explaining these (Bomback et al.,1975), (Hegedus, 1974), (Otto et al., 1974) and (Giacomazzi and Homfeld, 1973). Some of the results indicate that lead, phosphorus, and sulphur are deposited from the gas phase, whereas zinc and iron are deposited as particulates. The formation of an impervious layer of lead sulphate and phosphate and the penetration into the washcoat micropore structure seem to account for the poisoning effect which these elements have on catalytic activity.

Sulphur occurs naturally in crude oil, although in varying concentrations. Reducing the sulphur content of fuel by refinery processes is possible, but very costly. Phosphorus is intentionally added as a component in lead scavengers, valve seat antiwear agents, or detergents. As a result of lead omission, etc. phosphorus can easily be omitted.

The literature on removal of NO_x from exhaust is relatively sparse in comparison with the bulk on HC and CO up till 1970, when the progress on HC and CO removal was advanced enough, and the goals in sight attaining the 1975-76 standards, the main research emphasis shifted over to NO_x emissions control catalysts and devices for those. A few patents (see list) are based on the premise that there is not enough O_2 present to interfere with NO_x reduction. It has been shown that CO reacts with oxygen preferentially to NO over catalysts such as copper-cobalt-alumina (Baker and Doerr, 1964) and chromia (Shelef, M. et al., 1968). In the former study it is stated that sufficient CO must be present to consume all of the O_2 first with at least a stoichiometric amount of CO left for NO_x reduction. Obviously, for this to occur, the air-fuel mixture in the cylinders must contain less oxygen than required for complete combustion. When there was a sufficient excess of CO, NO_x removals of about 90% were obtained (Baker and Doerr). In the latter study (Shelef et al.) relatively poor conversions of NO to a mixture of N_2 and N_2O were obtained over chromia on alumina even in the absence of oxygen. It must be pointed out that the objective of the latter study was to develop a hypothesis to explain catalyst selectivity. Other investigators using catalysts of copper on silica (Sourirajan and Blumenthal, 1961) or barium promoted copper chromite (Ayen and Ng, 1966), obtained about 90% conversions of NO_x essentially in the absence of oxygen. These early studies showed clearly, where the main problem would lie. The maximum NO_x concentrations occur near to the stoichiometric air/fuel ratio and coincide with the minimum CO and HC concentrations. This is all the more awkward, bearing in mind that the power output of the engine and the highest fuel conversion efficiency are both at a maximum either at or slightly on the rich side of stoichiometric air/fuel ratios. The ideal emission control system from a power/fuel economy aspect would therefore be one which operates at or around the stoichiometric point. Theoretically, a perfect combustion should occur:

$$C_nH_m + x\,O_2 + 3.76x\,N_2 \rightarrow a\,CO_2 + b\,H_2O + c\,N_2$$

leaving only water, carbon dioxide, and nitrogen in the exhaust. Unfortunately, it doesn't happen that way. In addition to the water vapour, CO_2 , and N_2, many other products result, including undesirable ones:

$$C_nH_m + xO_2 + 3.76xN_2 \rightarrow aCO_2 + bH_2O + cN_2 + dC_nH_m + eCO + fNO + gO_2 + hH_2$$

As said before, some of the hydrocarbons pass through the cylinder without burning; incomplete oxidation results in the production of some carbon monoxide, some hydrogen present in the mixture always remains, and some of the nitrogen of the air combines with oxygen in various proportions.

So, perhaps the most objectionable of the combustion products results from reactions that shouldn't take place at all. Nitrogen is partially oxidized at the elevated temperatures in the engine cylinders. The resulting oxides of nitrogen contribute to the photochemical production of ozone (Altshuller and Bufalini, 1965), and the brownish nitrogen dioxide produced in the atmosphere is obnoxious itself. The oxides of nitrogen are produced in any combustion process. High pressure is not neccessary, so gas turbines as well as piston engines are similarly subject.

The extent to which this endothermic oxidation of the nitrogen takes place is a function of temperature. The relative amounts of oxides might seem to depend also on the air/fuel ratio, but because of the thermodynamics almost all of the oxide of nitrogen actually produced in the cylinder is nitric oxide (Heywood and Keck, 1973), NO. Some of this is later oxidized, in the atmosphere and to a minor degree beginning in the exhaust system, to nitrogen dioxide, NO_2. Analysis and laboratory results have shown that the most rapid production of nitrogen oxides occurs in the hottest region of the combustion chamber close to the spark plug. The first part of the charge to burn attains the highest temperature, and in the case of propane-air mixture with an equivalence ratio of 1.0 the concentration of nitric oxide has been found to reach temporary levels as high as one mole percent in the region around the spark plug (Benson, J.D., 1969), (Lawson, A., 1974), (Mayland, B.J., 1974). As the temperature decreases from its maximum the rate of oxide formation declines and the relaxation of the compounds accelerates, by the time the exhaust valve opens this portion of the gas in the cylinder contains about half or less that at peak concentration.

Thirty percent of the way across the combustion chamber the temperature never rises to the level it does at the spark plug, and the nitric oxide concentration reaches a lesser maximum. Expansion already has begun by that time, and temperature is falling, but since combustion of the charge is still in progress the decay is less rapid. About 2/3 of the distance across the combustion chamber the behaviour is similar, but the temperature reaches a much lower maximum.

The equilibrium constant of the controlling reaction for the formation of nitric oxide at the temperatures involved indicates that considerable NO can be expected to form during combustion but that the concentration should be down almost to zero at exhaust temperatures. Actually the concentration freezes at some quantity far above the equilibrium value for the exhaust temperature.

One practical measure that can be taken to promote reduction of nitric oxide at the exhaust ports is placement of the spark plug at a location removed from the center to keep the average temperature lower than it would be with the plug in the center.

Although design and operational changes have been necessary to meet the emission level limits specified in the past into the 1973 model year, these were evolutionary changes that could be made by applying engineering and scientific principles that are established ingredients of engine technology. In addition to the evaporation control system, modifications adopted were the closed positive crankcase ventilation system, the air injection reactor, changes to the ignition system and ignition timing control, improved carburettion, and internal engine design changes. Control of NO_x has introduced new complications and, with the 1973 model, exhaust gas recirculation (EGR), was introduced.

Engine modifications alone will nevertheless not suffice for the proposed NO_x controlled reduction of 1976-77 in the U.S. The efforts include calling on the assistance of a reducing catalyst.

The most practical and convenient method of removing NO is by catalytic reduction with CO or H_2, both of which are present in ample amounts in the exhaust gases. In practical systems, where NO, CO_2, H_2, and H_2O are simultaneously present, the following reactions may occur:

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \qquad (i)$$

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \qquad (ii)$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \qquad (iii)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (iv)$$

$$NO_2 + H_2 \rightarrow NH_3 + H_2O \qquad (v)$$

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad (vi)$$

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \qquad (vii)$$

While the products of both Equations (i) and (ii) are environmentally acceptable, the formation of ammonia by (iii) creates a major problem. In the dual converter approach for complete purification of auto exhaust, any ammonia produced in the reduction stage is reoxidized to NO in the second stage, thereby decreasing the overall effectiveness of the system. Although the formation of NH_3 from the reaction of NO with H_2 has long been recognized, it was largely overlooked during the early work in exhaust gas purification.

All of the common commercially available catalysts, which had been used for CO and hydrocarbon oxidation, produced large quantities of NH_3 during NO reduction in an exhaust gas environment. The extent of NH_3 formation over certain noble metals during the reduction of NO with H_2 has been researched into by various people (Meguerian and Lang, SAE 710291, 1970), (Shelef and Gandhi, 1972) and (Klimisch and Barnes, 1972). There is still not enough information existing concerning the competitive reduction of NO with mixtures of CO and H_2 in the presence of these catalysts. Furthermore, there is not general agreement as to the importance of NH_3 decomposition as a contributing step in NO conversion reactions where the overall NH_3 formation is low.

Some recent investigation of this selective reduction has lead to a hypothesis that the catalytic reduction of NO to N_2 in the engine exhaust is a 2-step process, in which ammonia is an intermediate product, i.e. (iii) → (vi). A possibility that cannot be ruled out for the second step, however, is a reaction between ammonia and more nitric oxide, i.e. (iii) → (vii), (Starkman,1974).

The two-step idea suggests that two catalytic components should be used to promote the two reactions. For instance, nickel has been found effective in promoting decomposition of ammonia, (Reed and Eisenberg, 1974), and reduction of NO to NH_3 could be catalyzed by copper, palladium, or platinum, (Chieu, 1973), (Sci. Am., 228, 44), (Johnson and Gallagher, 1973), (Libby, 1971), (Mayland, 1974), (Unland, 1973).

Ruthenium-containing catalysts have been found to have a pronounced selectivity for reduction to molecular nitrogen, and several laboratories have pursued recently the development of practical ruthenium-containing catalysts (Shelef and Gandhi, 1972), (Klimisch and Taylor, E.S.T., 7, 127, 1973), (Otto and Shelef, 1973).

With the use of ruthenium catalysts it soon became apparent that their stability under oxidizing conditions is poor. Analysis of spent catalysts revealed severe losses of the active component, readily explained by the formation and removal of the volatile tetroxide. However, for maximum effectiveness of the complete emission control system, it is very desirable that the reduction catalyst be able to function also as an oxidation catalyst, during the early warmup period. The heavy load this oxidizing period places upon the durability of the catalyst may in the case of ruthenium be difficult to handle.

The simplest way already available to meet U.S. 1977 standards for cars is to operate a two stage system with the first catalyst being used, under essentially reducing conditions, for NO_x control and subsequent introduction of secondary air before passing the exhaust gases through the oxidation catalyst as in the 1976 system. If the oxidation properties of the ruthenium-based catalysts can be utilized and, if exhaust gas composition is accurately controlled by keeping the air/fuel ratio within a narrow range (about 0.9-0.98), it is possible to operate a single bed system as there is sufficient oxygen present to oxidise CO and that part of the HC which is not used to reduce NO_x.

Selected Pre-1950 U.S. Patents Concerned with Catalytic Devices for Oxidizing HC and CO in Exhaust Gas

U.S. patent no., date of issue, inventor and assignee	Catalysis disclosed	Comment
1,522,111; Jan.6,1925 A.Franck-Phillipson	MnO_2	Catalyst in removable cartridge protected from particles by an upstream bed of light, porous material.
1,605,484; Nov.2,1926 C.E.Thompson	Pt or Pd on asbestos, CuO, zirconia	Filter and recycle portion of exhaust back through engine. All exhaust catalytically treated before discharge.
1,789,812; Jan.20,1931 J.C.W. Frazer	Chromite of a metal in Groups VI,VII,VIII	Directed primarily at CO removal.
1,867,325; July 12, 1932; H.A.Neville	Oxide of Fe, Co, or Ni plus one or more of another metallic oxide	Directed at catalyzing the water-gas shift reaction between CO and H_2O in exhaust gas.
1,902,160; Mar. 21, 1933; J.C.W.Frazer et al.	Copper chromite prepared by a specified method	Add additional air to exhaust. Omit air initially to reduce catalyst to lower its lightoff temperature
1,875,024; Aug. 30, 1932; Mine Safety Appliances	Oxides of Co, Ni,Mn,or Fe on pumice or asbestos	Two venturis to add air to exhaust. Larger venturi opened by thermostat to cool catalyst bed

2,071,119; Feb. 16, 1937; J.Harger	Oxides of Fe,Mn, Cr,Cu,or Ti singly or in combination on Al_2O_3	Remarkable grasp of problem. Radial flow reactor with venturi for secondary air, overtemperature bypass,spot heater for lightoff.

Selected Post-1950 U.S. Patents Primarily Directed at Catalyst Compositions for Oxidising CO and HC in Exhaust Gas. (Nomenclature as before)

3,220,794; Nov. 30,1965 Stiles to DuPont	Mangano-chromia-manganite ± metal oxide or chromate ± refractory interspersant	High Mn:Cr ratio lends selectivity for CO oxidation, low Mn:Cr for HC oxidation
3,228,746; Jan. 11,1966 Howk et al.to DuPont	Manganese chromite plus a chromite of Cu,Ni,Fe,Zn,Cd,Sn, or Bi	Considerable detail on process of preparation
3,230,034; Jan. 18,1966 Stiles to DuPont	List 108 catalytic materials which can be mixed with 35 refractory dispersants	High temperature stability obtained by building up catalyst from 1500Å crystallites of promoters and dispersants
3,282,861; Nov. 1,1966 Innes to American Cyanamid	Vanadia and cupria on alumina ± small amount of Pd.SiO_2 may be used to stabilize Al_2O_3 to heat	Discusses lead tolerance and crush strength versus catalyst pore volume and particle size

3,271,324; Sept. 6,1966 Stephens et al.to Ethyl	Alumina impregnated with Cu,Cu+Fe, Fe+Mn+Cu,Cu+Pd,Cu+Co, Cu+Co+V,or Cu+rare earth	Catalysts said to be heat stable and of low lightoff temperature. Road tested
3,346,328; Oct. 10,1967 F.J.Sergeys et al.	Copper exchanged crystalline zeolite Part of Cu^{2+} converted to CuO by NaOH	Ratio of Cu^{2+} to CuO said to govern selectivity for CO or HC oxidation
3,362,783; Jan.9, 1968 Leak to Texaco	Metal wool coated with Al_2O_3.Promoter then put on Al_2O_3 Refractory wools are disclosed	Better attrition resistance and lead tolerance is claimed
3,288,558; Nov. 29,1966 Briggs et al.to W.R. Grace	10% CuO,5% Cr_2O_3, and 0.02% Pd on gamma alumina	Road tested and said to have performed satisfactorily
3,249,558; May 3,1966 Kearbey to Esso	80% Al_2O_3, 10% V_2O_5,and 10% of either CuO,Ag_2O, Cr_2O_3, or MnO	Catalysts said to have excellent activity and lead tolerance
3,304,150; Feb. 14,1967 Stover et al.to W.C. Grace	0-4% CoO,0-4% CuO 12% MnO_2,0.02% Pd + 2-10% Fe_2O_3 on gamma alumina	The iron oxide is said to confer Pb tolerance to catalyst
3,409,390; Nov. 5,1968 Hoekstra to UOP	Stabilize with Ca, Ba,or Sr, metals of Groups VB,VIB or VIII singly or in combination on a support	Alkaline earth said to increase thermal stability and Pb tolerance

Selected U.S. Patents Directed at Device and Catalyst Improvements to Cause Lightoff at Lower Temperature (Nomenclature as before

2,898,202; Aug. 4,1959 Houdry et al. to Oxy-Catalyst	Pt,Cu, or Pd on alumina,beryllia, thoria,or magnesia	Inject fuel into upstram of device as needed to maintain catalyst above lightoff temperature
2,937,490; May 24,1960 Calvert to Oxy-Catalyst	Pt,Pd,CuO, or $CuO-CrO_3$ on alumina	Interrupt spark and cause misfires so that unburned fuel will cause catalyst bed to heat up rapidly
3,222,140; Dec. 7,1965 Scivally et al. to UOP	Metals of Groups I,V,VI,and VII singly or in combination ± refractory support	Direct flow of exhaust gas with dampers to save part of catalyst bed for lightoff only
3,224,831; Dec. 21,1965 Stephens to Ethyl Corp.	Metals Groups IB and VIII,5th,6th periods on Al_2O_3 plus 1-15% H_3PO_4	Phosphoric acid said to lower lightoff temperature
3,253,883; May 31,1966 Jaffe to Monsanto	Hydroxides of Cu, Co or Fe,Cr,and Zr and/or Hf, dried, tabletted,and calcined	Low lightoff and high strength claimed
3,254,966; June 7,1966 Block et al. to UOP	Pt,Fe,Cu and/or Cr on alumina plus Pt or Pd plated on alloy steel wire	Main bed of metal wool catalyst with pockets of alumina catalyst for lightoff

3,259,454; July 5,1966 Michalko to UOP	Pt group metal concentrated at periphery of alumina beads	Life and lightoff of catalyst said to be improved
3,291,564; Dec. 13,1966 Kearby to Esso	Metal oxidation promoter on support of alumina stabilized with barium chloride	Barium salt said to enhance thermal stability of Al_2O_3
3,310,366; Mar. 21,1967 Koepernik to Kali Chemie	Metal oxidation promoter on Al_2O_3 prepared by a special process	Claim high thermal stability and activity
3,375,059; Mar. 26,1968 Gerhold to UOP	Igniter catalyst of smaller particle size and higher promoter level	Igniter catalyst is minor component in device catalyst bed
3,378,334; Apr. 16,1968 Bloch to UOP	Igniter catalyst of higher promoter level but same size as rest of bed	Igniter catalyst said to facilitate lightoff

Selected U.S. Patents Related to Lead Deactivation of Catalysts

U.S. patent no.; date of issue; inventor and assignee	Technique disclosed	Comment
2,772,147; Nov. 27,1956 Bowen et al. to Oxy-Catalyst	External reservoir of catalyst to maintain catalyst level in catalyst bed	Use of partly filled bed: leaves room for catalyst to move and abrade away fouling deposits
2,867,497; Jan. 6,1959 Houdry et al. to Oxy-Catalyst	Leach Pt catalyst with dilute HNO_3 and Cu catalysts with ammonium acetate	Periodic leaching of lead salts from catalyst to restore activity
3,247,665; April 26,1966 Behrens to Texaco	Porous alumina coating containing phosphate or chromate on steel wool	Pretreat exhaust to remove lead as phosphate or chromate before entry to catalyst bed
3,259,453; July 5,1966 Stiles to DuPont	Chambered device with Pb scavenger upstream to catal.	Scavengers are sulphates of Na, K Li, NH_3 and Mg
3,024,593; Mar. 13,1962 Houdry to Oxy-Catalyst	Catalyst geometric surface of 115-250 in^2 per CID of engine	Geometric surface, bed thickness and bed cross-section ranges said to optimize lead tolerance of catalyst
3,025,133; Mar. 13,1962 Robinson to M&C Phillips	Granules of alumino-silicate activated with H_3PO_4	Pretreat exhaust to remove Pb as phosphate upstream of catalyst bed

3,053,612; Sept. 11,1962 DeRossit to UOP	Pellets containing metal above Pb in electromotive series and an alkali	Upstream half of catalyst bed replaced with pellets containing, e.g.Al and CaO to trap lead
3,072,457; Jan. 8,1963 Bloch to UOP	Regenerate Pb deactivated catalyst by heating in a reducing atmosphere	Presumably operable because Pb metal occupies less volume than equivalent amount of Pb salt
3,117,936; Jan. 14,1964 Michalko to UOP	Wash Pb deactivated catalyst with detergents to remove Pb salts	Extent of reactivation said to be unrelated to amount of Pb removal
3,162,518; Dec. 22,1964 Biggs et al. to W.R. Grace	Combination of cyclone separator and Pb absorbent bed	Cyclone for particulate lead salts and bed for vapourized lead salts
3,168,368; Feb. 2,1965 Mills to Air Products	Add $R{=}Mn(CO)_3$ to gasoline where R is methylcyclopentadienyl	Catalyst said to be protected from lead by an upstream cyclone separator
3,295,919; Jan. 3,1967 Henderson et al.to W.R. Grace	Alumina as Pb absorbent. Catalyst 10% CuO, 4% Cr_2O_3, and 0.02% Pd on Al_2O_3	Cooling loop in exhaust pipe to protect catalyst from overheating

Selected U.S. Patents Relating to Device Designs to Protect Catalyst

U.S.patent no; date of issue; inventor and assignee	Design Feature	Comment
3,215,507; Nov. 2,1965 Horstmann et al.	Multiple tubes for catalyst. Joints designed for differential thermal expansion	
3,297,400; Jan. 10,1967 Eastwood to Mobile Oil	Temperature activated valves to direct exhaust to either of two catalyst beds	If temperature too high, then bypass to atmosphere. Save first bed for light-off
3,303,003; Feb. 7,1967 Zimmer to W.R. Grace	Temperature sensor in catalyst bed to control speed of pump adding air to exhaust	Add air to cool catalyst bed, particularly during rich idle
3,223,491; Dec. 14,1965 Maillie et al. to Firestone	Improved design for bypass of bed and for withstanding heat warping	Compact design with provision for catalyst replacement
3,380,810; Apr. 30,1968 Hamblin to UOP	Layer of inert refractory next to catalyst support grit to prevent warping	Designs of radial and flat bed devices described
3,413,096; Nov. 26,1968 Britt to UOP		Prevent channeling of exhaust through bed in case catalyst volume lost by attrition or settling

3,094,394; June 18,1963 Innes et al.to American Cyanamid	Spring-loaded movable plate to prevent voids as catalyst settles and shrinks	Fusible cap for over-temperature protection. Voids permit catalyst attrition by movement

Patents related to NO removal

3,316,057; Apr. 25,1967 Houk et al.to DuPont	Mangano-chromia-manganites in a refractory matrix claimed to remove HC and CO with added air and NO when no air added	Use tandem reactors with air added in between. First reactor removes NO, second HC and CO
3,370,914; Feb. 27,1968 Gross et al.to Esso	20-50% Ni and 3-20% Ba on alumina. Catalyst must be in reduced state to remove NO. Disclose many metallic gasoline additives	Claim equilibration of CO,HC,H_2O,and NO through water-gas shift,steam reforming, and reduction to end up with N_2,CO_2, and H_2O

4. Catalytic Device Technology

A catalytic device is also a catalytic reactor. Chemical engineering as well as mechanical engineering skills are required to design an operable device. Such skills have been and are still being applied. Basic requirements for a device are now well known (De Rycke, D., 1963), (Innes, W.B. and K. Tsu, 1962), Innes, W.B. and R. Duffy, 1961). Two simple designs are shown, a flat catalyst bed in figure 1 and a radial exhaust flow device in figure 2. Neither of these is drawn in detail, of course. Even distribution of gas flow through the bed is important. Flow of gas into the dead-end center pipe of figure 2 or into the the simulated tidal bore of figure 1 gives rise to a ram effect. Most of the exhaust will flow through the downstream end of the catalyst bed, focussing the heat load of HC and CO combustion. Lead deposition on catalyst will similarly be focussed. Distribution of lead in the catalyst bed can be used to diagnose the flow pattern of exhaust gas through the bed. The device is detached while warm, plugged at one end, and filled with molten wax. After the wax has hardened, the device can be sectioned as desired with a metal saw and the lead distribution determined by X-ray photographs. The devices of figures 1 and 2 must be provided with baffles upstream of the catalyst bed is to distribute the the gas flow.

Pressure drop through the catalyst bed is theoretically influenced by bed thickness, catalyst support dimensions, and the per cent of hole area in the perforated steel sheet supporting the catalyst bed. High back pressure can be generated by a catalyst that crumbles to small pieces and cakes or by a catalyst

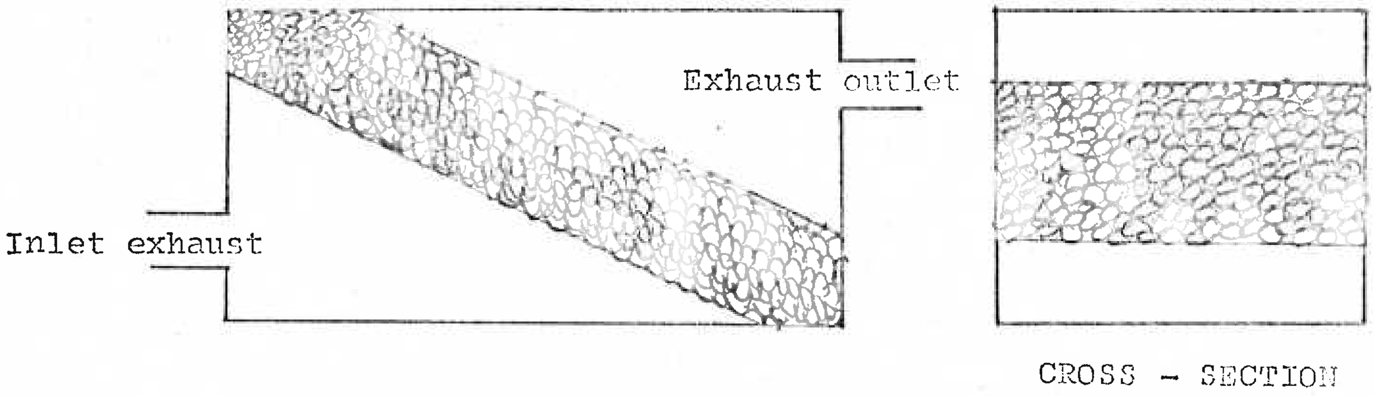

Fig. 1. Flat Bed Catalytic Device.

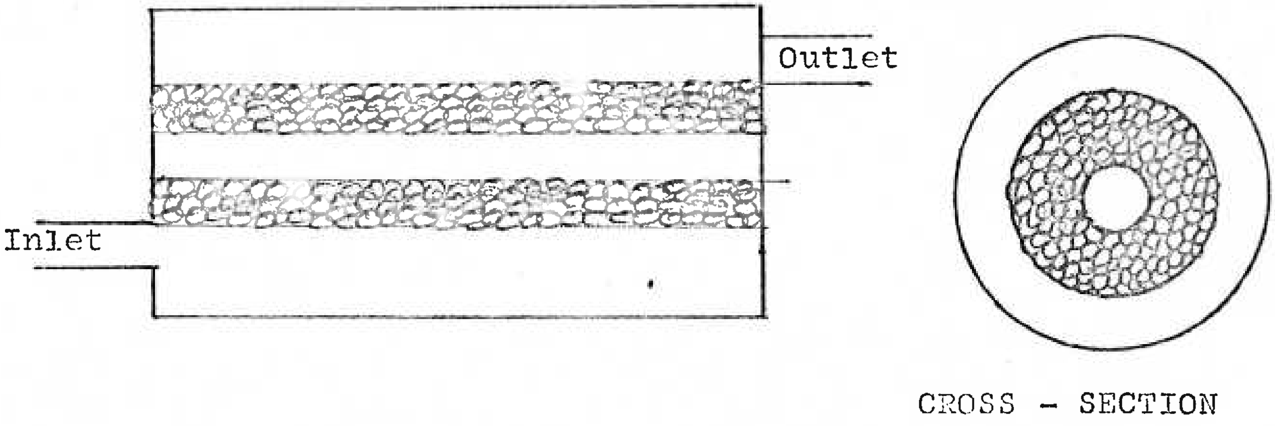

Fig. 2. Radial Flow Catalytic Device.

bed that has been partially fused. Normally the back pressure across a device is primarily controlled by the percent hole area in the catalyst support grid. This is because it is difficult to perforate alloy sheet steel with holes of small diameter. It is relatively easy to make a narrow-slot louver alloy sheet steel of relatively low percent hole area. High percent hole area can be attained with perforated stock but not with louvered stock.

When a car is started up on a cold winter morning, water vapour condenses in the exhaust system. The condensate contains dissolved SO_2, lead halides, plus a little hydrochloric and sulphuric acids. It is called "muffler acid". As the engine and the exhaust system become hot, the muffler acid evaporates or is blown out the tailpipe. When the car is allowed to cool, residual exhaust gases in the exhaust system condense to form muffler acid. Most mufflers corrode from the inside to the outside over a span of 1-4 years because of condensate. Any moving parts in the exhaust system, such as butterfly valve axles and heat riser valves, tend to corrode, rust, and become frozen unless constructed of special materials. Many exhaust catalysts are capable of withstanding regular leaching by muffler acid.

Location of a catalytic device in terms of distance from the exhaust manifold appears to be of marginal importance (Thomas,J.M. and W.J. Thomas, 1967). The cooling rate of exhaust gas in regular single-walled exhaust pipe has been measured. It varies from 30 to 150°F per linear foot as a function of exhaust gas flow rate and temperature. For double-walled or ceramic-coated exhaust pipe, the cooling rate can be close to nil.

Differential thermal expansion is another device-design problem. If the catalyst support grids of figures 1 and 2 are at 1200°F at the same time that the shell is at 600°F, the resulting stress will either crack the end plate weld seams or cause the grid supports to warp. Solutions to some of the foregoing problems are listed in chapter 2.

Device design modifications to provide protection to the catalyst against lead deactivation involve some sort of lead trap. Some of the lead traps described in chapter 2 are:

1) A bed of metal promoter or lead reactant on a porous support to scavenge lead from the exhaust gas upstream to the main catalyst bed,

2) The same but with the lead-entrapping material comprising the upstream portion of the catalyst bed,

3) A cyclone separator or filter to remove particulate lead upstream to the catalyst.

Mechanical lead filters and separators are generally ineffective because of the relatively low dewpoint of the lead halide salts in the exhaust. Some of the chemical lead traps, e.g., phosphoric acid and chromate, undoubtedly have stoichiometric limitations but that is not their major disadvantage. Any lead trap is a thermal luxury with respect to warmup of the catalyst bed. Should a lead trap be effective, the warmup problem would get worse with time. Assuming a vehicle that attains 20 miles per gallon using a premium gasoline containing 3 ml of TEL per gallon. Three milliliters of TEL is roughly equivalent to 3 g of elemental lead. In 12,000 miles of travel, about 4 lb of lead are converted to about 6 lb of lead halides. About 25% of this is either entrapped as exhaust system deposits or finds its way to the engine lubricating oils (Hirschler, D.A. et al.,1957). A portion of the remaining 75% or a maximum of about 4 lb as lead sulphate or phosphate could accumulate in the lead trap. This accumulation plus the mass of the trap itself acts as a heat sink. Essentially the same thing happens in a catalyst bed. Catalyst at the inlet side becomes leaded first. As the more distant parts of the catalyst bed begin to carry the conversion load, the leaded part of the bed extends the warmup time.

Very high temperatures can easily be reached in a catalyst bed because of its poor heat-rejection characteristics. Catalysts consisting of metal promoter on a porous refractory support are extremely poor conductors of heat. It is quite possible to measure a catalyst bed hot spot of 1500 °F within millimeters of catalyst at 700 °F. Heat rejection by radiation is insignificant in the desired temperature range, below about 1200 °F. Convection is the only heat-rejection mechanism remaining. Essentially all of the heat generated by combustion of HC and CO in a catalyst bed is removed as sensible heat by the exhaust gas.

The temperature potential of an exhaust gas stream is defined as the temperature increase resulting from complete combustion of the HC and CO contents of the gas stream. Temperature potential of an exhaust gas stream can be calculated by:

$$\text{Temp. potential} = \frac{((0.0062)\cdot(\text{ppm hexane}) + (4.1)\cdot(\%\ \text{CO}))}{0.02}$$

This includes several factors not readily apparent. One hidden approximation is that the CO-H_2 ratio in exhaust averages about 3:1. Another is that the parts per million of hexane as measured by hexane-sensitized, nondispersive infrared (HSNDIR) is only about two-thirds of the true value as measured by flame ionization detector (FID) (U.S. Department of Commerce, Dec.,1967). The heat capacity of exhaust gas is approximately 0.02 Btu/°F standard cubic foot.

Cars adjusted for rich idle, or with maladjusted spark timing or with a sticking choke, or worn distributor bearings, or any of a dozen other flaws, can have extraordinarily high emission levels of CO and HC. A rich idle may give rise to as much as 2000 ppm HC and 10% CO in the exhaust gas. As the above equation shows, these emission levels could cause a temperature rise in a catalyst bed of 2670°F. If a single cylinder is misfiring, the HC level in the exhaust may go to 10,000 ppm, equivalent to a temperature potential of about 3000°F.

Before engines were modified to reduce HC and CO emissions, catalytic devices had to be designed to handle, at least in part, the high emissions from rich idle, generously power-jetted acceleration and, worst of all, the high gasoline load from poor combustion during deceleration. Otherwise the device would not pass the California test. Penalties' were provided for the time that exhaust was bypassed around the device in the fleet tests of 1964. To illustrate the economics of the 1964 high-temperature problem, the absolutely essential combination of temperature sensor, bypass piping, bypass valve, and actuator for the bypass valve designed to reroute exhaust gas around the device when the catalyst bed exceeded about 1400°F would have cost about $30 in 1964 marketed through part distribution channels. At present. new car sales of about 10-15,000,000 per year, the cost to the nation would be well over $300,000,000 per year. This is an example of the economic waste of over-design referred to earlier.

Now that engines have been modified for lower HC and CO emissions, catalytic devices do not have to be designed to handle any high emission levels. The device still nedds protection against high temperature but this is a different and easier problem. High temperatures now occur only in unusual operating modes such as very high-speed cruise or rapid, prolonged acceleration. In normal operating modes, high temperature in a catalytic device would be a symptom of relatively severe engine malfunction. Malfunction is indeed the proper word because certification requirements are that engine modifications be capable of keeping emission levels at relatively low and steady level for 50,000 miles.

A catalytic device loaded with fresh catalyst operating as a part of a relatively simple power system design is capable of initially converting at least 70% of the HC and 80% of the CO in the engine exhaust to CO_2 and H_2O (Weaver, E.E., 1969). This is without added air using today's modified engines. Conversions are based on the seven-mode cycle cold-start test, as described before. As the vehicle is driven, the conversion percentages will drop, partly as a function of mileage but mainly as a function of the cumulative amount of tetraethyl lead fed to the engine in the gasoline (Yarrington, R.M. and W.E. Bambrick, 1970). In one particulas reference cited (Weaver, E.E.,1969), there was some loss in conversion attributable to loss of catalyst by attrition.

Since the CVS test procedure places considerable emphasis on cold-start performance, catalysts with lower density and higher oxidation activity at lower temperatures are required. Monolithic catalysts, which have more rapid warmup and lower pressure drop than pelletted catalysts, have been extensively evaluated in low emission vehicles. In addition, catalytic converters are often located quite close to the engine to further increase the warm-up rate.

As stated before, catalyst durability, in this more severe environment, is one of the current critical problems. Due to the higher operating temperatures associated with locating converters close to the engines, catalyst deterioration has often been observed in 1975-6 concept vehicles (SAE papers No. 720481, 720486, 720487, 720488, all from 1972). Occasionally, thermal failures (melting) have occurred during milage accumulation runs. The specific operational modes under which melting occurred were difficult to establish on concept vehicles.

Some attempts to prevent thermal failure by the use of protection devices have been reported (SAE 720486). These schemes have included bypassing the exhaust around the catalytic converter, dumping the secondary air supply, and feedback control of the air/fuel (A/F) ratio.

During certain acceleration-deceleration modes of the CVS test procedure, pulses of CO and HC are measured at the converter outlet, even when the catalytic converter is hot (emission breakthrough). Even though each breakthrough is relatively small compared to emissions during the cold-start portion of the CVS test procedure, their integrated contribution to the total CVS emissions can be significant.

Since both overtemperature and emission breakthrough occur when the converter is above 1000^{o}F (and not limited by catalyst activity), these phenomena are often dependent on the rates of heat and mass transfer processes in the catalytic converters. Several theoretical studies of these processes in pelletted catalysts have been reported (Kuo, Morgan and Lassen, 1971), (Harned, J.L., 1972). Kuo has developed a comprehensive mathematical model for monolitic catalytic converters which includes detailed heat and mass transfer relationships. Heat and mass transfer phenomena at a steady-state have been studied for several types of monolitic converter channel geometries (Hawthorne, R.D., 1972), (Votruba, J., et al., 1974). HC and CO emission breakthroughs associated with the secondary air supply system have also been reported. Kuo et al., 1972 reported breakthroughs resulting from insufficient oxygen during certain critical driving modes. Inoue et al. investigated the effect of secondary air distribution on catalytic converter performance (720487, SAE). The problems of thermal disintegration are still with us and a 1972 study by Ford reports that none of their concept vehicles were able to meet the IIEC (Inter-Industry Emission Control Program) low milage research emission targets established from the U.S. Clean Air Amendment of 1970 after providing for a very minimal depreciation in emission control with mileage (Campau, Stefan and Hancock, 1972). Other researchers have had better luck.

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5. Gasoline Engine Technology Related to Emission Control

Perhaps the best way to illustrate some of the optimization choices and remedial measures taken by or available to car manufacturers to minimize exhaust emissions is to trace the course of gasoline from carburettor bowl to tailpipe. The schematic diagram (next page) shows how filtered air flowing through a venturi throat creates a suction that inducts liquid gasoline from the carburettor bowl through the carburettor main jet into the intake manifold. Air flow is controlled by the throttle plate which in turn is controlled by the accelerator pedal. The rate of flow of gasoline into the airstream depends on the size of the metering orifice and the rate of flow of air through the venturi. As the air flow increases, the venturi suction also increases, thus pulling fuel through the carburettor jet at a greater rate (Taylor, C.F. and E.S. Taylor, 1961).

The physical state of the air-fuel (A/F) mixture as it proceeds from the carburettor has been particularly well described by investigators at Ford (Jones, J.H. and J.C. Gagliardi, 1967) who installed a window in the full length of the intake manifold of a six-cylinder engine. At idle, the A/F mix appeared to be a mist or fog. As the throttle was opened, droplets and globules of gasoline appeared. The interior surface of the intake manifold became wet with gasoline and actual puddles of gasoline appeared. When the throttle plate was closed and the engine began to pull a vacuum on the intake manifold the puddles of gasoline began to boil and the wetted surfaces became dry. Obviously, the A/F mixture going to the cylinders at this point was very rich. The actual driving condition simulated was a

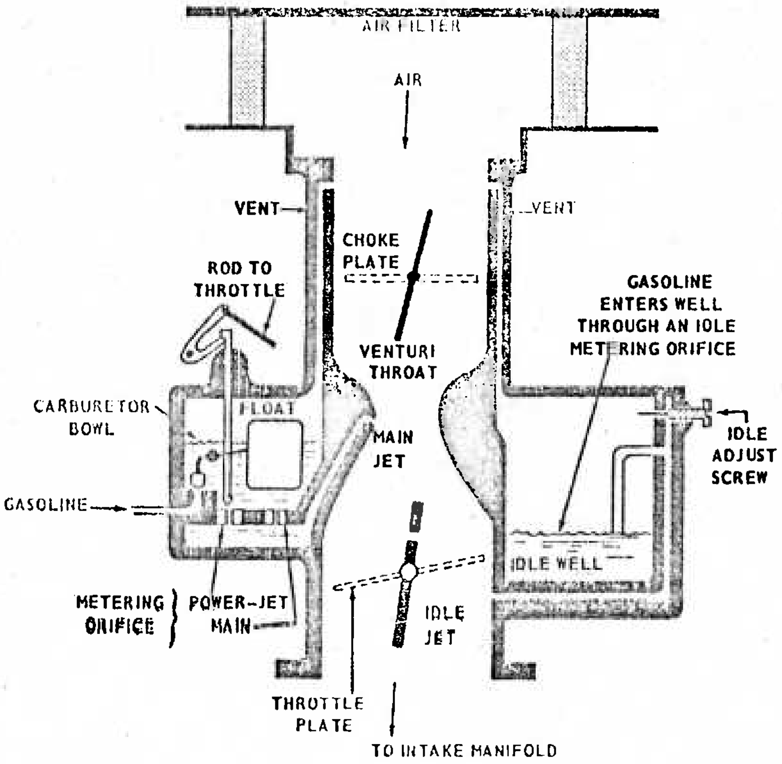


Fig. 3. Schematic Drawing of a Carburettor.

deceleration. During steady-state operation in idle or cruise modes the intake manifold equilibrates at a certain level of wetness. We have seen that a change of mode involving the closing of the throttle plate decreases the intake manifold wetness and enriches the A/F delivered to the cylinders. Conversely, acceleration which involves opening the throttle plate increases the intake manifold wetness and leans out the A/F mixture delivered to the cylinders. For cylinders farthest from the carburettor, the situation is worsened by the lower transport rate of liquid phase versus gas phase in the intake manifold. If the carburettor is designed to provide lean mixtures in the first place, then the further leaning in the initial phase of an acceleration will cause misfires in the cylinders. The resulting lack of power is called tip-in stumble, or lean-limit misfire.

The function of the power jet shown in the diagram is to permit the flow of sufficient gasoline both for power and for wetting the intake manifold when the throttle is opened. Emission control has necessitated reduction in the rate at which power jets formerly supplied gasoline to the intake manifold.

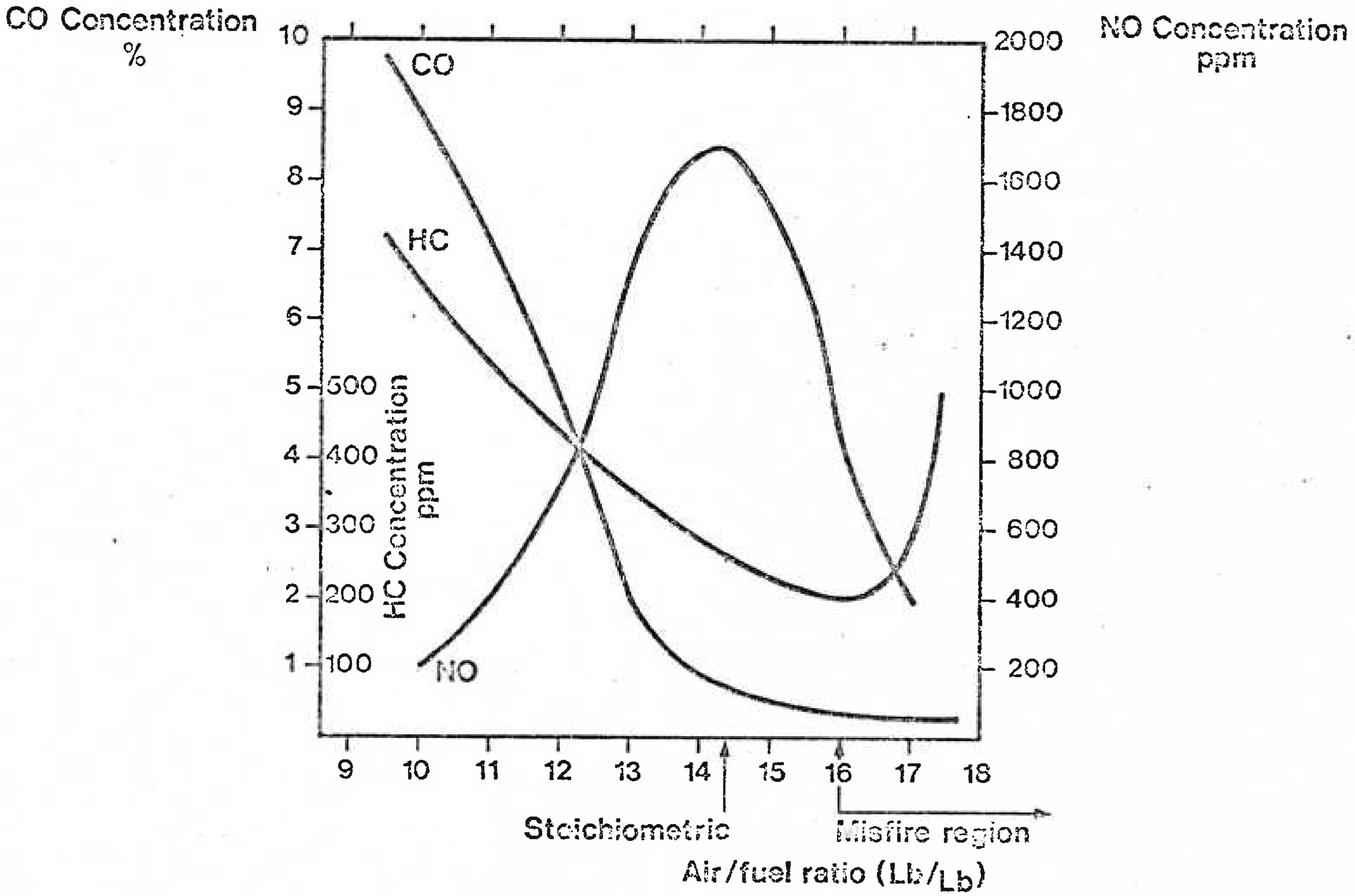
There are three commonly used measures of the air-fuel mixture. One is the A/F ratio which is the pounds of air per pound of fuel. The inverse of this, the F/A ratio, is also used. For the average gasoline the stoichiometric A/F ratio for theoretically complete combustion is approximately 14.6 or an equivalence ratio of 1.0, the third measure. An engine operating at an A/F ratio of 13.1 or (14.6-1.46) has an A/F equivalence ratio of 0.9 or is said to be 10% rich.

Two other terms of interest need also be defined. One is the mean break effective pressure (mbep) which is a measure of the useful power that can be got from a given engine. The other is the brake specific fuel consumption (bsfc) which for a given engine puts the constraint of fuel economy on power optimization. Other things being equal, the mbep is optimum at an equivalence ratio of about 0.9 or a 10% rich carburettion. The bsfc is optimum at an equivalence ratio of about 1.1 or about 10% lean carburettion. Until the advent of emission-control legislation, automotive carburettors were uniformly designed to deliver A/F mixtures on the rich side of the stoichiometric ratio thus maximizing power. Figure 4 shows roughly how HC, CO, and NO emissions can vary as a function of the A/F ratio (Agnew, J.T., 1967), (Eltinge, L., 1968), (Huls, T.A. and H.A. Nichol, 1967). Other factors are, of course, involved and will be discussed later.

Most interesting is the way in which various car manufacturers have coped with the problems of optimizing the induction system (carburettor plus auxiliaries) for emissions control without sacrificing car drivability. The automotive industry, associated industries, and universities have generated a great deal of data in a relatively short period of time. References a) - j) in the appendix list represent a selection of their work. The bulk of the references deal with much more than the induction system.

An essential change in carburettor appurtenances was a remodelled idle screw. With the earlier type idle screw, the idling jet could easily be opened wide, thus undoing the efforts of the car manufacturers toward emission control. One remedy (Toyota)

FIGURE 4



Effect of air/fuel ratio on HC, CO, NO_X emissions; 1300 cc engine, 3000 rpm road load is to put a stop on the idle screw limiting the adjustment to a range of about ± 1 on the A/F ratio (Toyoda, S., et al., 1967). Another way to achieve the same objective is to put an elongated tapered end on the idle screw (Chrysler). The tapered end fits into the idle jet and even when screwed out to the maximum does not provide adverse enrichment of the A/F mixture (indicated in fig. 3).

At idle, the air flow rate is low because the throttle is closed and the intake manifold vacuum is low. Linear velocity of the A/F mix is low, enhancing undesirable cylinder-to-cylinder variation in the A/F ratio. To remedy this, most engines are now set for higher idling speeds, about 550-650 rpm versus the former 500-600 rpm. In some cars the size of the intake manifold has been reduced to provide for more turbulence and better mixing of air and fuel. One manufacturer (Volvo) uses two throttle plates. At idle and low engine load, one throttle is closed and forces the A/F mixture coming through the first throttle plate to go through a heated labyrinth where theair and fuel becaome better mixed. At higher engine loads, the second throttle plate opens and bypasses the labyrinth (Larborn, A.O.S. and F.E.S. Zackrisson, 1968).

Other changes to the carburettor that have helped reduce exhaust emissions include some sort of air bleed into the intake manifold during deceleration. This can be done by drilling a hole in the throttle plate (see fig. 3) or by installing a throttle positioner to keep the throttle from closing completely. An engine is necessarily an effective air-pump because it must pump its air requirement in through the air filter and carburettor.

When the throttle plate is completely closed, the engine is pumping from a closed system. A vacuum of to 22-26 in. of mercury in the intake manifold can occur during a deceleration. This vacuum provides engine braking power. Air bleeds can only be used to reduce the intake manifold vacuum to about 22 in. of mercury. Even this reduction is of help in slowing the evapouration of liquid gasoline in the intake manifold. If the vacuum is further reduced, the reduction in engine braking power becomes noticeable (Larborn & Zackrisson, 1968) as does increased brake wear.

The choke plate in fig. 3 reduces the flow of air through the carburettor and permits the flow of gasoline through the jets to be increased by the intake manifold vacuum. Prolonged and tight closure of the choke plate can result in A/F ratios as low as 9:1 with exhaust emissions correspondingly rich in CO and HC. Duration and richness of choke have both been reduced in emission-controlled engines.

The form of spark ignition internal combustion engine most used operates on the Otto cycle. The four strokes of the Otto cycle are the intake, compression, power, and exhaust strokes. Position of a particular piston is given in terms of crank angle. This angle is between the axis of the cylinder and the specific crank in the crankshaft to which the piston is attathed. To indicate ascent or descent of the piston, the angle is described as degrees before top dead center (btdc) or degrees after top dead center (atdc). Similar terms involve the bottom dead center.

As a piston at top dead center starts downward on the intake stroke, the exhaust valve is still open and stays open until the crank angle is about 15-30° atdc. In the combustion chamber above the piston there is residual gas from the previous stroke. Additional exhaust gas is sucked back through the exhaust valve until it closes. The intake valve opened earlier at about 15-30° btdc. Valve overlap is the period when both valves are open. At about 15-30° abdc the intake valve closes. For an engine running at 3000 rpm, the elapsed time for the intake stroke is 10 msec. Elapsed time for each of the other strokes is of course the same. At an engine idling speed of 600 rpm, the time for the intake stroke is 50 msec. Because the piston is in harmonic motion, it has maximum speed at 90° before or after tdc. Most of the actual flow of A/F into the cylinder therefore effectively occurs in less than the time of the full intake stroke. Turbulence of flow of A/F into the cylinder varies considerably as a function of engine speed, manifold vacuum, and the size of the intake valve port (Stivender, D.L., 1968).

After the piston passes the bdc position, the compression stroke has begun. Timing the spark to ignite the A/F mixture is crucial both to engine power and to emissions control. For best power the combustion should be complete by about 15-30° atdc. Delay past this point encounters the possibility of the flame being quenched in the expansion or power stroke. The speed of propagation of the flame front from the spark plug out to the walls of the combustion chamber is obviously a key factor. Remarkably and fortunately the flame front travels faster and faster as engine revolutions per minute increase (Taylor & Taylor, 1961). Combustion is completed in the 10 msec available at 3000 rpm as well as in the 50 msec available at 550 rpm. The correspondence is not exact and may be compensated for by relatively small but important changes in spark timing (Taylor & Taylor, 1961). The increased turbulence of the A/F mixture at higher engine speeds is the reason for the increased flame speeds. Eddies and vortices small in size relative to the flame front enhance the propagation of the flame (Taylor & Taylor,1961).

A number of interesting phenomena occur in the flame front. Bulk temperature in the combustion chamber reaches about 1500°F as measured at the nose of the spark plug. Flame front temperatures have been calculated at 4000-5000°F. At these temperatures the equilibrium constant and the k_1 rate of the below equation are favorable for NO formation (Newhall, H.K. and E.S. Starkman, 1967).

$$N_2 + O_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2\ NO$$

As soon as the flame front has passed, the burned gases cool by expanding against the unburned gases (Graiff, L.B., 1966). At the bulk temperature of the burned gases k_2 is sufficiently low that the NO concentration is frozen at its highest level. There is some disagreement whether the highest level is an equilibrium NO concentration. One investigator has reported that addition of NO to the A/F charge of a cylinder did not increase the NO output of the cylinder after firing (Newhall & Starkman, 1967).

While a number of engine variables affect NO emission level (Huls, T.A. and H.A. Nichol, 1967), it is apparent that major reduction in NO must involve a lowering of the flame-front temperature. This can be done by adding inert material to act as a heat sink. In an earlier day, excess gasoline, i.e. rich mixtures, served this purpose. Exhaust gas recycled to the intake manifold can also serve (Kopa, R.D., 1969). Experimental work indicates reduction of about 80% of NO emission levels by recycling of exhaust up to about 25% of the cylinder charge (Deeter, W.F. et al., 1968), (Newhall, H.K., 1967). The practical implications of this, however, turned out not to be as promising. Water injection into the intake manifold also lowers flame-front temperature (Nicholls, J.E. et al., 1969). At an injection rate of 1.25 lb of water per pound of fuel, NO emissions were reduced by more than 90% and with some improvement in power and fuel consumption. This hasn't either been developed into a practical system for the reduction of NO emission levels. Further development work on exhaust recycle encountered problems of fuel economy and drivability of test vehicles (Benson, J.D., 1969)

The level of NO_x in exhaust depends primarily on cylinder flame-front temperature. CO level is primarily a function of A/F ratio. HC emissions have a more complex dependency. Only during misfires and poor combustion during deceleration does the composition of exhaust HC's closely correspond to fuel composition (Hurn, R.W. et al., 1960). A considerable amount of analytical work (Hurn, 1960), (Hurn, R.W. et al., 1962) is summed up in the statement that about 50% of the photochemically reactive hydrocarbons in exhaust are due to low molecular weight combustion products not present in gasoline (Papa, L.J., 1967). An additional conclusion is that exhaust hydrocarbons are made up of about 60% combustion products and 40% fuel components (Papa). Theoretically, one would expect all the HC to burn up in the cylinder if there were enough air present. A theory to explain the presence of low molecular weight combustion products and unburned fuels was developed and substantiated in a series of studies conducted at General Motors (Daniel, W.A. and J.T. Wentworth, 1962), (Wentworth, J.T., 1968) conducted over a number of years. A paper by (Daniel, W.A., 1967) illustrates the technique. A single cylinder engine using propane as fuel was equipped with a gas-sampling valve. During engine operation samples were taken from the cylinder. Sampling occurred immediately before and after flame-front passage. The sampling valve was adjustable to withdraw gas out to varying distances from the cylinder wall. Analysis was carried out by GC. The results showed clearly that right at the cylinder wall the propane concentration was very high. Within about 0.001-0.005 in. of the wall were cracked propane products such as methane, ethane, ethylene, and propylene. Further out from the cylinder walls, combustion was relatively complete. The zone of cracking is called the quench zone. It has effects on NO and CO as well as on HC (Starkman, E.S. et al., 1969). Post-flame reaction continues to oxidize both CO and HC at a rate depending on the time-temperature exposure and oxygen concentration of the gases during and after the expansion and exhaust strokes (Agnew, J.T., 1967), (Daniel, W.A., 1967). Continuance of this homogeneous non-flame oxidation of CO and HC in the exhaust manifold is the basis for the Ford Thermactor and the GM AIR (Air Injection Reactor) devices. In both devices the exhaust manifold is enlarged to provide residence time and insulated to keep the temperature up. Air is injected at the exhaust ports to supply an excess of oxygen. The devices operate at about 1100^{O}F and are capable of oxidizing about half the HC and a lesser proportion of the CO. As with catalytic devices, overtemperature protection must be provided, although their conversion capability does not decline with lead deposits and cumulative time at high

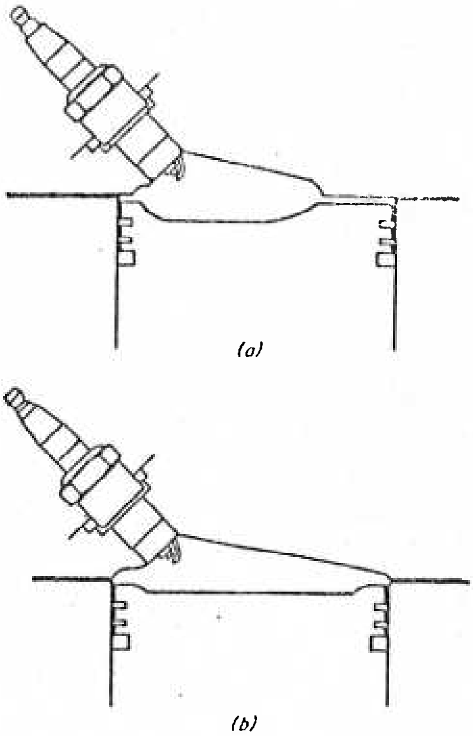


Fig. 5. Cross Section of 232 CID Combustion Chamber,

a) quench, and

b) low quench.

temperature. Manifold air injection became feasible only when a suitable air pump became available. Development of such a pump by GM was a considerable engineering achievement (Thompson, W.B., 1966).

During the work on quench zones, additional factors were observed to affect HC emissions. The combustion flame front does not penetrate crevices with one small dimension. For example, the crevice representing the clearance between cylinder and piston down to the piston rings is not penetrated by the flame front. Significant amounts of HC are trapped there and in various other crevices (Wentworth, J.T., 1968) during the compression stroke. They escape during the expansion and exhaust strokes. The American Motors Company have taken an advantage of this (Hitter, D.L. and L.R. Hamkins, 1968). Fig. 5b shows most of the crevices eliminated by their redesign of combustion chamber. The initial design, fig. 5a, with center-well in the piston, called a squish piston, formed numerous crevices with the cylinder head. In fig. 5b, the present design, the surface-to-volume ratio of the combustion chamber has been decreased. The equivalent of crevice volume is apparently supplied by porous lead deposits in cylinders because such lead deposits have been shown to cause an increase in HC emission (Gagliardi, J.C., 1967). There is some disagreement on the size of the increase with one study (Dupont) indicating an emission increase of about 5% (Pahnke, A.J. and J.F. Conte, 1969) and another study (Ford) indicating about 20% (Gagliardi, J.C. and F.E. Ghannam, 1969). Both studies agree that engine deposits do not affect CO or NO emissions level.

To cut a long story short, the reciprocating piston engine has dominated the automotive engine scene for more than 60 years and until very recently, at least to most realists, seemed unlikely to ever be displaced. Although the piston engine has served its users well for many years and is likely to continue to do so for some years to come, it does have a number of shortcomings which are becoming more serious as ever greater numbers come into use and as we become enlightened on social values. It is a major contributor to air and noise pollution. It is also relatively inefficient and has a narrow fuel tolerance, consuming large amounts of highly refined petroleum.

The early phases of an expected long-term energy crisis are now upon us. The era of abundant low cost energy is over. Much higher prices are certain and there might be some rationing in the future. The need to greatly increase efficiency rather than trade off efficiency for emission control is therefore emerging. Before the end of the century, petroleum may be replaced as the dominant fuel for mobile powerplants.

Although much progress has been made in reducing automotive emissions, it has been achieved at the price of increased fuel consumption. Much further reductions in emissions are needed to meet the requirements of the U.S. Clean Air Act of 1970. Growing, but of somewhat lesser importance is the issue of noise pollution.

Wankel, Stirling, turbine, stratified charge and diesel engines are the most serious contenders to replace or supplement today's piston engines. Electric vehicles are not considered serious contenders because of grossly inadequate technology and steam engines have too low an efficiency.

In addition to the three social parameters, (fuel consumption, emissions and noise) there are seven other major engine selection parameters:

1. Flexibility (torque-speed characteristics and drivability),
2. Smoothness,
3. Cost,
4. Weight,
5. Size,
6. Maintenance requirements,
7. Durability.

The table below lists these parameters in order of importance for passenger cars as of 1973. Both fuel consumption and noise are now (1975) much higher in the list, probably on even terms with 'Emissions',' The five contenders are compared on these ten parameters with the 4-cycle gasoline piston engine.

Relative Importance of Selection Parameter vs. Piston Engine.

	Wankel	Turbine	Stirling	Stratified Charge	Diesel
1.	-	+	+	0	-
2.	+	++	++	0	-
Emissions	0	+	++	+	+
3.	-	-	-	?	-
Noise	0	+	++	0	-
4.	+	+	0	-	-
5.	+	0	-	-	-
6.	0	+	+	0	+
Fuel Consump.	-	-	++	+	++
7.	-	?	+	0	+

The Wankel, despite prior praise, has little to offer in the three important social areas and uses substantially more fuel. It is also a more costly and less flexible engine and has poorer durability characteristics.

The Wankel is smaller and lighter, but nowhere near as much as often claimed. These advantages are not readily convertible into major reductions in vehicle size and weight. Design studies indicate that several of the most compact cars using transverse engines would have to increase in length if a Wankel engine were substituted.

The turbine engine is quieter and can have very low emissions but has higher fuel consumption. It is lighter, smoother and more flexible, should require less maintenance, but is costly and its durability has not been proven extensively enough (automotively). The turbine requires considerable additional development before it could enter volume production.

The Stirling engine has the lowest fuel consumption, lowest emissions, and the lowest noise of any known engine. It is potentially capable of burning any fuel, since it is an external combustion engine. It is becoming increasingly apparent that petroleum consuming mobile powerplants must be supplemented or replaced within the next 10 to 20 years. Stirling engine also has flexibility, smoothness, maintenance and durability advantages, but tends to be somewhat bulky and costly. It is in an early stage of development. Introduction in high volume production is not likely until at least the early to mid-1980's.

Stratified charge engines could be introduced relatively quickly into production as it is a variation of today's piston engine. The stratified charge engine provides a better trade off between fuel consumption and exhaust emissions, the engine appears to be capable of meeting the interim 1975 and 1976 emission standards while equalling or bettering today's engines' fuel economy.

Stratified charge engines have a disadvantage in that their specific power output is somewhat less than conventional engines, resulting in lower performance cars or an increase in engine size. Ultimately this disadvantage may be overcome by turbocharging but at least the first generation of stratified charge engines are not likely to use turbochargers.

Diesel engines have low fuel consumption and low emissions of controlled pollutants but high emission of smoke, odour and noise. They require less maintenance and have a long life but are at a disadvantage in all other characteristics.

On balance therefore, the stratified charge reciprocating engine appears to be the leading near-term challenger and the Stirling engine, the leading long-term contender.

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6. Fuel Technology Related to Emission Control

The oil industry has a major stake in the fate of the gasoline engine. It has been briefly stated that the energy to run the Western economy is supplied in the ratio of about 40% by oil, 40% by gas, 20% by coal and 0.2% by food (Larsen, R.I., 1966). This has been changing slightly in the most recent years, but still the oil industry will be expected to and will desire to supply directly or indirectly the energy to power the vehicles of the near future whatever the nature of their engines. A handicap common to both the oil and automotive industries is that their scale of operation necessitates a large investment, i.e., a large capital mass of inertia. Changes in their direction or rate of motion require the application of correspondingly large forces. For gasoline specifically, any significant change in present oil refinery configuration (the combination of processing equipment to produce a particular product spectrum) is virtually certain to entail severe economic penalties.

As described earlier, gasoline and exhaust gas do have quite different although not entirely unrelated compositions. However, for evaporative emissions of gasoline vapour from carburettor bowl and gas tank, the composition of the gasoline is obviously important. California has limited the olefin content of gasoline. Significant reductions in evaporative emissions could be achieved by widespread use of gasoline of lower volatility (Nelson, E.E., 1969). To change refinery configurations to reduce gasoline volatility, an API task force (Lawson, S.D., 1968) estimated would entail new refinery investments of one to three billion dollars and add one to 2.3 cents per gallon to the cost of gasoline. Devices containing activated charcoal for redirecting evaporative emissions to the intake manifold have been described and tested (Joyce, R.S. et al., 1969), (Deeter, W.F. et al., 1968). However, the economic choice does not appear to be between devices and gasoline volatility reduction. An API-sponsored study (Esso-API, 1968) clearly shows severe starting and warmup problems for carburetted engines operating on gasoline of low volatility. Probably an engine with fuel injection and throttled intake valves could successfully use a fuel of low volatility (Stivender, D.L., 1968). Hence the economic choice really appears to be either devices or gasoline volatility reduction plus engine modification. The odds in such a choice favour devices. The before quoted study by E.E. Nelson showed satisfactory startup and drivability in the equitable climate of Los Angeles for a group of 1800 cars using a low volatility gasoline. Evaporative emissions could be reduced an estimated 50% in the Los Angeles basin by changing the Reid vapour pressure of gasoline supplied to the area from the present 10 psi average to about 7 psi. Since the all the urban areas of the world do not enjoy Los Angeles average temperatures, weather conditions nor topography there still appears to be a niche for evaporative emission control devices.

Alternative fuels to gasoline would undoubtedly involve more capital expense than gasoline volatility reduction. It has been shown (Lee, R.C. and D.G. Wimmer, 1968) that the use of methane or propane instead of gasoline reduces exhaust emission levels of HC, CO, and NO_x significantly. The cost to produce and market either methane or propane instead of gasoline is dismaying to contemplate.

Historically the sequence has been to develope or improve fuels after a new or improved engine has been developed. The invention of TEL antiknock additive might be considered an exception. Without TEL the introduction of high compression engines would undoubtedly have been delayed. As mentioned before, in order to achieve the slower, more even burning of fuel necessary to eliminate engine knock in high-compression engines, high octane fuel is essential. TEL has offered the least expensive means of increasing this octane number. The poisoning action of lead in gasoline on emission control catalysts has been described.

Automobile manufacturers therefore in 1970 (U.S.) decided to produce 90% of their 1970 models to operate on 91 research octane number (RON). This means that these vehicles could use low-lead or lead-free fuels. (Lead-free gasoline is defined by the NAS study as having less than 0.03 g/gal lead, 0.04% sulphur by weight, and 0.005 g/gal phosphorus). This change was not without a cost: it necessitated a drop in average engine compression ratios from 9.5 to 8.5. Since higher-compression engines are more efficient in terms of energy conversion than lower-compression engines, according to the U.S. Department of Commerce's study of automobile fuels, lower-compression ratios alone resulted in fuel penalties of 5% .

Besides reduction in catalyst poisoning, the effects of lead removal include:

1) Reduced emission control system maintenance. The Dept. of Commerce study cites lead salts and scavengers as causes of corrosion in thermal exhaust reactor materials and as causes of plugging in some recirculation systems proposed for oxides of

nitrogen (NO_x) control.

2) Reduced hydrocarbon emissions. HC emissions increase with mileage with either leaded or lead-free gasoline. But they increase more and faster with leaded gasoline. Though there is disagreement on the magnitude of this effect, a study by the Coordinating Research Council comparing leaded and unleaded 91 RON gas stated that the 'net lead effect' increases hydrocarbon emissions by 7% under typical driving conditions (Dept. of Comm., p.43).

3) Possible increased valve wear. Lead acts as a high-temperature lubricant and helps to prevent fusing of the valve and valve seat, which may occur under severe engine loading. This phenomenon will affect only a small number of cars now on the road and can be eliminated by valve inserts.

4) Reduced health hazard due to lead in the atmosphere. In assessing this factor, it is important to bear in mind that the health hazard of lead at levels near present ambient concentrations has not been demonstrated. Data on physiological effects at threshold values or concentrations versus effects at low concentrations are not available.

The technological pros and cons are not decisive, except for catalyst poisoning. The compelling reason for EPA regulation of leaded fuel was the decision by automobile manufacturers to rely upon catalytic converters to meet the 1975-76 federal emission standards. This decision dictating lead-free gasoline had economic consequences.

The U.S. average clear pool RON is 88.5. The clear pool is the total stock of raw gasoline after refining and before mixing. Once the decision was made to prohibit TEL additives, other ways of raising the RON from 88.5 to 91-94 had to be used. The octane rating can be raised in the following ways:

a) Shifts in clear-pool components- the higher octane components of the clear pool could be used to make a lead-free 91 RON fuel. But the leftover, low-octane components of the clear pool would then have to be used to produce 100 RON fuel. Consequently, more lead would have to be added to raise the octane rating to 100 than previously. The response of the RON to lead addition is highly nonlinear. The first 0.5 gram of lead added per gallon increases the octane rating by three numbers, while it takes 1.5 grams per gallon to raise it the next three numbers. This is reflected in an EPA study by the consulting firm Bonner and Moore.

b) Reforming- there is not enough high-octane clear-pool volume to meet the demand for lead-free gasoline. The next most popular means of raising the RON is the addition of aromatics - six carbon-ringed molecules, such as benzene, toluene and xylene, which have high octane numbers (xylene has an octane rating of 110). Present gasolines contain approximately 25% aromatics. To reach a 94-octane rating without lead would require an estimated increase to 35%. Aromatics are obtained by reforming, which, under heat and pressure, reshapes heavy low-octane hydrocarbons. At present, 20% of all crude oil is processed by reforming, in 1980, 30% will be so processed.

The refiner and ultimately the consumer pays an economic penalty for reforming. The extra cost is not so much in processing as in capital investment amortization and product losses. A large refinery, processing 200,000 barrels (bbl) of crude oil per day, may have to increase its reforming capacity by 30,000 bbl/day at a capital cost of $10 million. The major loss comes from the fact that only 85-90% of the raw feed becomes gasoline component products. The remaining 10-15% comes out as gases with low market value, or is used as fuel in the operation of the reformer.

C) Alkylation- involves the linking of gaseous short-chain hydrocarbons to form long-chain hydrocarbons with octane numbers up to 94. At present, in the U.S., 7% of the gasoline feed stock is processed by alkylation, this is projected to rise to 12% by 1980. This process also involves an economic penalty. In order to provide more gases for alkylation, catalytic crackers must be run to produce more gases and less gasoline components. These gases, used in alkylation, are not completely converted into high-octane gasoline components. The result is both decreased gasoline yield and increased cost for the alkylation processing.

d) Isomerization- currently, 10% of the refiners' clear pool consists of light, straight, five and six carbon hydrocarbons, i.e. pentanes and hexanes. The components have very low octane ratings but are very responsive to lead addition. Normal lead addition boosts their octane rating by as much as 20 points. Without lead addition, they can be increased in octane by isomerization, which involves changing the straight-chain molecules to branched versions of the same molecule. The octane boost is dramatic. Normal pentane has an octane rating of 61, while iso-pentane has an octane rating of 92. Unfortunately, the costs are also dramatic. A 15,000 bbl/day unit costs approximately $12 million, twice the cost of a reformer of equal capacity. In addition, the small fraction of the pool which can be isomerized means that the octane rating of the clear pool can be raised at most by two points.

The situation is summarized by C.G. Gerhold of Universal Oil Products: "Virtually all the things the refiner does to get higher octane to replace lead, he does at the expense of yield, which is why he has to run more crude to produce the same amount of gasoline". To make the same amount of gasoline requires the processing of 6% more crude oil. The other petroleum fractions from the refining process are of low value. The cost to the petroleum industry, according to a study by the Pace Company, a Houston-based consulting firm, will be between $300 million and $600 million annually in additional capital expenditures through 1980, over and above the present $800 million annual construction figure. One-half to two-thirds of this additional cost will be for octane-boosting units and the remainder will be for capacity to produce extra gasoline needed to compensate for the lower efficiency of new automobiles. For the least demanding schedule of lead reduction, the study by Bonner and Moore predicted a capital investment of an additional $2 billion by 1980 and increased cost to motorists of $6.5 billion per year. For the fastest feasible schedule, the capital costs would increase by $4 billion and motorist costs by $8 billion annually (economics from McGraw-Hill's 1972 Report on Business and the Environment, ed. F. Price, New York : McGraw-Hill, 1972, pp.8-23) This cost to the motorist amounts to $65-$80 per vehicle per year.

An issue of major importance not detailed in the major studies mentioned (NAS, Dept. of Commerce, etc.,) is the relationship between the technology used in emissions abatement and the $2-4 billion capital investment on the part of the refiners needed to meet the lead-free fuel requirements. By ignoring the details of the gasoline refining situation, the NAS and other studies imply that any solution would involve lead-free gasoline. It is certain that any system involving catalysts would require large investments in capital and increased gasoline consumption from 5-25%, depending on the system. But the NAS study makes it clear that some present and future technologies do not presuppose lead-free gasoline. The West Germans reduced the lead content of their petrol in January, 1976. So far, no apparent ill-effects economically have been demonstrated. The large oil companies generally do not accept that automotive lead does the population any harm when airborne. The British Government does not compel a reduction of lead in petrol and their agreement with the oil companies is on a voluntary basis. The EEC, which has supra-national powers to control pollution, is incapable of reaching any agreement on the matter.

Lead can kill, though nowadays it rarely does. Enough is known about the symptoms of acute lead poisoning and the dosages that can produce it to have reduced industrial deaths from lead from an average of 30 a year at the turn of the century to zero for the past 20 years.

Much less is known about subclinical lead poisoning. It is known that lead can damage the brain, central nervous system and the heart, and that it might cause genetic injury. Symptoms can include headaches, depression, lassitude, anxiety, loss of appetite, bloody-mindedness or even delirium. Children, who are particularly vulnerable, can develop "disturbed" behaviour. The trouble is that most of these symptoms are virtually andemic in modern industrial man, and it would take an exceptionally canny doctor to isolate lead rather than "stress" as the cause. Matters are further complicated by the fact that lead is, and always has been, "naturally" present in our bodies, ingested via a food chain which begins with plants absorbing lead from the soil. One school of thought ascribes the decline of Ancient Rome to the practice of using leaden wine vessels and water pipes.

A good deal of research has been done on subclinical lead poisoning. The concept of how much lead constitutes a danger is still arbitrary. The Russians, for instance, fix the maximum exposure levels of industrial workers at one-fifteenth of the British level. They also forbid the addition of any lead to petrol sold in major cities.

Approximately 10,000 tons of lead are discharged into the atmosphere in the form of minute particles from the exhausts of British motorists every year. Official Government thinking on the matter is enshrined in a Department of the Environment publication "Lead in the Environment and its Significance to Man", (1974). It concludes that there is no reason to question existing safety levels; that lead from petrol is not a major source of the lead in our bodies; and that, while it is always desirable to reduce the amount of lead in the environment, and while its removal from petrol is a tempting solution, the technological problems and cost would handsomely outweigh the uncertain benefits.

What has happened since then is that the medical assumptions of the report have become more tenuous and the technological arguments against which they were balanced have been virtually demolished

The medical evidence remains inconclusive, just as, for that matter, the link between smoking and lung cancer is still inconclusiv But subsequent research suggests that the DoE underestimated the amount of airborne lead originating from petrol, and how much we absorb. Evidence is also arriving, particularly from the United States, which supports the Russian belief that much smaller amounts of lead than those we have hitherto believed dangerous can cause psychological disturbance. Nowaday, many city dwellers have lead bloodlevels perilously close to these.

It is interesting to look at the West German experience. On January 1st, 1976, the legal limit of lead in petrol was reduced to 0.15g/l, well below the limit anywhere else in Western Europe, and 0.40g/l below which the DoE accepts British industry cannot reasonably be asked to go. The current legal limit in Britain is 0.64g/l though, in November 1974, the Government obtained a voluntary agreement from the oil companies to restrict themselves to 0.55g/l. This was pretentious. No petrol, not even five-star, had more than that in 1974, when the average lead content of all petrol sold was 0.52g/l. In 1971 it was 0.46g/l. In banning lead for health reasons, the Bonn Government rode rough-shod over the objections of the oil companies and of its fellow EEC members.

The British oil companies are unmoved by the German experience. The Institute of Petroleum, a clearing house for industry informatior says that the reason why the Germans have not experienced all the problems predicted is that they are a rich nation prepared to pay the extra refining costs and believes this will ultimately be reflected in the pump price of petrol. A few extra pennies will be well worth spending though, if the health risk is reduced.

D. Fuel Technology - Alternatives.

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7. Auto Exhaust Emission Standards

From the point of view of those working on remedial measures for air pollution, the quantitative standards and the test methods are the immediate concern. Standards are, however, but one element in a mesh of continuing operations for air pollution control. The major operations for most pollution control situations are:

1) Data gathering-air samples are periodically taken and analyzed to define distribution, concentrations, sources, and fate of pollutants.

2) Criteria writing-supporting data are assembled to show adverse time-concentration effects of pollutants.

3) Control method review-feasibility and effectiveness of available control technology are summarized.

4) Standards setting-air quality standards and emission standards are set using considered judgement, preferably in the light of information from the three above operations.

5) Standards enforcement-a policing apparatus is needed to enforce compliance with established standards. Part of its work includes the gathering of some data.

6) Legislation enactment-funding and the force of the law are essential for pollution control.

7) Research and developement-new knowledge is required to pave the way for continued purification of our atmosphere.

8) Public education-the citizenry must be informed and concerned for acceptance of enforcement and to preclude unrealistic

expectations.

The above listing is not intended to be complete nor is there any implication that the real-life application of these stages necessarily follows a logical or inviolable sequence.

The magnitude of the automotive exhaust problem in relation to our total air pollution can be seen in the table to follow. These figures are estimates based on a 90,000,000 with uncontrolled evaporative, crankcase, and exhaust emissions. The indicated multipliers in the reference where this table comes from (U.S. Dept. of Commerce, "The Automobile and Air Pollution: A Program for progress", Part II, Dec., 1967), are the pounds of pollutants discharged per year. These may be approximately calculated from the appropriate data in table I, chapter 2 and the appendix to complement this chapter. Emission of hydrocarbons from cars is roughly 55% from the exhaust, 25% from the crankcase, and 20% from evapourative losses. The average car is presently driven about 10,000 miles per year and consumes about 700 gallons of gasoline. In 1962 the mileage was about the same but about 800 gallons of gasoline were consumed (Jones, J.H. and J.C. Gagliardi, 1967). Gasoline averages about 0.05% sulphur and 2.5 ml of TEL per gallon. As stated earlier, 1 ml of TEL contains about 1 g of Pb which ends up as lead salts.

Estimated Total U.S. Emissions of Various Pollutants in Millions Tons per Year

	Auto exhaust	Nonautomotive	Total
CO	66	5	77
HC	12	7	19
NO_x	6	7	13
SO_2	1	25	26

Lead	0.2	-	0.2
Particulates	1	11	12

Nonautomative sources include industrial operations, heat and power generation, and waste incineration. They comprise the source of about one-third of the pollution in the U.S. The two-thirds share of automobiles has already been significantly reduced. Installation of positive crankcase ventilation (PVC) has eliminated about 25% of the HC emitted by cars since the 1966 model year. Exhaust emissions have been reduced as indicated in chapter 2 starting with the 1968 model year. Offsetting these gains is the increase in car population. Car sales in the U.S. are now at a rate of about 10,000,000 per year. Life of a car is about 10 years. In this year (1975) the U.S. car population has exceeded 100,000,000. California accounts for the purchase of about 10% of new cars sold in the States and has had crankcase emissions controlled since 1963 and exhaust emissions controlled since 1966.

The size of the figures in the table above becomes even more alarming when one realizes that these tonnages are not evenly spread out but are concentrated in the cities and suburbs. Our populous areas vary widely in the amount of ventilating winds and cleansing rains they receive. Some correspondences must be established between pollutant levels in the adverse effects such as vegetation damage, eye irritation, increase of lead and combined CO levels in the blood of people, and impairment of visibility. Still more difficult to determine are the synergistic effects of pollutants or their absolute contribution to chronic illnesses amongst populations. The need for data gathering, research, and criteria writing is immediately obvious. An enormous amount of work has been done and is partly cited in the list of references to go with this chapter, as well as some in the other chapters. The authoritative summaries of the information as these, support the establishment of standards for ambient air qualities for the different areas. Air quality standards involve dosage, i.e., the time duration of a concentration of a pollutant. As an example, the California Department of Public Health has set CO standards calling for less than 30 ppm CO for an eight-hour exposure or 120 ppm CO for one-hour exposure. Colorado's Air Pollution Control Act of 1967 declares unacceptable an NO_x level of 0.1 ppm for one hour and a total oxidant level of 0.1 ppm for one hour.

Emission standards for specific pollutant sources could be set by summing average emission times and rates of the pollutant from all sources in an area, subtracting the amount of pollutant removed assuming an average rate of removal, and comparing the result with the air quality standard for the volume of affected air over the geographical area in question. Emission standards so set do not preclude aggravated localized situations or incidents of poor air quality caused by nonaverage weather affecting pollutant removal rates. After an agency has defined the existing air quality and identified the source of pollution in a region, a determination can begin as to how much to reduce existing emissions to reach the national air quality standards.

A simple mathematical calculation permits a general estimate of the percentage of reduction necessary throughout the region. Three facts must be known, as mentioned before, i.e.:

1) the existing concentration of a pollutant,
2) the air quality standard for that pollutant,

3) the background level of that pollutant in the region.

This is the "rollback" technique:

$$\text{Percentage of Emission Reduction} : \frac{(A-C) - (B-C)}{(A-C)}$$

A: existing concentration
B: air quality standard
C: background concentration

Once the percentage of rollback has been determined, the emission control strategy may be devised. This strategy is expressed in regulations and timetables for the prevention, abatement, and control of a pollutant.

The first automotive emission standards were set in California (cf. chapter 2) with the objective of attaining by 1970 an air quality equivalent to air quality in 1940 (Maga, J.A. and J.R. Kinosian, 1967), (Nissen, W.E., 1963). The records apparently indicate that smog was not a serious problem in California prior to 1940.

For purposes of data gathering and standards enforcement, adequate analytical methods are available for all the major pollutants (see reference index of this chapter). Those are not without international complications. In some places, hydrocarbons are analyzed by HSNDIR (hexane sensitized non-dispersive infrared). Results are expressed as parts per million of HC as hexane. Because the infrared spectrophotometer is sensitized to the C-H group in paraffins it does not register in full other exhaust components such as olefins, acetylenes, and aromatics. Other instruments such as a Flame Ionization Detector (FID) are capable of registering all the carbon-containing components of exhaust.

Seven mode cycle HC test results by HSNDIR must be multiplied by a factor of about 1.5 to arrive at the real (FID) HC emissions. The multiplying factor varies from mode to mode and is larger during the acceleration and cruise modes when the olefin content of exhaust is higher. Olefinic HC has been shown to be a primary raw material in the formation of photochemical smog in atmospheric inversion situations similar to Los Angeles (Haagen-Smit, A.J., 1952), (Leighton, P.A., 1961). On the basis of photochemical reactivity, smog indices have been developed for individual hydrocarbons (CRC Report No. 398, 1966), (Reckner, L.R. and W.E. Scott, 1968). The work on indices was performed by mixing the pure individual HC with NO and air followed by irradiation in a smog chamber. There is general recognition that the automotive HC emission standard should eventually be based on reactive HC. However, there is still considerable disagreement in the scientific community on where to draw the line between reactive and unreactive HC. Virtually all agree that methane is unreactive. Most agree that ethane too is unreactive. Many would also include propane and benzene in the unreactive category. Considering the rest of the HC in exhaust gas as reactive, the sticking point is the assignment of numerical values to smog indices or molar reactivity constants. There is some evidence that changes in the molar ratio of HC to NO_x may significantly increase the reactivity constant of HC formerly considered unreactive (Altshuller, A.P., et al., 1967, 1970). While studies continue the fact is that all legislated HC emission standards are in terms of total HC without regard to reactivity considerations.

During the catalytic oxidation of HC in exhaust, olefins are more completely oxidized than methane, ethane, propane, or benzene (Innes, W.B., and K. Tsu, 1962), (Weaver, E.E., 1969). Obviously, analytical methods directed at measurements of reactive HC in exhaust would more accurately reflect the contribution of a catalytic device to smog reduction.

The sequence described above goes for reduction below smog formation levels, in terms of corresponding pollutants. There is no reason why the accepted level for those could not go further down if another criteria were adopted, e.g. the carcinogenicity of some of the compounds involved, supported by adequate clinical and epidemiologic data.

The research effort on air pollution generally and on automotive air pollution in particular is enormous and data piling up. (Agnew, W.G., 1968), (Altshuller, A.P., 1969). There is little question but that our pollution control technology and knowledge of air pollution will be greatly augmented by research and development already in progress or projected. Of more concern is the area of public education. The automobile of a driver who prefers theacceleration-deceleration modes may have up to ten times the pollutant emission levels of the same automobile operated by a driver who prefers steady cruising (Duckstein, L. et al., 1968). Regulation of traffic flow patterns to induce steady cruise driving is obviously desirable. Education of drivers toward a steady cruise preference is likely to be difficult, particularly since it is counter to Detroit's historic advertising emphasis.

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7a. Appendix

Dynamometer procedure-the vehicle shall be tested from a cold start. Four warmup cycles and five hot cycles make a complete dynamometer run. Exhaust emission measurements for hydrocarbons and carbon monoxide will be performed during the four warmup cycles and during the sixth and seventh (hot) cycles. The dynamometer cycle is broken down in an earlier chapter.

Calculations (Exhaust Emissions)-the final reported test results shall be derived through the following steps:

1) Exhaust gas concentrations shall be adjusted to a dry exhaust volume containing 14.5 mole percent carbon atoms by applying the following dilution factor to the individual mode data.

$$\frac{14.5}{\%CO_2 + (0.5)\%CO + (1.8x6)\%HC}$$

Since hydrocarbons, carbon monoxide, and carbon dioxide all are measured with the same moisture content, no moisture correction is required to convert the results to a dry basis.

2) The adjusted mode data of paragraph 1 shall be weighed in proportion to the time spent in each mode during a typical metropolitan trip by applying the appropriate "weighting factor" (shown in a table to follow).

3) Composite hydrocarbon and carbon monoxide concentrations are determined for each cycle by summing up the respective weighted mode data of paragraph 2.

4) The composite cycle data of paragraph 3 shall be weighted in proportion to the time spent in each cycle, classified according

to "warmup cycle" and "hot cycle", during a typical metropolitan trip by applying the appropriate "weight factor" shown in another table to follow and a calculation example.

5) Composite hydrocarbon and carbon monoxide trip concentrations are determined by summing up the respective weighted cycle data of paragraph 4.

6) The overall composite concentration values of paragraph 5 shall be converted into mass emission values by substituting in the appropriate formula given in paragraph 7.

7) Formulas for converting concentration into mass:

a) For light duty vehicles, excluding off-road utility vehicles.

i) For hydrocarbons:

$$HC_{mass} = \frac{HC_{conc}}{1{,}000{,}000} \times (1.8 \times 6) \times \frac{\text{Exhaust volume}}{\text{mile}} \times \text{Density}_{HC}$$

ii) For carbon monoxide:

$$CO_{mass} = \frac{CO_{conc}}{100} \times \frac{\text{Exhaust volume}}{\text{mile}} \times \text{Density}_{CO}$$

b) Example calculation of composite cycle concentrations.

Mode	Conc as measured HC	CO	CO_2	Dilution factor	Adjusted HC	CO	Weighting fact.	Weighted HC	CO
Idle	99	1.2	14.0	14.5/14.8	97	1.2	0.042	4.1	0.05
0-25	125	0.6	13.5	14.5/13.9	130	0.6	0.244	31.7	0.15
30	159	0.6	13.6	14.5/14.1	164	0.6	0.118	19.4	0.07

30-15	93	1.2	14.0	14.5/14.7	92	1.2	0.062	5.7	0.07
15	90	1.0	14.1	14.5/14.7	89	1.0	0.050	4.4	0.05
15-30	116	0.3	13.5	14.5/13.8	122	0.3	0.455	55.5	0.14
50-20	210	1.3	13.6	14.5/14.5	210	1.3	0.029	6.1	0.04
Sum				(cycle composite)				127	0.57

or, for a metropolitan driving cycle:

Cycle	Concentration as determined HC	Concentration as determined CO	Weighting factor	Weighted HC	Weighted CO
1	319	4.68	0.35/4	27.9	0.41
2	136	0.66	0.35/4	11.9	0.06
3	127	0.57	0.35/4	11.1	0.05
4	128	0.48	0.35/4	11.2	0.04
5	Not read				
6	122	0.46	0.65/2	39.6	0.15
7	133	0.58	0.65/2	43.2	0.19
Sum		(trip composite)		145	0.90

c) Example Calculation of Mass Emissions Values

Assuming: 1970 model light-duty vehicle with automatic transmission, equipped with evaporative emission control system and tested with a 3,500-lb dynamometer inertia wheel (W = 3,500):

$$HC_{mass} = \frac{(145-20)}{1,000,000} (1.8 \times 6)(-6.69 + 0.0277 \times 3,500 - 0.00000201 \times 3,500^2) \times (16.33) = 1.45 \text{ g/mile}$$

Assuming: Another model with manual transmission, tested with a 4,500-pound dynamometer inertia wheel (W = 4,500):

$$CO_{mass} = \frac{(0.90 \times 0.85)}{100} (-6.00 + 0.0249 \times 4,500 - 0.00000181 \times 4,500^2) \times (33.11) = 17.6 \text{ g/mile}$$

8. Engine-Device Systems and their Future

As stated earlier the problem of exhaust emission control will be solved by a series of economic choices between feasible alternatives. The table to follow gives the range as determined feasible by representatives of the U.S. Government, industry, and academic experts for the period 1967-1975. The economic basis has since then altered, with the result that some of the projected goals for 1975 will not be reached this year, i.e. as swiftly as expected. The improvement over this period is, however, tremendous. Two columns of numbers under a date represent a choice between either lowering HC and CO or lowering NO_x.

	Demonstrated technical feasibility,'67		Commercial feasibility				Ultimate feasib.
			1967	1970	1975		
	Either	Or			Either	Or	
Hydrocarbons, ppm (as hexane)	50	275	275	180-200	275	50	<25
Carbon Monoxide, %	0.7	1.5	1.5	1.0-1.2	1.5	0.5	<0.25
Nitrogen Oxides, ppm	500	350	1500	600-800	350	350	<100

In speculation for new device systems, there is undoubtedly room for improving manifold air injection devices. Speculating further, perhaps carburettion problems will disappear with adoption of fuel injection. On the other hand, considerable progress has already been made in carburettor and intake manifold design. Hence it may be economically preferable to continue with an improved carburettor and treat the somewhat higher emissions with an improved manifold reactor. Since manifold reactors are less effective in converting CO and HC than catalytic devices, a catalytic device might be preferable. Over the life of a car the cost of a manifold reactor may probably be lower than the cost of a catalytic device. Counterbalancing this the catalytic device might provide a relatively easy and reliable way for motorists to pass emissions inspection tests. It might be that two catalytic devices, one to convert NO_x and the other to convert HC and CO will provide the ultimate feasibility levels of the table above. It would be preferable, though, from many points of view, if this could be achieved by one device.

Catalytic devices were thoroughly evaluated and dismissed by a member (Ford) of the automobile industry in 1962 (Schaldenbrand, H., and J.H. Struck, 1962). In retrospect, this conclusion was economically inevitable considering the early stage of development of emission control by motor modification. At this time catalytic devices are being reevaluated in all respect by Ford utilizing the advances in engine technology made since 1962 in a systems approach. It is not presently possible to state that catalytic devices will or will not appear worldwide and survive in the marketplace. One thing is certain; within the next few years the gasoline engine will be pushed to the wall with respect to emissions control. Car manufacturers will need to use all the resources at their disposal to meet this challenge. It is not altogether worrying for them, since it will be the customer who pays the research and developement cost in the end.

Recent economic developments in the western world, particularly in the United States have forced pollution control issues back, so the intended emission limits for 1975 have had to be cancelled and put back, aiming for 1978 - 1982 instead. This was reported in the Federal Register, E.P.A., March, 1976. Future developments in the motor industry will, however, take into account the emission control constraints and work towards a permanent solution for vehicular air pollution control.

PART II

A Correlation of Emissions in Relation to Source.

1. Introduction.

In part I, we have seen how a practical problem has been tackled by various concerns and how the different solutions have been affected by the economic and political situations that have arisen in and after the "oil crisis". Most of the action in catalyst technology has been in the United States, where some of the urban areas are frequently hit by patches of serious air pollution. It is the aim of part two of this thesis to examine the actual need for such action in Britain. Various automotive air pollutants are monitored at three sites; two urban ones and one rural. The pollutants are then related to each other to assess what fraction of the total environmental air pollution actually is from automotive sources. The manifestation that carbon monoxide can be used as an indicator of airborne lead concentration is tested and a new method for determination of organic lead in air is tested out for its stability.

2. Experimental Set-up, and sampling procedure.

Use was made of the Public Health Engineering Mobile Laboratory, which is specially equipped for air pollution monitoring. Among the instruments included are:

1) A sampling pump and duct system (see fig. 6 and plate 2)
2) An Air Quality Chromatograph (see fig. 7 and plate 2)
3) A smoke analyser
4) Air filters for sampling inorganic lead compounds
5) A dual-pen chart recorder
6) A dual-column gas chromatograph
7) A collapsible mast supporting an anemometer and wind-vane linked to a directional sampler and recorder
8) A wet and dry bulb thermometer
9) An aneroid baromenter

The instruments used in the laboratory for further analysis are:-

1) A double beam atomic absorption spectrophotometer
2) A heated graphite atomiser
3) A deuterium arc background corrector

Main Instruments and facilities used for this survey will now be described in more detail:

2.1 Air Sampling Duct - intake of ambient air is projected 300 mm above the roof of the mobile laboratory (see fig. 6 and plate 2). A continuous stream of air is drawn through the duct by a pump situated at its base. Sub-samples of air can then be withdrawn isokinetically from several points on the duct.

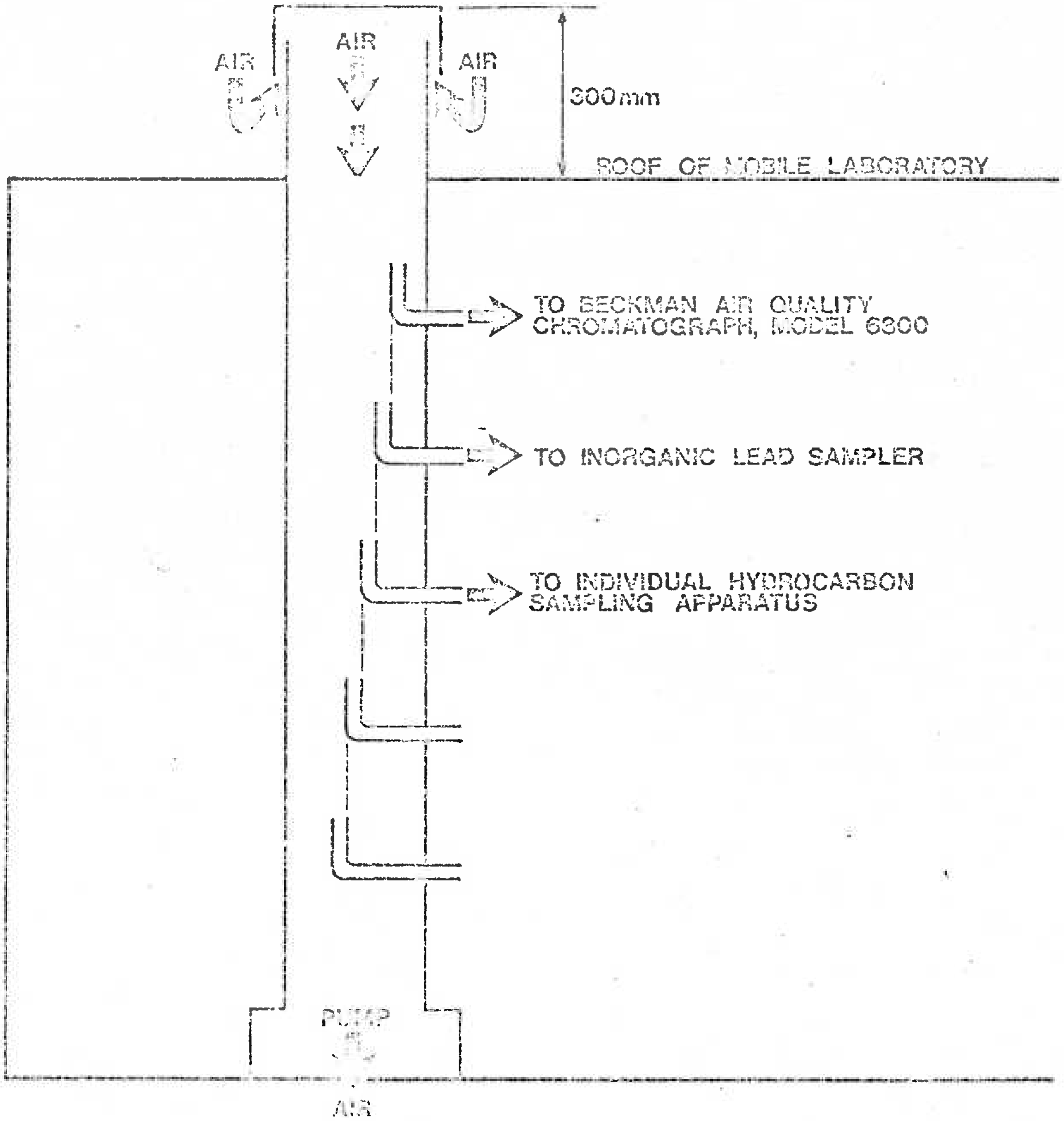


Figure 6. Mobile Laboratory Sampling Duct.

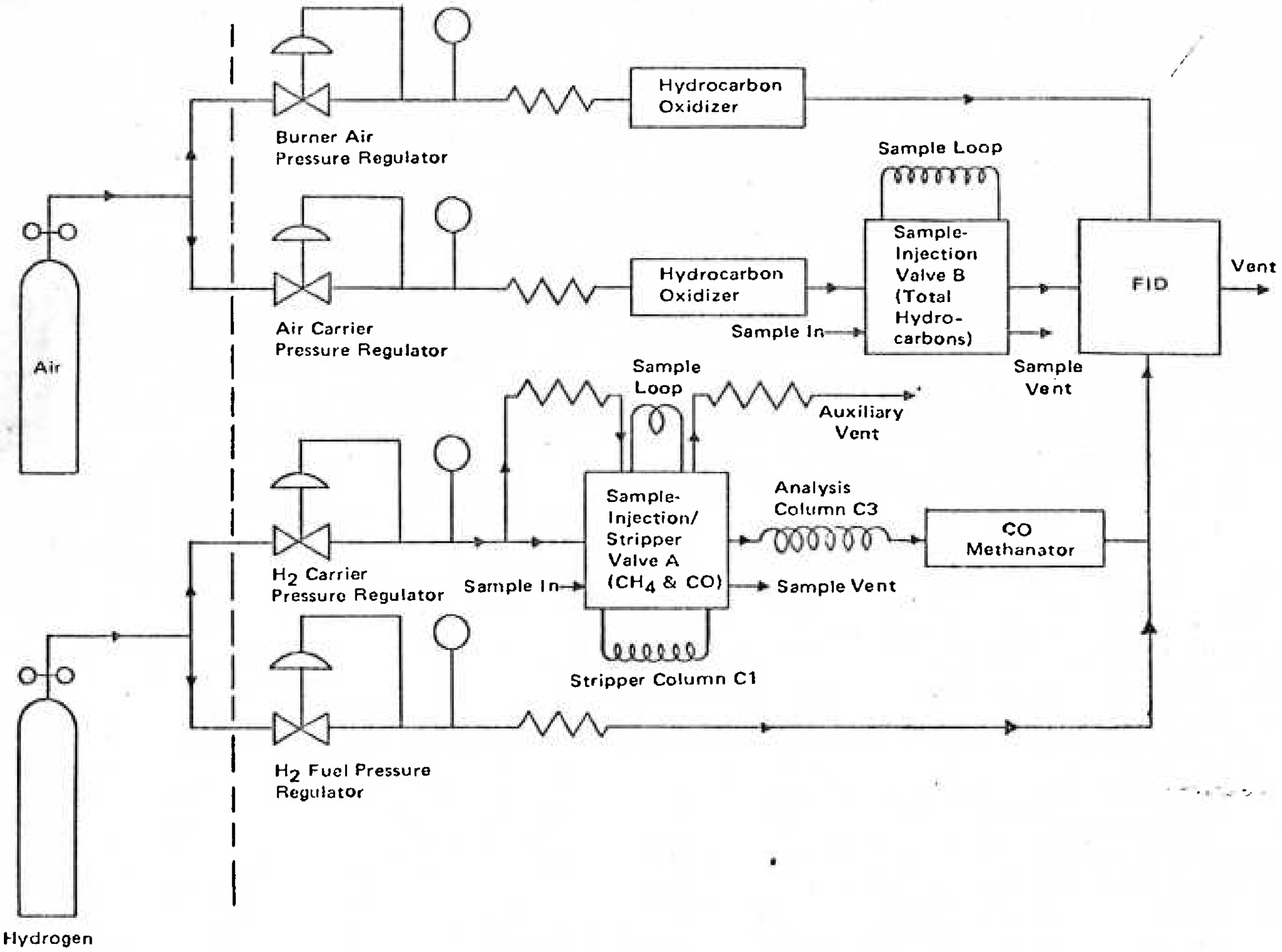


Figure 7. Schematic Diagram of Air Quality Chromatograph.

Plate 1.   The Mobile Laboratory.

Plate 2. Interior of mobile laboratory showing sampling duct and Beckman Air Quality Chromatograph Model 6800.

Two of these points are linked to the Air Quality Chromatograph and the inorganic lead filter respectively ensuring that a sample of the same mass of air is delivered to each of the instruments for analysis.

2.2 The Air Quality Chromatograph - The model 6800 Beckman Air Quality Chromatograph is an integrated, modular analysis system for automatic, continuous, unattended monitoring of low-level atmospheric pollutants. The instrument is equipped to perform a three-component analysis that measures the concentrations of total hydrocarbons, methane, and carbon monoxide in ambient air.

Atmospheric sample is drawn into the analyser by an internal suction pump. Within the instrument, components are separated by column chromatography. The column effluent is routed to a flame-ionization detector (FID). Solid state electronic circuitry measures the detector signal and provides outputs for chromatogram or bar graph and trend data-presentation. The Model 6800 consists of three sections:

i) Gas Control Section,
ii) Chromatographic oven section,
iii) Electronic control section.

Gas Control Section - On the rear panel of the gas control section are all the inlet and outlet gas connections. On the front panel are pressure regulators and associated gauges for air and hydrogen carrier gases, hydrogen fuel and air support gases for the FID, and service air to operate the slider valves in the chromatographic oven.

Chromatographic Oven - The chromatographic oven is a heated, temperature-controlled compartment. It contains the following elements:-

1. Chromatographic columns used to separate the sample components.

2. Pneumatically-actuated slider valves that perform the sample-injection and the stripping functions.

3. Flame-ionization detector

4. A fan at the rear of the compartment, which circulates air to equalize temperature throughout the oven.

Electronic Control Section - Includes circuitry for the following functions:-

1. Ignition of flame in FID.

2. Measurement of the output signal from the FID.

3. Automatic control of all time-related functions, including auto zero.

4. Trend and continuous analog presentation of data.

5. Power Supplies.

Instrument Theory - Principle of operation:

Chromatographic analysis involves a separation based on the differing solubilities of various components of a sample passing through a packed column.

A measured amount of sample is injected into the column and is swept along by a continuous flow of inert carrier gas. Individual components emerge from the column, at different times, as elution bands diluted with carrier gas.

The column effluent is monitored continosly by the flame ionization detector (FID). The output signal from the FID is processed electronically and is applied to the recorder or other data-presentation device.

Flow System - The flow configuration of the 3-component analysis system is shown in simplified form in fig. 7 , and in greater detail in fig. 8 . This system provides determination of total hydrocarbons, methane, and carbon monoxide.

Analysis Channel for Carbon Monoxide and Methane Determinations -

To initiate the analysis, valve A (see fig. 9) is actuated, either by manual closure of the front-panel switch designated VALVE A or by automatic command from the programming circuitry. The valve slider is now retracted, resulting in the sample-injection/stripper-foreflush condition (see fig. 10). Hydrogen carrier sweeps the contained sample from the sample loop and into stripper column C 1.

The stripper column, C 1, is used to separate the fast-eluting desired components (methane and carbon monoxide) from the slower-eluting undesired components (CO_2, H_2O, C_2-and-heavier hydrocarbons, etc.). This separation permits discarding the undesired components to prevent their entry into, and resultant contamination of, analysis column C 3.

Methane and carbon monoxide elute from C 1 as a single, undifferentiated peak, which would be followed within 15 to 20 seconds by the CO_2 peak. During this brief interval before the CO_2 would elute, stripping must be initiated by deactuating Valve A, thus returning it to the sample-purge/stripper-backflush condition, fig. 9 . Selection of the proper moment to deactuate Valve A is rather critical; if stripping is initiated too late, CO_2 would enter and contaminate Analysis Column C 3. In practice,

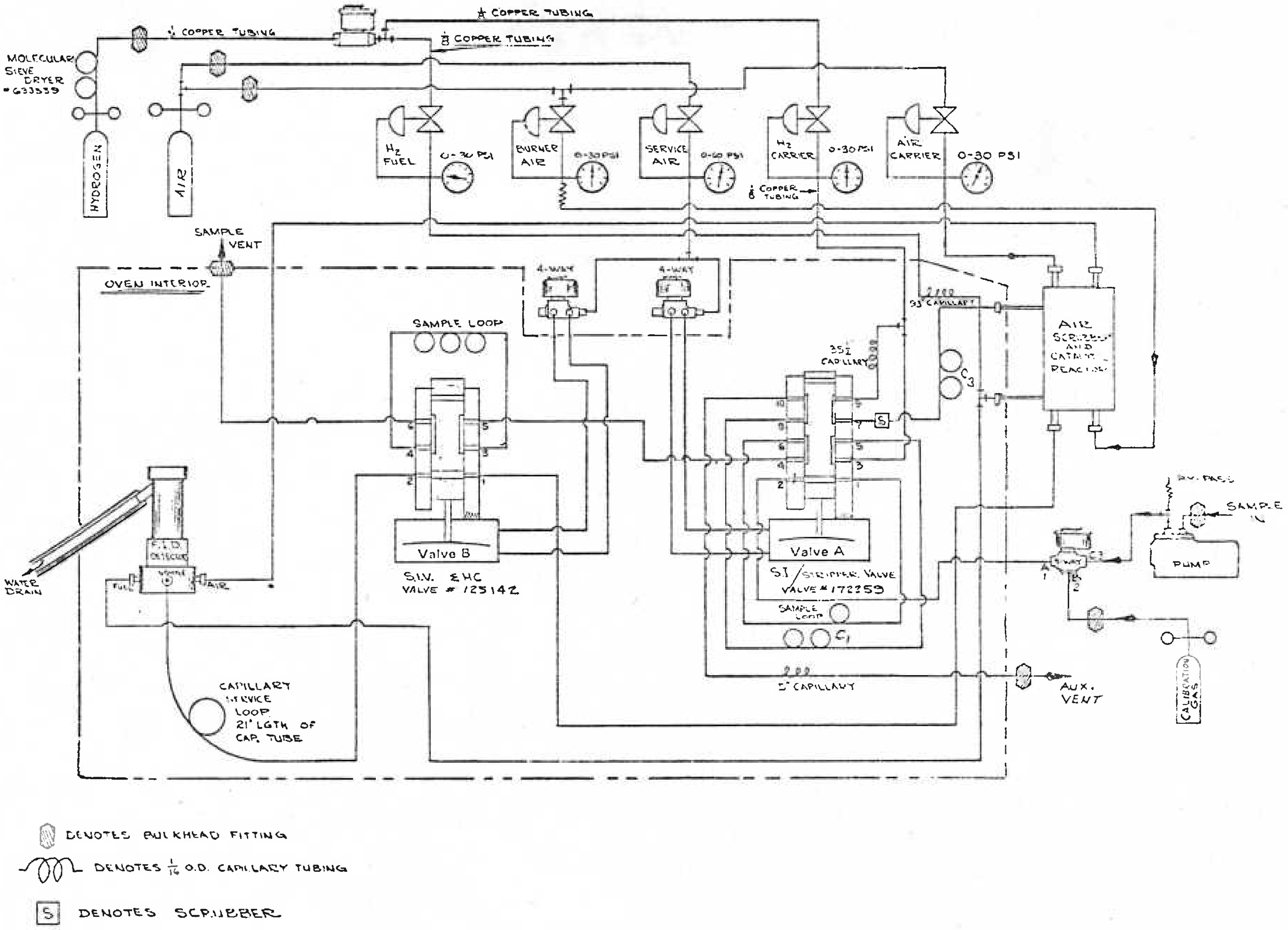


Figure 8. A Detailed Flow Diagram of a Three Component Air Quality Chromatograph System.

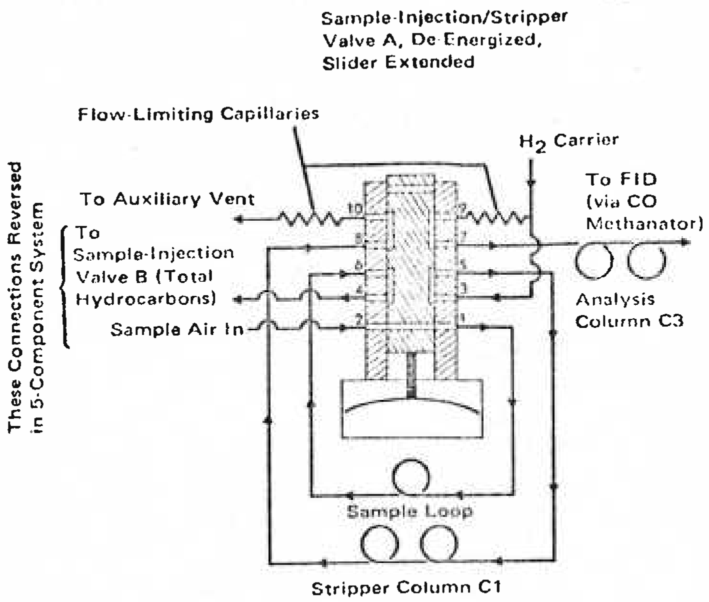


Figure 9. Sample-Purge Stripper Backflush Condition

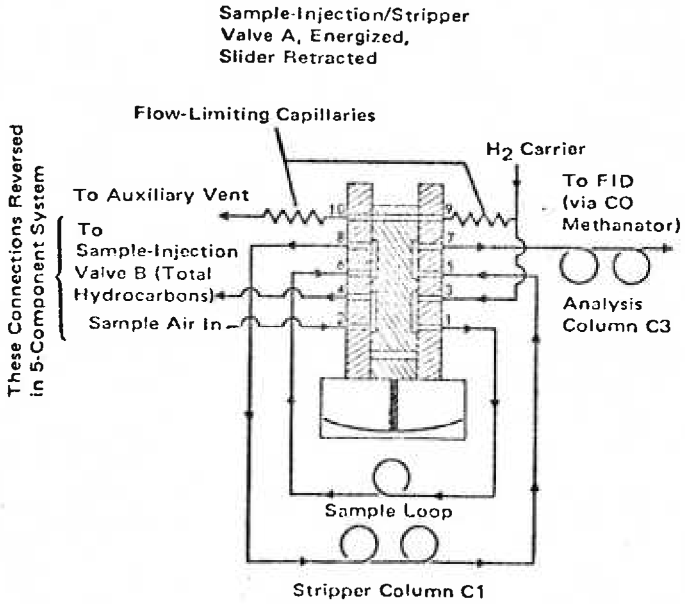


Figure 10. Sample-Injection/Stripper Foreflush Condition.

the proper time to deactuate Valve is determined experimentally. With stripping initiated at the correct time, the undifferentiated methane/carbon monoxide peak enters analysis column C3 while the undesired components have not yet emerged from column C1. The undesired components are now backflushed to an auxiliary vent. Backflushing continues throughout the remainder of the analysis cyrcle, to clear the undesired components from the stripper column and prevent their interference with subsequent analyses. During backflushing, flow to the auxiliary vent is controlled by a flow-limiting capillary to prevent excessive consumption of of the hydrogen carrier. An auxiliary flow of hydrogen carrier is supplied to analysis column C3 through another capillary, which is sized to maintain hydrogen flow to the FID at a constant rate, regardless of the status of Valve A.

After the methane and carbon monoxide emerge, now resolved, from analysis column C3, they pass through a catalytic methanator, Here the carbon monoxide is converted into methane to permit its detection by the flame ionization detector. As the sample components pass through the detector, the recorder registers two peaks, the first is due to methane originally present in the sample, the second is due to methane obtained from conversion of carbon monoxide into methane.

Analysis Channel For Total Hydrocarbons Determination.

High purity air supplied to the ANALYZER AIR inlet is routed, via the AIR CARRIER pressure regulator, to an oxidizer for removal of the trace hydrocarbon contaminants normally present in even the cleanest available cylinder air. The resultant Hydrocarbon-free carrier air is routed to sample-injection Valve B.

Normally, Valve B is de-energized, slider extended, resulting in the purge condition (see fig. 11). Sample air flows continuously through the sample loop and out through the rear-panel SAMPLE VENT. A continuous flow of hydrocarbon-free carrier air passes directly through the valve to the carrier air inlet on the FID (see fig. 13).

To inject sample, the valve is actuated, either by manual closure of the front panel switch designated VALVE B, or by automatic command from the programming circuitry. The slider now retracts, placing the valve in sample-inject condition,(fig. 12) Carrier flow now sweeps the contained sample out of the loop, directly to the FID. New incoming sample now passes directly through the valve to the SAMPLE VENT.

After sample injection, the valve is de-energized, returning it to the purge condition (fig. 11).

Flame Ionization Detector (FID)

The principal components of the FID (fig. 13) are the manifold, the burner jet, and the collector.

Streams of air carrier, hydrogen carrier mixed with hydrogen fuel, and air support gas are delivered by the chromatograph flow system (see description before) and are routed through internal passages in the manifold and into the interior of the FID. Here the carrier air and the hydrogen stream pass through the burner jet and into the flame; the stream of support air flows around the periphery of the flame. The burner jet and the collector function as electrodes. The jet is connected to the positive terminal of the 90-Volt power supply. The collector is

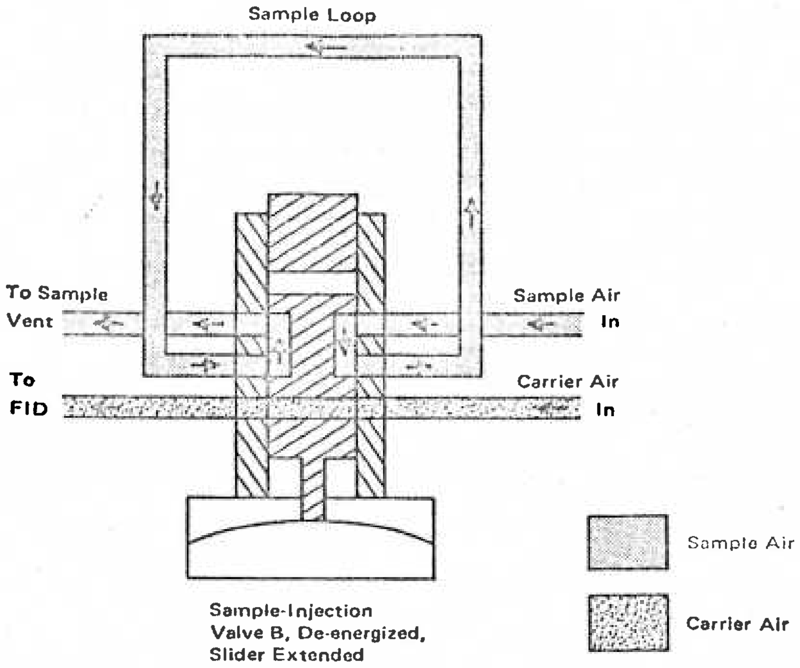


Figure 11. Flow Diagram of Sample-Injection Valve B and the Total Hydrocarbons Analysis Channel Valve Purging.

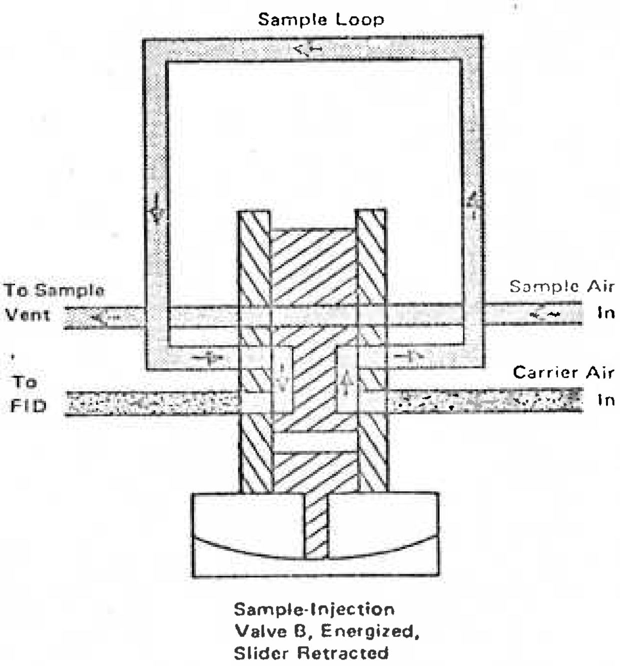


Figure 12. Same as fig. 11, Sample Injection.

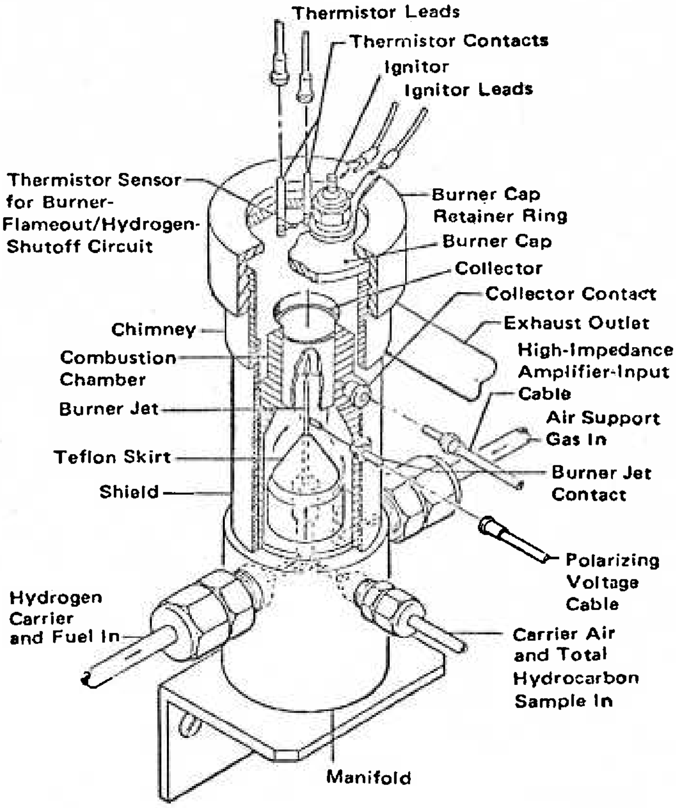


Figure 13. Sectional View of a Flame Ionization Detector.

connected, via the flame amplifier to the negative terminal. The two polarized electrodes establish an electrostatic field in the vicinity of the flame. The field causes the charged particles formed during combustion to migrate. Electrons go to the burner jet; positive ions go to the collector. Thus, a small ionization current flows between the two electrodes. Magnitude of the current depends on the concentration of carbon atoms in the carrier. The burner current serves as the input signal to the electronic measuring circuitry.

Mounted with the burner cap are: i) thermistor sensor for burner-flameout/hydrogen-shutoff circuit, and ii) igniter, used by flame ignition circuit.

Electronic Circuitry - Summary

The electronic control section contains all circuits for:-

1) Ignition of flame in FID,
2) Measurement of the signal from the FID,
3) Automatic control of all time-related functions,
4) Data presentation.

The Beckman automatic instrument measures total hydrocarbons, methane and carbon monoxide at five minute intervals, the concentration of non-methane hydrocarbons being calculated from the total hydrocarbon and methane results. Calibration is achieved by the use of a standard gas mixture supplied by British Oxygen (9.5 ppm methane, 8.5 ppm carbon monoxide). The total hydrocarbon results were thus expressed on a methane basis. The detection limit is 0.05 ppm for each of the three components, whilst the operating range is 0.05 - 300 ppm.

2.3 Atomic Absorption Spectrophotometer.

The basic principle of atomic absorption can be described as the inverse of that of emission methods for determining metallic elements. In all emission techniques, the sample is excited to make it give off radiation of interest. At the same time, the sample cannot be prevented from giving off radiation which is not of interest. The appropriate type of filtering system is employed to select the radiation which the analyst wants; the radiation intensity is measured; and by comparison with standards, the concentration of the desired element in the compound is found.

In atomic absorption, the opposite process takes place. The element of interest in the sample is not excited, but is merely dissociated from its chemical bonds, and placed into an un-excited, un-ionised "ground" state. It is then capable of absorbing radiation at discrete lines of narrow bandwidth, i.e. the same lines as would be emitted if the element were excited.

When the atomic vapour is illuminated by an appropriate light beam, a ground state atom absorbs a photon of light, and the energy of the latter causes a change in the distribution of an electron in the atom, bringing it into the so-called excited state. The difference in energy between the two states is equal to the energy of the absorbed photon.

Each species of atom may only exist in certain excited states with definite energies, consequently only photons having specific energies are absorbed; these energies corresponding to lines of the atomic absorption spectrum of the element.

This process is quantitative; thus the percentage absorption of an atomic vapour (such as might be present in a combustion flame) at the resonant frequency of a given element is a direct

[redacted]

[redacted]

Plate 3. Perkin Elmer Atomic Absorption Spectrophotometer equipped with HGA 72 Furnace.

measure of the number of atoms of that element in the vapour.

The basic instrument used for the analysis of the metal concentrations is the Perkin-Elmer 305, Double Beam Atomic Absorption Spectrophotometer to which has been added a Heated Graphite Atomizer HGA 70 for the detection of trace elements at very low concentrations and a Deuterium Arc Background Corrector to remove unwanted absorption.

The basic Double Beam instrument is a development of the more extensively used Single Beam a.c. system in which a source light from a hollow catode lamp is chopped producing an alternating current and the flame light left unchopped. The chopped light produces alternating current in the detector. Because the amplification is arranged to be selective to alternating current, the light from the flame is ignored. In the double beam instrument, the rotating chopper is replaced by a rotating sector mirror, which passes the beam from the lamp alternately through the flame (sample beam), and past the flame (reference beam). The sample and reference beams are recombined by a half silvered mirror and then passed together through the rest of the system. The electronics are designed to measure the ratio of the two beams. The readout is the fraction produced by the sample beam as numerator and the reference beam as denominator. Changes in lamp emission, detector sensitivity, and electronic gain appear in numerator and denominator and are cancelled out.

The double beam system thus gives a stable baseline almost immediately, and has the following advantages:-

i) lamps can usually be inserted and operated at once with little or no wait for warm up;

ii) the stability of the baseline makes it possible to see small departures from it, thereby improving detection limits over the single beam method.

iii) a stable baseline implies good analytical precision.

2.4 Heated Graphite Atomizer.

The usual method of dissociating the element being investigated from its chemical bond is by burning the sample in a flame, giving detection limits as low as 0.001 g for cadmium. However, by using a heated graphite atomizer for atomizing the sample, detection limits down to 10^{-13} g are possible.

The atomizer is situated in the measuring beam of the spectrophotometer and the sample to be analysed is brought into the atomic state in a white hot graphite tube. The free atoms remain in the tube for periods of up to one second or longer. This is about 1000 times longer than in an open flame where, due the gas flow, the atoms are carried through in a few milliseconds. Consequently, a larger number of atoms are stimulated to light absorption, thus allowing the use of very small sample amounts or the detection of very small absolute trace amounts. Atomisation in the graphite tube is also free from interferences such as oxidation found in a flame, as the atomisation procedure is carried out in an inert gas atmosphere.

The entire sample dosed into the graphite tube is atomised and the measurement result is a direct measure of the absolute weight or amount of the element being analysed. This is of great advantage for samples with very low concentrations, as increasing the sample amount dosed also increases the measurement signal. On the other hand, for samples of higher concentration, very small sample amounts (down to the nanolitre range) are sufficient.

Inert Gas - The inert gas prevents the graphite tube from burning and flushes vaporized and atomised materials from the tube. The flow rate is set at about ten times the volume of the graphite tube per second (1,5 to 1.7 liters/min) when the pressure gauge on the gas cylinder is set at 15 p.s.i. There will be some gas loss through the injection hole of the graphite tube (about 20% when the tube is new) and care must be taken to see that there is no gas escape elsewhere, particularly during a measurement sequence, either from connecting hoses or badly fitted observation tube as this will significantly affect the peak height recorded. The influence of fluctuations in gas flow can be minimised by the use of Argon gas (very high purity; <5 v.p.m. oxygen). The full interruption of the inert gas flow (Gas Stop facility) during the atomisation stage leads to a longer period of stay of the atoms formed in the beam path, particularly for the easily atomised elements (Zn, Cd) with a consequential increase of up to five times in the sensitivity of the instrument and also an improvement in the detection limits. However, it is not necessary to use this facility in all cases.

Programmed Measurement Sequence - Unlike the flame technique in which the process of drying the sample through to atomisation takes place in very rapid sewuence, the graphite atomiser is programmed to carry out the stages more slowly and in stepwise sequence. The control unit of the H.G.A. allows the sample to be prepared in up to four independent time-temperature circuits.

The purpose of pre-treatment of the sample in the graphite atomiser is to free the element as far as possible from accompanying material which might give rise to interferences during the atomisation stage, and this is accomplished by programmes for drying, ashing and atomisationof the sample injected.

1. Drying - The drying is controlled by temperature and time. A temperature is selected which is just under the boiling point of the solvent of the solution to prevent spitting and possible loss of metals out of the end of the tube. Complete drying is essential and a rule of thumb guide of 1.5 - 2 seconds/µl of the sample is recommended. For an injection of 25µl a drying time of 30 sec is considered to be adequate for complete drying of the sample.

2. Thermal Destruction of the Matrix (Ashing) - The purpose of this stage is to free the element from accompanying material. At higher temperatures, organic substances char with the formation of smoke or soot; inorganic substances distil, sublime, or decompose with the formation of mist. If this takes place during the atomisation of the element then the element's specific signal will be completely masked by non-specific signals caused by the light scattering. the thermal dastruction temperature is dependant upon the nature of the matrix and the volatility of the element of interest, and a temperature is selected near or slightly above that at which the matrix distils, sublimes or is decomposed. Recommended time and temperature programmes are available from the Perkin-Elmer manual for the elements being investigated.

3. Atomisation- After it has been released from interfering accompanying material, the element of interest can be thermally dissociated into its atoms. The temperature of dissociation has a direct influence on the peak height of the signal, but an optimum temperature has to be selected which is consistent with signal height (maximum temp.). Recommended temperatures and times were obtained from the Perkin-Elmer manual.

2.5 Deuterium Arc Background Corrector.

The Deuterium Arc Background Corrector is designed for use in a Perkin-Elmer double beam atomic absorption spectrophotometer to remove the effects of unwanted absorption or light scattering. The accessory consists of a deuterium arc optical assembly and a power supply module.

The continuum radiated by the deuterium arc replaces the ordinary reference beam of the double beam system, which is automatically cut off by a shutter when the arc is turned on. A motor driven variable attenuator (graded neutral density filter) serves to balance the reference beam' energy radiated by the deuterium arc and the sample beam energy of the hollow cathode lamp.

Since the unwanted (background) absorption is of equal intensity in the two beams, its effect on the signal is cancelled when the two beams are balanced. This leaves the sample beam absorption due to the element of interest as a corrugated signal.

2.6 Air Sampling Equipment and Inorganic Lead Analysis.

A measured volume of air was drawn by a Charles Austen pump (Type DY Mk. 1) from the sampling duct through a 0.22µm membrane filter (Millipore Type HAWP 04700, 47mm dia.). The filtered air was then fed onwards to the Air Quality Chromatograph for gaseous analysis. The filter was held by a filter holder connected to a gas meter, equipped with a pressure indicator (vacuum meter) and a temperature indicator, for the correction of the air volume measured. All the interconnecting leads were made out of teflon tubing. The sampling flow rate is approximately 5.0 l/min to ensure that there is never any dead space in the flow to the A.Q.C.

The filters were brought back to the central laboratory and treated in the following manner: (see method described by R.M. Harrison et al., 1974)

The Millipore filter is transferred to a covered polypropylene beaker. (All handling of filters is by tweezers, cleaned out in dilute nitric acid). 5 ml of an aqueous 10% hydrogen peroxide (B.D.H. High Purity Aristar, 100 vol.)/ 10% nitric acid (B.D.H. Aristar 70% w/w) solution is added to the beaker. The filter is given a good swirl in the mixture and then left for 30 minutes. 25 µl are then taken from the solution and analysed by atomic absorption at 283.3 nm using the following time-temperature programme:

Cycle 1 :15 minutes at 53°C - Drying

Cycle 2 : 1 minute at 82°C - -

Temperature Programming : 5 126 (increase to 500°C at rate 5)

Cycle 3 : 5 seconds at 2000°C - Atomising

Cycle 4 : 1 minute at ambient - this is to standardise period between consecutive injections.

Standard lead solutions were prepared in an aqueous 10% hydrogen peroxide/ 10% nitric acid medium and a blank value obtained from an unused filter was subtracted from the analytical results. All the apparatus used was rinsed with 35% nitric acid and washed with distilled water prior to use. New standards were prepared daily from a stock of 1000µg/ml lead solution. It has been shown by Atomic Absorption Spectrophotometry workers aqueous solutions of metal salts with this concentration remain stable for periods of up to twelve months, whereas dilute aqueous solutions of 0.1 µg/ml can possibly experience a change in concentration of 2 or 3% in a couple of days due to adsorption of the metal on the glass.

2.7 Selection of sites.

Originally, the intention was just to compare a rural with an urban situation as regards the atmospheric pollutants mentioned before. These were the sites at Prince Consort Road, London, S.W. 7, near the college and sites north of the River Tees, Teeside during a larger monitoring survey of hydrocarbons that the college undertook. When the preliminary results had been obtained and processed, it was felt necessary to fill in the data with a survey from a site with a higher gaseous pollution concentration than obtained before. This data substantiated further the overall conclusions of this part of the work. The site selected was the entrance of Olympia Car Park, London, W.14.

3. Results and Data Handling.

Measurements of Carbon Monoxide, Methane and Total Hydrocarbons were carried out every 5 minutes by the automatic Air Quality Chromatograph. These can be plotted to show the diurnal variations (see graphs 1 - 4), and also expressed in terms of their ranges and means over the sampling period. The intention with this work was, however, to examine to what an extent they were correlated with airborne lead. If there were significant correlations, the four pollutants were likely to originate from the same source.

The 5 minute samples were therefore expressed as averages over the relevant lead sampling period (standard deviation given), thus giving a common basis for comparison. The data are tabulated hereafter, giving time of day when accumulated, concentrations in ppm for the gases and $\mu g/m^3$ for the lead. Averages are also given with standard deviations, for the gases.

A. Prince Consort Road/Exhibition Road, June 3rd, 1975.

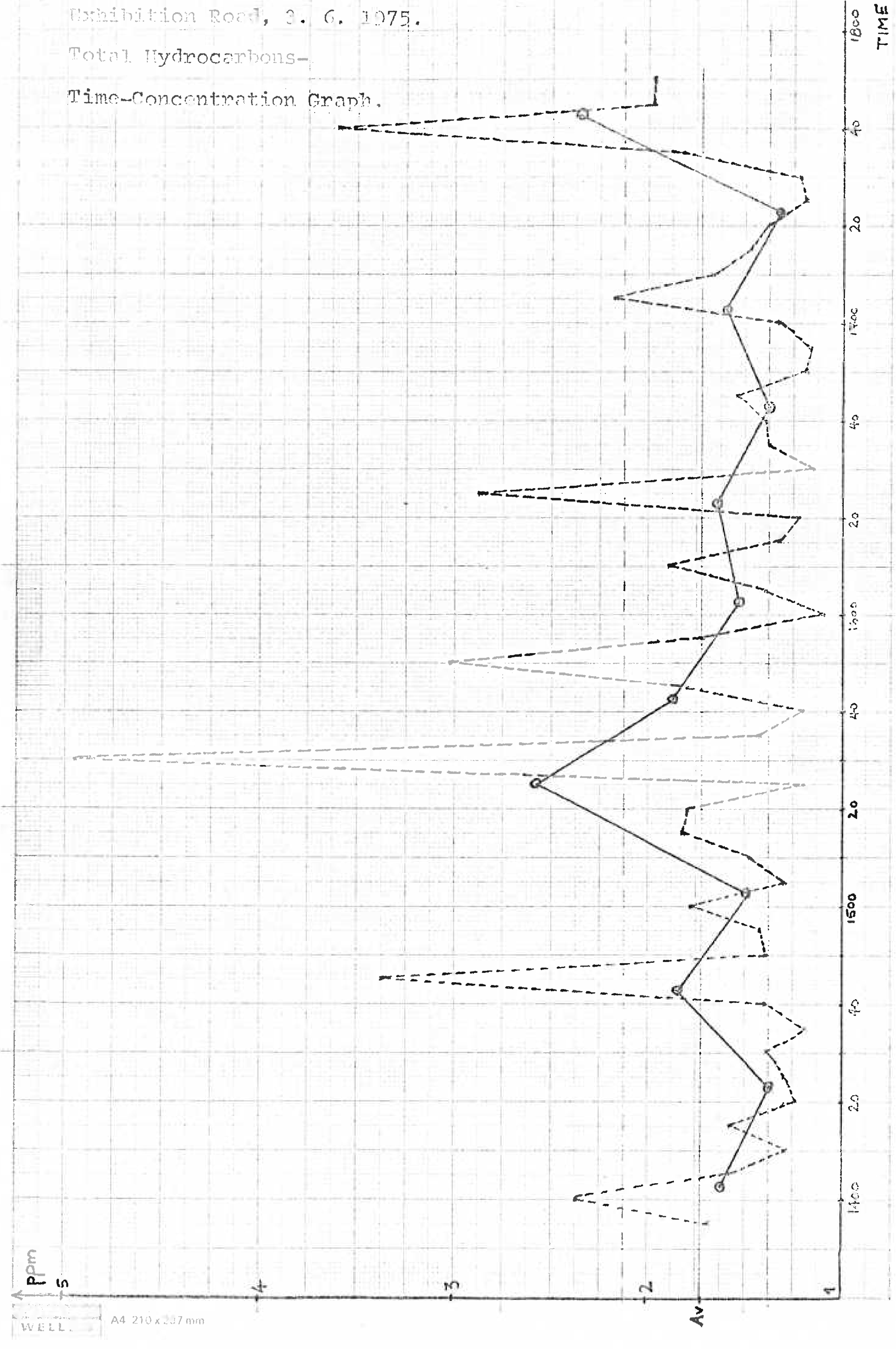
Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1355	1.68	1.60	3.14				
1400	2.38	1.30	1.24	1.73 ±0.46	1.38 ±0.15	1.43 ±1.18	4.1
1405	1.58	1.30	0.76				
1410	1.29	1.31	0.57				
1415	1.58	1.30	0.76				
1420	1.23	1.35	1.42	1.37 ±0.15	1.32 ±0.02	1.04 ±0.38	1.4
1425	1.29	1.32	0.66				
1430	1.39	1.29	1.33				

1.

Exhibition Road, 3. 6. 1975.

Total Hydrocarbons-

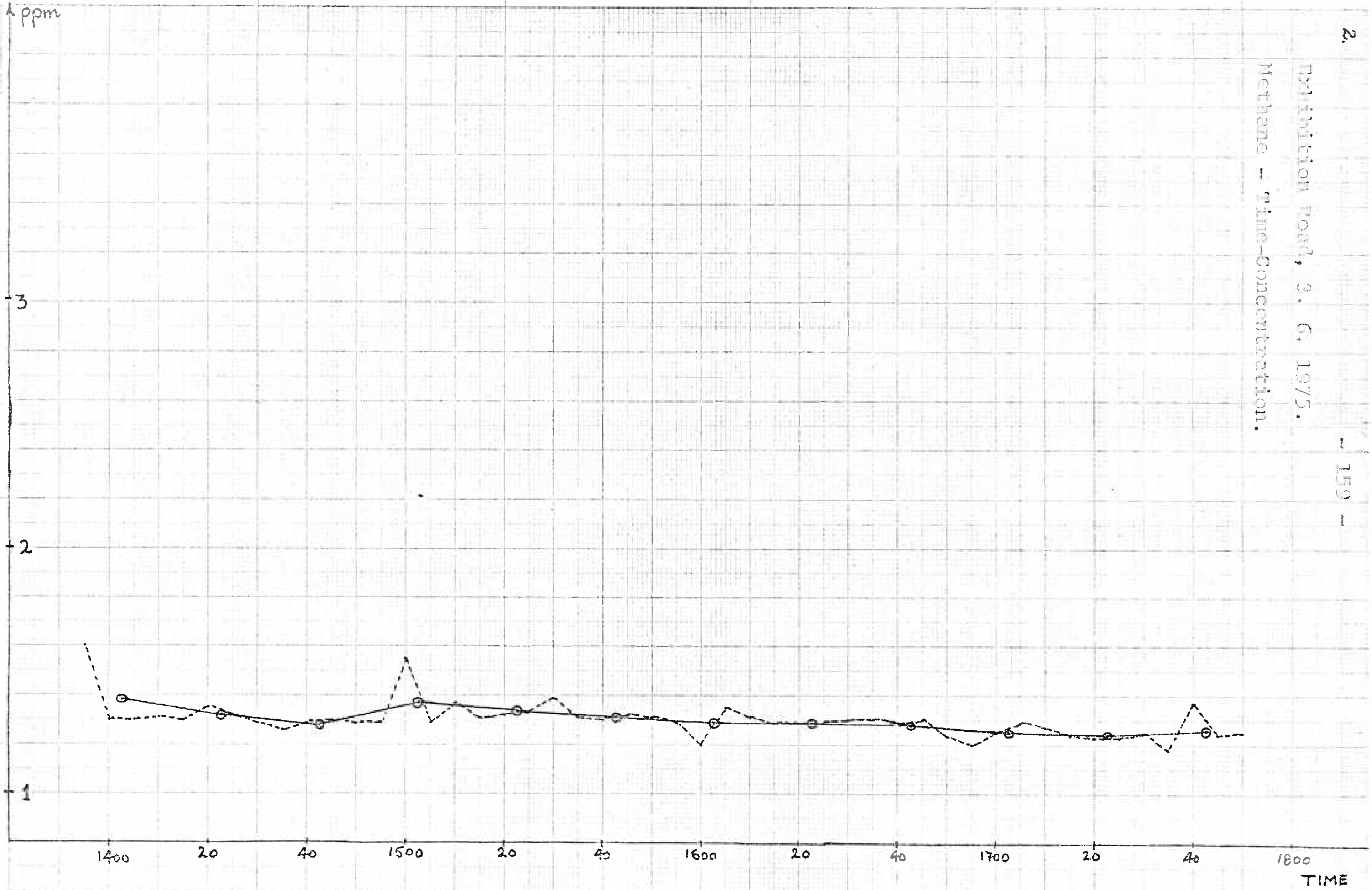
Time-Concentration Graph.



2.

Exhibition Road, 3. 6. 1975.

Methane - Time-Concentration.

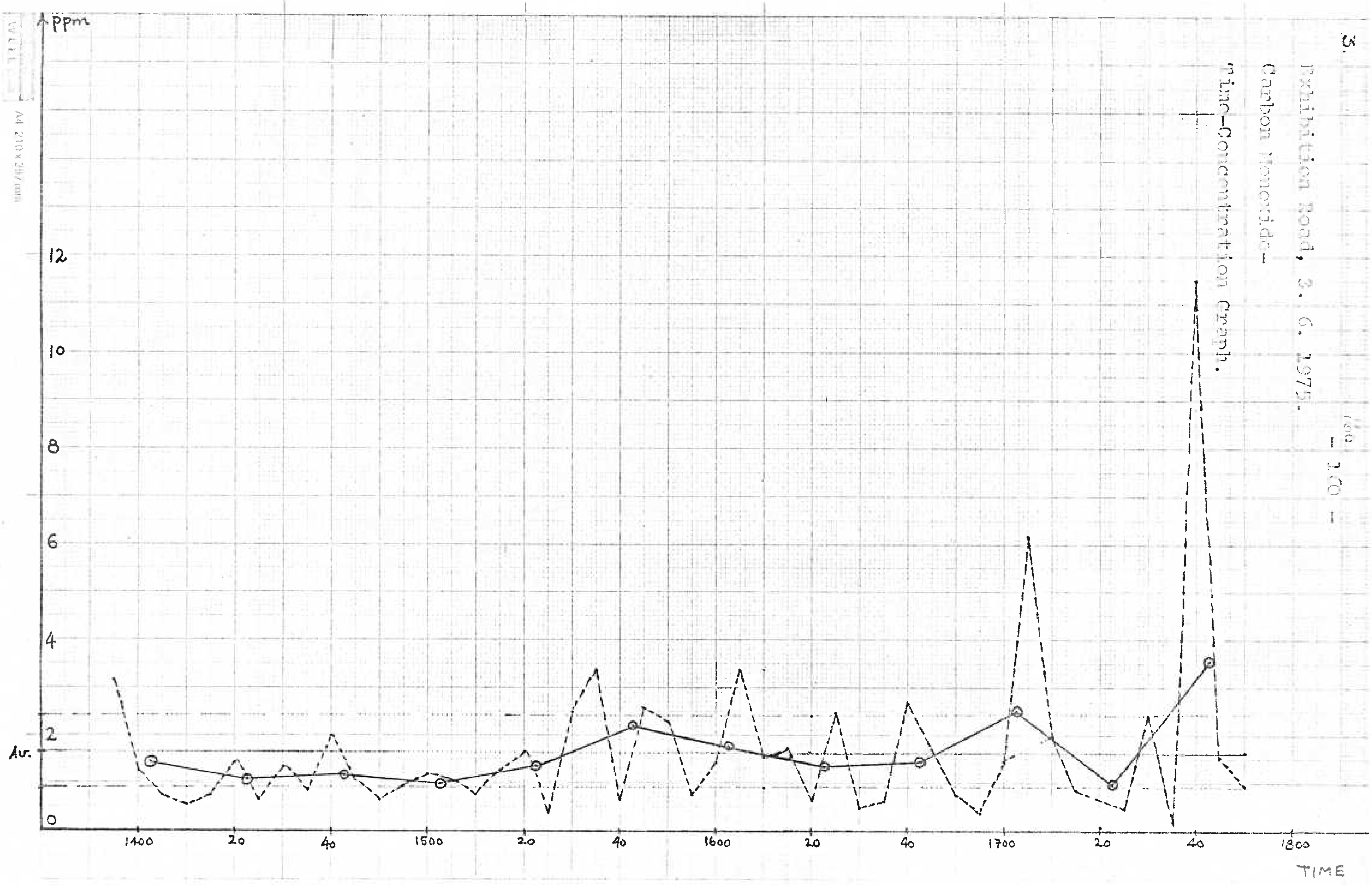


3.

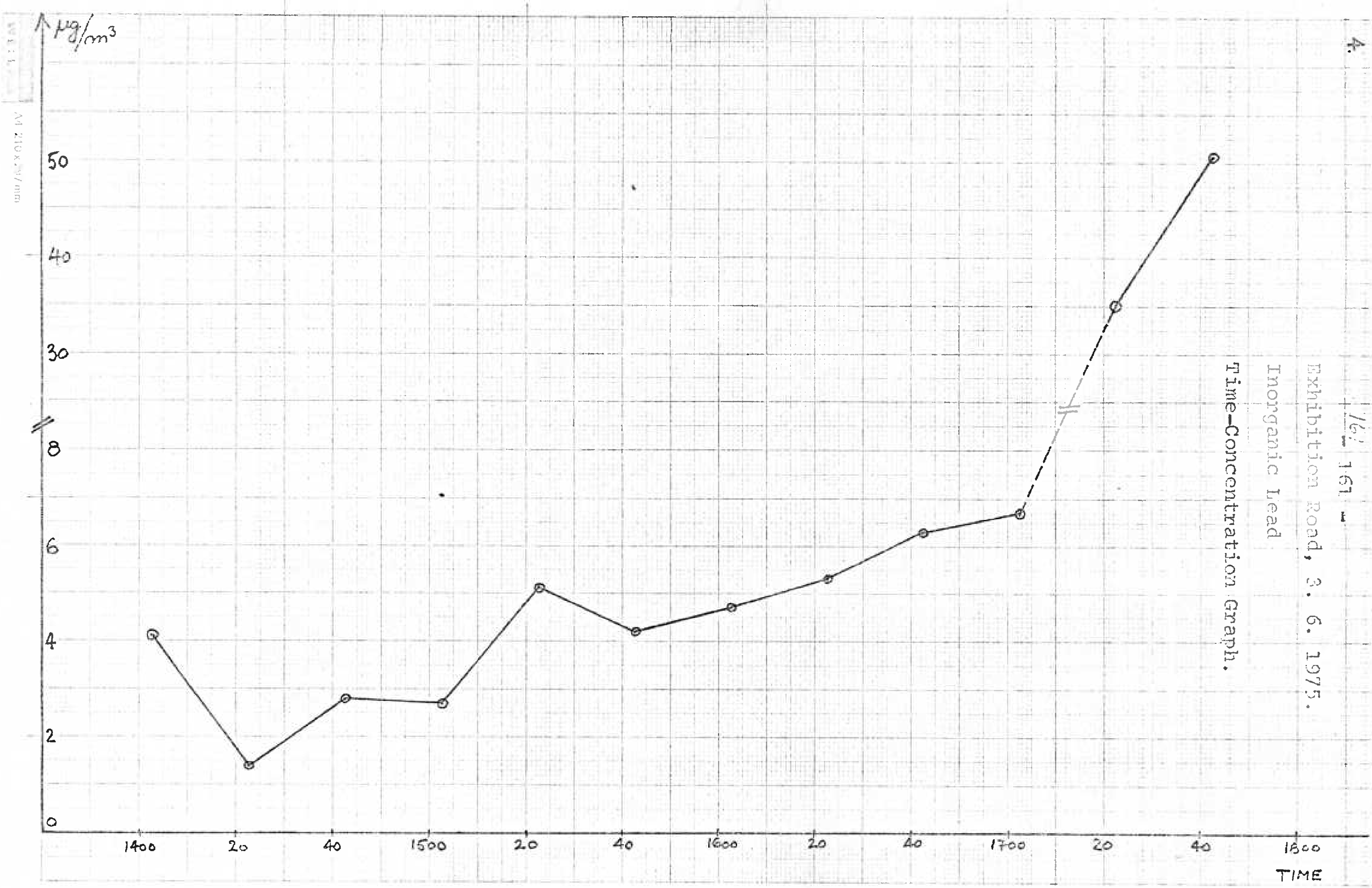
Exhibition Road, 3. 6. 1975.

Carbon Monoxide—

Time-Concentration Graph.



4.



Exhibition Road, 3. 6. 1975.

Inorganic Lead

Time-Concentration Graph.

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1435	1.19	1.26	0.86	1.84 ± 1.02	1.28 ±0.02	1.14 ±0.59	2.8
1440	1.39	1.29	2.00				
1445	3.37	1.30	1.04				
1450	1.39	1.29	0.66				
1455	1.42	1.29	0.95	1.49 ±0.21	1.37 ±0.12	0.98 ±0.18	2.7
1500	1.78	1.55	1.18				
1505	1.29	1.29	1.04				
1510	1.48	1.37	0.76				
1515	1.82	1.31	1.24	2.58 ±1.70	1.34 ±0.04	1.44 ±0.87	5.1
1520	1.84	1.32	1.67				
1525	1.19	1.33	0.38				
1530	4.95	1.39	2.47				
1535	1.42	1.31	3.34	1.87 ±0.82	1.31 ±0.01	2.21 ±1.13	4.2
1540	1.21	1.30	0.66				
1545	1.80	1.32	2.56				
1550	3.03	1.31	2.28				
1555	1.72	1.29	0.76	1.52 ±0.52	1.29 ±0.06	1.77 ±1.12	4.7
1600	1.09	1.20	1.42				
1605	1.39	1.35	3.36				
1610	1.89	1.31	1.52				
1615	1.33	1.29	1.71	1.64 ±0.82	1.29 ±0.00	1.32 ±0.94	5.3
1620	1.22	1.29	0.63				
1625	2.87	1.29	2.47				
1630	1.15	1.30	0.48				
1635	1.37	1.30	0.61	1.37 ±0.14	1.28 ±0.03	1.44 ±0.95	6.3
1640	1.39	1.29	2.66				
1645	1.54	1.30	1.71				
1650	1.19	1.23	0.76				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1655	1.17	1.20	0.38				
1700	1.33	1.25	1.42	1.59 ±0.45	1.25 ±0.07	2.50 ±2.54	6.7
1705	2.18	1.29	6.18				
1710	1.68	1.27	2.00				
1715	1.48	1.24	0.86				
1720	1.39	1.23	0.10	1.32 ±0.14	1.24 ±0.00	0.96 ±1.00	35.1
1725	1.19	1.23	0.48				
1730	1.23	1.25	2.38				
1735	1.82	1.18	0.20				
1740	3.60	1.37	11.50	2.35 ±0.84	1.26 ±0.08	3.54 ±5.34	50.6
1745	1.98	1.24	1.52				
1750	1.98	1.25	0.95				
Overall averages : for whole period				1.72 ±0.39	1.30 ±0.04	1.65 ±0.76	10.75 ±15.53

a. Percentile standard deviation.

Samples	THC	CH_4	CO
1	26.6	10.9	82.5
2	10.9	1.5	36.5
3	55.0	1.6	51.7
4	14.1	8.8	18.4
5	65.9	3.0	60.4
6	43.8	0	51.1
7	23.7	4.7	63.3
8	50.0	0	71.2
9	10.2	2.3	66.0
10	35.4	5.6	101.6
11	10.6	0	104.2
12	35.8	6.4	150.8
Average	31.8	3.7	71.5
"Standard deviation"	19.0	3.6	35.0

D. Prince Consort Road, June 19th, 1975

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1200	2.24	1.78	4.02	2.50	1.77	3.76	10.71
1205	2.77	1.76	3.05				
1210	1.90	1.41	6.80	1.91	1.46	5.90	5.45
1215	1.92	1.52	5.00				
1220	2.42	1.52	9.62	2.25	1.58	6.05	3.44
1225	2.08	1.63	2.47				
1230	1.98	1.25	1.46	2.10	1.40	1.76	3.08
1235	2.22	1.54	2.06				
1240	1.48	1.58	1.96	1.44	1.48	1.50	3.19
1245	1.39	1.39	1.03				
1250	2.18	1.31	1.85	1.90	1.50	2.10	4.74
1255	1.62	1.68	2.35				
1300	1.94	1.68	1.26	2.01	1.74	1.70	5.00
1305	2.08	1.79	2.14				
1310	1.78	1.85	2.27	1.73	1.60	2.01	2.78
1315	1.68	1.36	1.75				
1320	1.62	1.33	1.75	1.95	1.54	3.92	3.69
1325	2.28	1.74	6.08				
1330	1.58	1.52	14.00	1.70	1.44	7.44	3.12
1335	1.82	1.36	0.87				
1340	1.74	1.76	1.46	2.56	1.81	3.36	4.16
1345	1.88	1.88	2.60				
1350	2.61	1.85	2.88				
1355	4.08	1.75	6.49				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1400	1.78	1.59	2.68	1.86	1.64	2.99	2.81
1405	1.98	-	-				
1415	-	1.83	3.60				
1420	1.88	1.67	2.37				
1425	1.80	1.46	3.30				
1430	1.82	1.63	4.35	2.37	1.54	3.72	3.48
1435	2.28	1.34	1.69				
1440	2.81	1.64	5.67				
1445	2.57	1.56	3.19				
1450	2.02	1.88	1.85	2.07	1.62	3.10	3.53
1455	2.08	1.47	3.71				
1500	2.16	1.65	2.41				
1505	1.98	1.54	4.43				
1510	2.10	1.54	3.09				
1515	2.20	1.65	2.99	2.21	1.54	4.67	4.11
1520	2.44	1.63	3.32				
1525	2.57	1.34	6.28				
1530	1.62	1.53	6.08				
1535	1.98	1.60	2.02	1.88	1.60	2.78	2.73
1540	1.98	1.80	4.16				
1545	1.59	1.48	3.30				
1550	1.98	1.54	1.63				
1555	1.98	1.52	9.27	2.24	1.43	4.56	2.93
1600	2.48	1.48	2.37				
1605	1.68	1.22	1.61				
1610	2.81	1.51	4.98				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1615	2.67	1.48	5.03	2.06	1.59	3.80	2.82
1620	1.83	1.64	3.03				
1625	1.62	1.70	4.57				
1630	2.08	1.52	2.58				
1635	1.98	1.70	3.79	2.30	1.52	3.65	4.48
1640	2.61	1.35	3.50				
1645	1.68	1.56	5.29	2.20	1.48	3.02	3.22
1650	2.71	1.41	0.74				
1655	1.40	1.42	4.33	1.43	1.52	3.05	3.99
1700	1.46	1.63	1.77				
1705	1.90	1.35	7.68	2.02	1.53	5.72	3.06
1710	2.14	1.71	3.77				
1715	1.98	1.71	2.58	2.01	1.48	1.50	3.09
1720	2.04	1.25	0.41				
1725	1.72	1.30	0.62	1.95	1.41	7.25	3.87
1730	2.18	1.52	13.88				
1735	1.58	1.33	2.27	1.90	1.35	2.52	2.90
1740	2.22	1.36	2.76				
1745	2.20	1.42	2.53	1.99	1.42	2.89	2.46
1750	1.78	1.43	3.25				
1755	1.52	1.38	2.55	1.63	1.33	2.13	4.44
1800	1.74	1.28	1.71				
1805	1.82	1.39	3.56	1.94	1.37	3.58	4.06
1810	2.06	1.35	3.60				
1815	1.96	1.36	3.15	2.12	1.33	3.68	4.62
1820	2.28	1.29	4.22				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1825	3.07	1.67	3.81	2.88	1.48	3.50	3.00
1830	1.88	1.30	3.19				
1835	1.92	1.43	6.08	2.07	1.42	4.12	2.68
1840	2.22	1.42	2.16				
1845	2.04	1.45	2.06	2.01	1.44	2.36	2.94
1850	1.98	1.44	2.66				
Overall averages for whole period :				2.04 ±0.30	1.51 ±0.12	3.56 ±1.56	3.77 ±1.48

b. Percentile standard deviation.

Samples	THC	CH_4	CO
1	14.8	0.6	18.1
2	0.5	5.5	21.6
3	10.7	5.1	83.7
4	8.1	14.3	25.9
5	4.2	8.8	44.0
6	21.0	17.4	16.7
7	5.0	4.6	36.5
8	4.0	21.9	18.4
9	24.1	18.8	78.0
10	10.0	7.6	124.8
11	40.5	3.3	65.0
12	4.8	9.1	18.8
13	17.7	9.1	45.5
14	3.4	9.9	32.6
15	19.0	9.1	37.5
16	10.6	8.8	41.7
17	22.3	9.8	76.0
18	21.8	6.3	31.1
19	19.1	16.5	5.5
20	33.2	7.4	106.5
21	2.8	9.9	59.4
22	8.4	16.4	48.3
23	2.0	21.6	102.0
24	16.4	11.4	129.3
25	23.7	1.5	13.9
26	15.1	0.7	17.6

27	9.8	5.3	27.7
28	8.8	2.2	0.8
29	10.9	3.8	20.6
30	29.2	17.6	12.6
31	10.2	0.7	67.3
32	2.0	0.7	17.8
Average	13.6	8.9	45.1
"Standard deviation"	9.8	6.3	34.8

C. Teeside, July, 1975.

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1210	1.39	1.27	0.70				
1215	1.40	1.17	0.70				
1220	1.61	1.12	0.63				
1225	1.36	1.12	0.46				
1230	1.36	1.15	0.43				
1235	1.32	1.18	0.75	1.40 ±0.08	1.16 ±0.04	0.55 ±0.12	0.57
1240	1.45	1.16	0.53				
1245	1.32	1.16	0.42				
1250	1.44	1.14	0.40				
1255	1.38	1.15	0.54				
1300	1.40	1.17	0.52				
1305	1.41	1.17	0.70				
1310	1.35	1.15	0.80				
1315	1.42	1.12	0.41				
1320	1.36	1.10	0.42				
1325	1.47	1.14	0.39				
1330	1.33	1.13	0.37				
1335	1.29	1.13	0.37	1.36 ±0.06	1.14 ±0.02	0.44 ±0.18	1.04
1340	1.44	1.11	0.34				
1345	1.35	1.10	0.39				
1350	1.33	1.11	0.22				
1355	1.31	1.10	0.24				
1400	1.30	1.17	0.61				

Time	THC	CH_4	CO	THC_{av}	CH_{av}	CO_{av}	Pb
1455	-	1.20	0.29				
1500	1.49	1.26	0.61				
1505	1.44	1.23	0.36				
1510	1.43	1.28	0.36				
1515	1.45	1.21	0.34				
1520	1.41	1.24	0.38				
1525	1.46	1.28	0.43	1.46 ±0.04	1.25 ±0.03	0.43 ±0.10	0.36
1530	1.43	1.26	0.49				
1535	1.53	1.28	0.56				
1540	1.51	1.26	0.55				
1545	1.46	1.24	0.38				
1550	1.46	1.23	0.42				
1555	1.44	1.24	0.47				
1705	1.40	1.26	0.31				
1710	1.59	1.21	0.38				
1715	1.48	1.18	0.29				
1720	1.44	1.24	-				
1725	1.33	1.18	0.26				
1730	1.33	1.22	0.34	1.40 ±0.08	1.21 ±0.02	0.34 ±0.09	0.43
1735	1.33	1.22	0.30				
1740	1.42	1.20	0.35				
1745	-	1.20	0.58				
1750	1.34	1.22	0.26				
1755	1.38	1.20	0.30				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1100	1.63	1.44	0.37				
1105	1.59	1.43	0.41				
1110	1.70	1.62	0.44				
1115	1.54	1.40	0.43				
1120	1.60	1.51	0.36				
1125	1.67	1.56	0.46				
1130	1.66	1.50	0.37	1.55 ±0.08	1.44 ±0.08	0.39 ±0.03	0.92
1135	1.52	1.42	0.38				
1140	1.46	1.34	0.40				
1145	1.49	1.37	0.37				
1150	1.47	1.39	0.36				
1155	1.48	1.36	0.36				
1200	1.46	1.37	0.36				
1210	1.41	1.33	0.42				
1215	1.41	1.26	0.38				
1220	1.42	1.27	0.37				
1225	1.44	1.33	0.33				
1230	1.38	1.28	0.40	1.42 ±0.02	1.30 ±0.03	0.37 ±0.03	0.74
1235	1.41	1.28	0.35				
1240	1.39	1.29	0.36				
1245	1.46	1.33	0.38				
1250	1.44	1.32	0.39				
1255	1.41	1.28	0.34				
1505	3.37	1.34	0.73				
1510	1.53	1.34	0.40				
1515	1.84	1.35	2.00	2.05 ±0.76	1.33 ±0.03	1.00 ±0.60	0.47
1520	1.57	1.28	0.97				
1525	1.92	1.34	0.86				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1540	2.04	1.34	0.71				
1545	2.36	1.26	0.84				
1550	1.53	1.33	0.35				
1555	3.61	1.36	0.64				
1600	3.92	1.45	-				
1605	2.65	1.41	1.36				
1610	3.06	1.51	1.13	2.48 ±0.70	1.38 ±0.07	0.85 ±0.44	0.47
1615	2.26	1.35	0.68				
1620	1.92	1.40	0.62				
1625	1.94	1.30	0.44				
1630	2.24	1.32	0.38				
1635	2.22	1.46	1.81				
1640	2.00	1.42	1.22				
1100	1.59	1.43	0.40				
1105	1.55	1.42	0.39				
1110	1.55	1.42	0.44				
1115	1.55	1.42	0.38				
1120	1.55	1.42	0.38				
1125	1.55	1.43	0.33	1.58 ±0.06	1.43 ±0.02	0.39 ±0.03	0.45
1130	-	1.44	0.43				
1135	1.55	1.41	0.37				
1140	1.68	1.45	0.37				
1145	1.70	1.47	0.39				
1225	1.58	1.48	0.35				
1230	1.62	1.50	0.24				
1235	1.58	1.54	0.34	1.55 ±0.06	1.44 ±0.09	0.34 ±0.05	0.25
1240	1.55	1.48	0.40				
1245	1.53	1.35	0.35				
1250	1.44	1.32	0.36				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1435	1.54	1.34	0.37				
1440	1.46	1.31	0.38	1.48 ±0.05	1.31 ±0.02	0.39 ±0.02	1.99
1445	1.44	1.29	0.41				
1545	1.42	1.25	0.25				
1550	1.40	1.29	0.37				
1555	1.40	1.29	0.37				
1600	1.38	1.24	0.30	1.39 ±0.02	1.25 ±0.03	0.31 ±0.04	0.73
1605	1.38	1.22	0.29				
1610	1.38	1.21	0.31				
1615	1.38	1.23	0.30				
1645	1.37	1.31	0.33				
1650	1.49	1.31	0.46				
1655	1.35	1.30	0.35				
1700	1.37	1.26	0.31	1.37 ±0.05	1.29 ±0.04	0.33 ±0.08	0.57
1705	1.37	1.24	0.25				
1710	1.33	1.25	0.25				
1715	1.33	1.33	0.41				
Average over 3 days:				1.58 ±0.33	1.30 ±0.10	0.47 ±0.21	0.69 ±0.45

c. Percentile standard deviation.

Samples	THC	CH_4	CO
1	5.7	3.4	21.8
2	4.4	1.8	40.9
3	2.7	2.4	23.2
4	5.7	1.6	26.5
5	5.2	5.5	7.7
6	1.4	2.3	8.1
7	37.1	2.3	60.0
8	28.2	5.1	51.7
9	3.8	1.4	7.7
10	3.9	6.2	14.7
11	3.4	1.5	5.1
12	1.4	2.4	12.9
13	3.6	3.1	24.2
Average	8.2	3.0	23.4
"Standard deviation"	11.1	1.6	17.6

D. Teeside, September, 1975.

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1115	1.56	1.64	0.33				
1120	1.50	1.60	0.32				
1125	1.58	1.65	0.39				
1130	1.48	1.62	0.44				
1135	1.48	1.62	0.53				
1140	1.46	1.58	0.50	1.48 ±0.06	1.60 ±0.06	0.43 ±0.13	0.97
1145	1.46	1.67	0.57				
1150	1.38	1.61	0.58				
1155	1.50	1.48	0.43				
1200	1.38	1.49	0.18				
1235	1.40	1.39	0.12				
1240	1.37	1.40	0.37				
1245	1.37	1.38	0.46				
1250	1.39	1.40	0.39				
1255	1.42	1.40	0.28	1.38 ±0.02	1.39 ±0.01	0.29 ±0.12	1.05
1300	1.37	1.36	0.16				
1305	1.37	1.38	0.31				
1310	1.38	1.38	0.24				
1410	1.37	1.46	0.42				
1415	1.43	1.35	0.22				
1420	1.37	1.37	0.20				
1425	1.44	1.35	0.29				
1430	1.40	1.38	0.61				
1435	1.36	1.36	0.29				
1440	1.38	1.37	0.30				
1445	1.39	1.41	0.56				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1450	1.49	1.49	0.58				
1455	1.66	1.51	0.70				
1500	1.62	1.51	0.58	1.55 ±0.17	1.41 ±0.05	0.42 ±0.16	0.76
1505	1.74	1.45	0.53				
1510	1.77	1.45	0.28				
1515	1.45	1.36	0.23				
1520	-	1.39	0.33				
1525	1.64	1.42	0.38				
1530	1.86	1.42	0.51				
1535	1.72	1.40	0.58				
1540	1.76	-	-				
1610	-	1.42	0.26				
1615	1.52	1.43	0.39				
1620	1.64	1.37	0.32				
1625	1.42	1.40	0.29				
1630	1.48	1.40	0.42				
1635	1.57	1.41	0.42				
1640	1.49	1.40	0.34				
1645	1.54	1.40	0.32	1.49 ±0.07	1.39 ±0.04	0.59 ±0.54	0.73
1650	1.48	1.27	1.47				
1655	1.42	1.40	0.32				
1700	-	1.40	0.36				
1705	1.41	1.41	0.32				
1710	1.44	1.42	1.15				
1715	1.53	1.38	2.10				
1720	1.42	1.37	0.32				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1150	1.56	1.56	0.35	1.50 ±0.03	1.55 ±0.02	0.40 ± 0.03	0.64
1155	1.53	1.53	0.35				
1200	1.51	1.54	0.35				
1205	1.51	1.57	0.41				
1210	1.50	1.58	0.42				
1215	1.45	1.53	0.38				
1220	1.52	1.56	0.42				
1225	1.53	1.57	0.41				
1230	1.52	1.56	0.44				
1235	1.49	1.55	0.44				
1240	1.47	1.53	0.41				
1245	1.50	1.50	0.39				
1250	1.44	1.56	0.44				
1255	1.52	1.51	0.39				
1345	1.54	1.39	0.20	1.39 ±0.06	1.38 ±0.04	0.22 ±0.06	0.19
1350	1.47	1.49	0.41				
1355	1.46	1.38	0.17				
1400	1.41	1.40	0.19				
1405	1.42	1.42	0.20				
1410	1.40	1.37	0.19				
1415	1.40	1.39	0.22				
1420	1.34	1.37	0.20				
1425	1.35	1.35	0.18				
1430	1.34	1.37	0.21				
1435	1.33	1.35	0.19				
1440	1.35	1.36	0.26				
1445	1.35	1.35	0.23				
1450	1.33	1.32	0.21				
1455	1.33	-	-				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1600	-	1.43	0.40				
1605	1.48	1.40	0.38				
1610	1.46	1.38	0.20				
1615	1.46	1.42	0.26				
1620	1.53	1.41	0.32				
1625	1.43	1.46	0.36				
1630	1.43	1.41	0.27	1.45 ±0.04	1.42 ±0.06	0.30 ±0.06	0.51
1635	1.43	1.44	0.31				
1640	1.51	1.60	0.38				
1645	1.44	1.35	0.24				
1650	1.42	1.44	0.29				
1700	1.46	1.40	0.27				
1705	1.37	1.39	0.22				
1130	1.32	1.41	0.23				
1135	1.31	1.41	0.15				
1140	1.33	1.40	0.20				
1145	1.30	1.22	0.24				
1150	1.36	1.37	0.22				
1155	1.31	1.37	0.26	1.33 ±0.03	1.38 ±0.05	0.24 ±0.04	0.37
1200	1.36	1.38	0.27				
1205	1.31	1.38	0.31				
1210	1.38	1.40	0.27				
1215	1.34	1.38	0.27				
1220	1.35	1.41	0.29				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1315	1.39	1.42	0.59				
1320	1.41	1.42	0.29				
1325	1.46	1.38	0.27				
1330	1.45	1.38	0.39				
1335	1.44	1.39	0.21				
1340	1.74	1.40	0.32				
1345	1.37	1.38	0.32				
1350	1.66	1.42	0.41				
1355	1.40	1.40	0.29	1.49 ±0.15	1.40 ±0.02	0.43 ±0.32	0.64
1400	1.56	1.38	0.25				
1405	1.51	1.38	0.26				
1410	1.55	1.40	0.50				
1415	1.77	1.42	0.32				
1420	1.55	1.41	0.51				
1425	1.61	1.39	1.58				
1430	1.37	1.36	0.24				
1555	1.54	1.44	0.36				
1600	-	1.50	0.29				
1605	1.88	1.50	1.05				
1610	1.36	1.46	-				
1615	1.80	1.44	0.99				
1620	1.10	1.40	0.29	1.52 ±0.27	1.45 ±0.04	0.80 ±0.56	2.57
1625	1.40	1.44	1.17				
1630	1.36	1.41	0.72				
1635	1.34	1.48	1.95				
1640	1.40	1.43	0.35				
Average over 3 days:				1.46 ±0.07	1.44 ±0.08	0.41 ±0.17	0.34 0.66

d. Percentile standard deviation.

Samples	THC	CH_4	CO
1	4.4	4.0	29.5
2	1.3	1.0	39.9
3	11.1	3.7	38.0
4	4.6	2.7	92.7
5	2.1	1.6	8.2
6	4.5	2.9	27.0
7	2.9	4.2	21.7
8	2.0	4.0	18.3
9	10.2	1.3	74.2
10	17.5	2.4	70.0
Average	6.1	2.8	42.0
"Standard deviation"	5.2	1.2	27.7

E. Olympia Car Park, October, 22nd, 1975.

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1300	3.65	2.28	5.05	4.43 ±0.78	2.23 ±0.09	7.65 ±3.32	5.13
1305	5.12	2.28	8.69				
1310	5.37	2.28	6.06				
1315	4.63	2.28	13.95				
1320	4.38	2.17	6.27				
1325	3.41	2.07	5.86				
1335	4.15	2.17	4.04	4.02 ±1.08	2.24 ± 0.25	7.55 ±6.47	4.59
1340	6.09	2.38	10.31				
1345	3.90	2.68	19.40				
1350	3.41	2.17	3.64				
1355	3.41	2.07	5.86				
1400	3.16	1.97	2.02				
1410	4.38	2.07	6.06	4.23 ±0.12	2.19 ±0.19	7.12 ±1.51	5.33
1415	4.15	2.07	7.07				
1420	4.38	2.07	5.15				
1425	4.15	2.07	6.67				
1430	4.15	2.48	8.89				
1435	4.15	2.38	8.89				
1440	3.90	2.17	12.73	4.30 ±0.56	2.26 ±0.14	8.77 ±2.65	4.97
1445	4.83	2.48	8.69				
1450	4.02	2.17	6.97				
1455	3.53	2.17	5.15				
1500	4.87	2.17	10.51				
1505	4.63	2.38	8.59				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1510	3.66	2.07	4.45				
1515	3.66	2.17	5.46				
1520	4.38	-	7.28				
1525	3.90	2.28	5.05	4.06 ±0.40	2.22 ±0.09	6.35 ±1.60	5.24
1530	4.15	2.28	7.28				
1535	4.63	2.28	8.59				
1540	6.34	2.68	8.69				
1545	3.90	2.38	15.97				
1550	5.12	2.38	9.70				
1555	3.90	2.48	10.51	5.00 ±0.95	2.34 ±0.24	9.67 ±3.51	4.92
1600	5.37	2.07	7.28				
1605	5.37	2.07	5.86				
1610	4.38	2.17	8.89				
1615	4.38	2.48	13.95				
1620	3.53	2.17	5.66				
1625	6.09	2.17	12.93	4.63 ±0.86	2.26 ±0.12	10.46 ±3.35	6.50
1630	4.38	2.28	8.19				
1635	5.00	2.28	13.14				
1640	5.37	2.28	8.59				
1645	6.09	3.12	11.52				
1650	7.06	2.58	19.60				
1655	4.02	2.28	6.67	6.07 ±1.22	2.61 ±0.41	12.28 ±5.62	8.41
1700	7.31	3.12	18.90				
1705	6.58	2.28	8.39				
1710	6.09	2.48	12.33				
1715	5.60	3.00	12.53				
1720	5.24	2.90	10.11				
1725	4.15	2.28	5.86	4.84 ±0.95	2.60 ±0.28	8.79 ±3.26	4.49
1730	4.27	2.48	6.37				
1735	3.66	2.48	5.56				

Time	THC	CH_4	CO	THC_{av}	CH_{4av}	CO_{av}	Pb
1740	3.78	2.17	6.67	5.24 ± 1.58	2.64 ± 0.58	11.69 ± 8.99	4.45
1745	3.78	2.17	5.05				
1750	4.63	2.28	9.50				
1755	7.80	3.21	29.31				
1800	5.12	2.48	7.28				
1805	6.34	3.52	12.33				
1810	5.00	2.90	8.89	8.55 ± 2.73	2.92 ± 0.43	26.78 ± 12.80	11.27
1815	7.68	2.68	24.25				
1820	13.16	3.21	27.28				
1825	8.28	3.52	45.88				
1830	7.43	2.28	19.20				
1835	9.75	2.90	35.17				
1840	6.34	3.12	27.28	6.24 ± 2.00	2.78 ± 0.23	15.36 ± 7.38	6.62
1845	10.12	2.80	21.42				
1850	6.09	2.90	13.74				
1855	4.87	2.48	9.70				
1900	5.12	2.80	9.09				
1905	4.87	2.58	10.91				
Overall averages for whole period :				5.13 ± 1.30	2.44 ± 0.25	11.04 ± 5.57	5.99 ± 2.02

c. Percentile standard deviation.

Samples	THC	CH_4	CO
1	17.6	4.0	43.3
2	26.3	11.2	85.7
3	28.3	8.7	21.2
4	13.0	6.2	30.2
5	9.8	4.1	25.2
6	19.0	10.5	36.3
7	18.6	5.3	32.0
8	20.1	15.7	45.8
9	19.6	10.8	37.1
10	30.2	22.0	76.9
11	32.0	14.7	47.8
12	32.0	8.3	48.0
Average	22.2	10.1	44.1
"Standard deviation"	7.4	5.3	19.5

3.2 Summary of Results - Ranges.

Exhibition Road, June 3rd, 1975.

Pb	1.40 - 50.6 $\mu g/m^3$	(20 min average)
CO	0.10 - 11.50 ppm	(5 min average)
	0.96 - 3.54 -	(20 - -)
THC	1.09 - 4.95 ppm	(5 min average)
	1.37 - 2.58 -	(20 - -)
CH_4	1.18 - 1.60 ppm	(5 min average)
	1.24 - 1.37 -	(20 - -)

Exhibition Road, June 19th, 1975.

Pb	2.46 - 10.71 $\mu g/m^3$	(10-20 min averages)
CO	0.41 - 14.00 ppm	(5 min average)
	1.50 - 7.44 -	(10-20 -)
THC	1.39 - 4.08 -	(5 min average)
	1.43 - 2.88 -	(10-20 -)
CH_4	1.22 - 1.88 ppm	(5 min average)
	1.33 - 1.81 -	(10-20 -)

Teeside, July, 1975.

Pb	0.25 - 1.99 $\mu g/m^3$	(Hourly averages)
CO	0.20 - 2.00 ppm	(5 min average)
	0.31 - 0.85 -	(1 hr -)
THC	1.29 - 7.24 ppm	(5 min average)
	1.36 - 2.48 -	(1 hr -)
CH_4	1.10 - 1.62 ppm	(5 min average)
	1.14 - 1.44 -	(1 hr -)
$THC-CH_4$	0.00 - 2.47 -	(5 min average)
	0.09 - 1.11 -	(1 hr -)

Teeside, September, 1975.

Pb	0.19 - 2.57 $\mu g/m^3$	(Hourly averages)
CO	0.12 - 2.10 ppm	(5 min average)
	0.22 - 0.80 -	(1 hr -)
THC	1.10 - 1.88 ppm	(5 min average)
	1.33 - 1.55 -	(1 hr -)
CH_4	1.22 - 1.67 ppm	(5 min average)
	1.38 - 1.60 -	(1 hr -)

Olympia Car Park, October 22nd, 1975.

Pb	:	4.45 - 11.27 µg/m^3	(25 min average)
CO	:	2.02 - 45.88 ppm	(5 - -)
	:	6.35 - 26.78 -	(25 - -)
THC	:	3.16 - 13.16 ppm	(5 min average)
	:	4.02 - 8.55 -	(25 - -)
CH_4	:	1.97 - 3.52 ppm	(5 min average)
	:	2.19 - 2.92 -	(25 - -)
N_{tpv}	:	162 - 286	(25 min average)
N_{pvg}	:	5 - 105	(- - -)
N_{tpdv}	:	195 - 308	(- - -)

N - number of vehicles
tpv - total petrol vehicles in area
pvg - petrol vehicles from car park exit
tpdv - total vehicles in area

3.3 Statistical Data Handling.

American investigators (Brief, R.S., et al., 1960) have established a correlation between lead concentrations and traffic intensity and carbon monoxide concentrations and traffic intensity. They suggested the following possible relationship between lead and carbon monoxide in street air:

$$Pb = 0.516 + 0.268\ CO$$

where Pb - lead concentrations in $\mu g/m^3$

CO - carbon monoxide concentration in ppm by volume.

It was decided to use my data to try this theory out. Data was subjected to a statistical test and a multiple regression curve fitting (see computational program in Appendix I).

F - test: In some problems the possibility that a given source of variation has had no effect has to be considered. In other words, we may want to know whether the estimates of two variances differ significantly,-more than can be reasonably explained on the grounds of error in the estimates. This is done by taking the ratio of the mean square between samples - called the F-ratio - and referring to F-tables. A significant value of F discredits the Null Hypothesis. When the observations are distributed normally, the ratio of the two mean squares is distributed exactly as F and depends only on the degrees of freedom of the mean squares. This is also sufficiently close to the truth even when the distribution of the observations departs markedly from the Normal form, provided the number of analyses on each sample do not differ widely.

When applying a test of significance we calculate the probability P that a given result would occur if the Null Hypothesis were true. If this probability is equal to or less than a given value α, the result is said to be significant at the level α. The appropriate level of significance will depend on the particular problem under consideration. Usually the value $P = 0.05$ gives sufficient assurance, but in certain circumstances a higher degree of assurance may be required, while in others a lower degree of assurance corresponding to 0.10 may be sufficient. When $P = 0.05$ the result is usually referred to as "significant" and when $P = 0.01$ as "highly significant".

Multiple Regression Analysis - There is a class of problems in descriptive statistics involving two or more related variates where the main interest is not in estimating one variate from another, but in the joint distribution of the variates and in the extent of association between them. This is the class of problem in which correlation methods are most useful.

The correlation can be negative or positive. When it is positive, one variate tends to increase as the other increases; when it is negative, one variate tends to decrease as the other increases. A correlation coefficient determines the degree of fit of a calculated graph to given data. It can be readily shown that the correlation coefficient cannot take values outside the limits -1 and +1. A high absolute value of "r" (term for the correlation coefficient) indicates a close relationship and a small value, a less definite relationship. When the absolute value of r is unity, the points fall exactly on a straight line and the relationship is perfect. When $r = 0$ the points scatter in all directions, and the variates are linearly independent.

Where a linear representation of the relationship between observed values of two variables appears inadequate, an equation of higher order may be sought to improve the fit.

This will be of the general form:

$$Y = A_o + A_1x + A_2x^2 + \dots + A_px^p$$

A similar generalisation of the multiple regression equation, involving powers and products of the several independent variables, is also possible. In the context of this data handling, only the curvilinear approach is used.

The order of the equation required will not, in most cases, be known or predictable in advance. It is usual, therefore, to introduce successive powers of "x" into the representation and to test for the significance of the additional effect of each. The fitted equation is taken to that order beyond which the addition of extra terms produces no significant reduction in the residual variance. For the purpose of this work, it was decided not to go beyond $p = 4$ for the sake of:

a) the testing of the linear case is the most important;

b) the size of the sample population is not big enough for reliably using higher order.

The regression coefficients attached to the separate powers of "x" will generally be highly correlated with one another. Thus the standard errors of the coefficients are, in themselves, of little value as measures of the precision with which the overall effect of "x" has been estimated. The analysis of the computer printouts will, therefore, place primary significance on the confidence limits given by the "F-test", and in cases of significant results, take further notice of "r". The pollution parameters are all analysed in relation to each other to obtain a correlation matrix. The individual results are given hereafter in addition to a summary of the matrices for the various sites and the various dates.

4. Computer print-outs and their interpretation.

Exhibition Road, 3. 6. 1975.

$X = CO$

$Y = Pb$

Linear regression: F-value : 4.32, hence $P > 0.10$

: insignificant correlation.

Square regression: F-value : 13.45, $0.10 > P > 0.05$

: slight correlation.

$$Y = 16.63X^2 - 60.22X + 56.23$$

$$r = 0.85$$

Cubic regression : F-value : 0.0001, $P > 0.01$

: insignificant correlation.

Quartic regression: F-value : 0.93, $P > 0.10$

: insignificant correlation.

```
   X            Y
1.43000      4.10000
1.74000      1.41000
1.14000      5.00000
 .93000      2.70000
1.44000      5.10000
2.21000      4.25000
1.77000      4.00000
1.32000      5.30000
1.44000      6.30000
2.50000      5.70000
 .96000     35.10000
3.54000     52.60000


      Y=   -.759592E+01    .110873E+02 X
REGRESSION COEFFICIENT =   .548077
VARIATION          DEG OF F         SUM OF SQ        VAR EST           F VALUE


LIN EFFECT            1             .789267E+03     .789267E+03      .431600E+01
OVERALL EFF           1             .789267E+03
DEVIATION            10             .182866E+04     .182866E+03
TOTAL                11             .261793E+04


      Y=    .562324E+02  -.612224E+02 X    .165351E+02 XX
REGRESSION COEFFICIENT =   .849515
VARIATION          DEG OF F         SUM OF SQ        VAR EST           F VALUE
LIN EFFECT            1             .789267E+03     .789267E+03
QUAD EFFECT           1             .109559E+04     .109559E+04       .134505E+02
OVERALL EFF           2             .188485E+04
DEVIATION             9             .733077E+03     .814530E+02
TOTAL                11             .261793E+04


      Y=    .559654E+02  -.599575E+02 X    .157656E+02 XX    .665258-01 XXX
REGRESSION COEFFICIENT =   .848510
VARIATION          DEG OF F         SUM OF SQ        VAR EST           F VALUE
LIN EFFECT            1             .789267E+03     .789267E+03
QUAD EFFECT           1             .109559E+04     .109559E+04
CUB EFFECT            1             .111142E-01     .111142E-01       .121181E-03
OVERALL EFF           3             .188486E+04
DEVIATION             8             .733066E+03     .916333E+02
TOTAL                11             .261793E+04


      Y=    .334099E+03  -.710661E+03 X    .559381E+03 XX   -.185041E+03 XXX    .222217E+02 XXXX
REGRESSION COEFFICIENT =   .867724
VARIATION          DEG OF F         SUM OF SQ        VAR EST           F VALUE
LIN EFFECT            1             .789267E+03     .789267E+03
QUAD EFFECT           1             .109559E+04     .109559E+04
CUB EFFECT            1             .111142E-01     .111142E-01
QUART EFF             1             .863659E+02     .863659E+02       .934879E+00
OVERALL EFF           4             .197123E+04
DEVIATION             7             .646703E+03     .923858E+02
TOTAL                11             .261793E+04
```

Exhibition Road, 3. 6. 1975.

X : Total hydrocarbons

Y : Pb

Linear regression : F-value : 0.73, $P > 0.10$

insignificant correlation.

Square regression : F-value : 0.52, $P > 0.10$

insignificant correlation.

Cubic regression : F-value : 15.12, $0.025 > P > 0.001$

significant correlation,

$Y : -282.7X^3 + 1639.4X^2 - 3069.3X + 1869.6$

$r : 0.83$

regression of doubtful value, Y cannot ever take a negative value.

Quartic regression : F-value : 1.90, $P > 0.10$

insignificant correlation.

```
      X              Y
  1.7[illegible]     [illegible].1[illegible]
  1.37[illegible]    1[illegible]
  1.5[illegible]     3.[illegible]
  1.4[illegible]     2.7[illegible]
  2.5[illegible]     5.1[illegible]
  1.37[illegible]    4.2[illegible]
  1.52[illegible]    4.7[illegible]
  1.64[illegible]    5.7[illegible]
  1.37[illegible]    6.3[illegible]
  1.5[illegible]     5.7[illegible]
  1.32[illegible]   35.1[illegible]
  2.35[illegible]    5.6[illegible]


     Y=   -.6893[illegible]E+01    .102[illegible]7[illegible]E+02 X
REGRESSION COEFFICIENT =    .2[illegible]5
VARIATION          DEG OF F        SUM OF SQ       VAR EST        F VALUE
LIN EFFECT             1          .17778[illegible]E+03    .177787E+03    .72[illegible]5[illegible]4[illegible]E+0[illegible]
OVERALL  EFF           1           177787E+03
DEVIATION             10          .244[illegible]14[illegible]E+04    .244[illegible]14E+03
TOTAL                 11          .2617[illegible]3[illegible]E+04


     Y=   .[illegible]5545[illegible]E+02  -.[illegible]6[illegible]E+02 X    .24[illegible]77E+02 XX
REGRESSION COEFFICIENT =    .[illegible]45[illegible]
VARIATION          DEG OF F        SUM OF SQ       VAR EST        F VALUE
LIN EFFECT             1          .1777[illegible]7[illegible]E+03    .177787E+03
QUAD EFFECT            1          .134[illegible]1[illegible]E+03    .134010E+03    .522[illegible]E+0[illegible]
OVERALL  EFF           2           3117[illegible]7[illegible]E+03


DEVIATION              9          .2[illegible]613[illegible]E+04    .256237E+03
TOTAL                 11          .261793E+04


     Y=   .1[illegible]6[illegible]5[illegible]E+04  -.3[illegible]6[illegible]2[illegible]E+04 X    163[illegible]3[illegible]E+04 XX  - 2[illegible]266[illegible]E+03 XXX
REGRESSION COEFFICIENT =    .[illegible]
VARIATION          DEG OF F        SUM OF SQ       VAR EST        F VALUE
LIN EFFECT             1          .1777[illegible]7[illegible]E+03    .177787E+03
QUAD EFFECT            1          .134[illegible]1[illegible]E+03    .134[illegible]1[illegible]E+03
CUB  EFFECT            1           15[illegible]47[illegible]E+04     15[illegible]47[illegible]E+04    .151[illegible]2[illegible]E+02
OVERALL  EFF           3          .1[illegible]2[illegible]26[illegible]E+04
DEVIATION              8          .7[illegible]76[illegible]7[illegible]E+03    .997[illegible]84E+02
TOTAL                 11          .261793E+04


     Y=   [illegible]14467[illegible]E+04    [illegible]161[illegible]E+04 X   -.[illegible]16165[illegible]E+04 XX    .174682[illegible]E+04 XXX   -.2[illegible]141[illegible]E+03 XXXX
REGRESSION COEFFICIENT =    .[illegible]71921
VARIATION          DEG OF F        SUM OF SQ       VAR EST        F VALUE
LIN EFFECT             1          .1777[illegible]7[illegible]E+03    .177787E+03
QUAD EFFECT            1           134[illegible]1[illegible]E+03     134[illegible]1[illegible]E+03
CUB  EFFECT            1          .15[illegible]847[illegible]E+04    .15[illegible]847E+04
QUART EFF              1          .17[illegible]E+03    .17[illegible]9[illegible]E+03    .18960[illegible]3E+01
OVERALL  EFF           4          .1[illegible]27[illegible]E+04
DEVIATION              7          .627659[illegible]E+03    .[illegible]96655[illegible]E+02
TOTAL                 11          .2617[illegible]E+04
```

Exhibition Road, 3. 6. 1975.

X : CH_4 - CH_4 (background)

Y : Pb

Linear regression : F-value : 4.00, $P > 0.10$
insignificant correlation.

Square regression : F-value : 2.73, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.05, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.32, $P > 0.10$
insignificant correlation.

```
 )
 .1[illegible]        4.1[illegible]
 .12[illegible]       1.4[illegible]
 .[illegible]         2.8[illegible]
 .17[illegible]       2.7[illegible]
  14[illegible]       5 1[illegible]
 .11[illegible]       4.2[illegible]


 .[illegible]         4.7[illegible]
 .33[illegible]       5.[illegible]
 .0[illegible]        5.30[illegible]
 .15[illegible]       6 7[illegible]
 .04[illegible]      30.1[illegible]
 .06[illegible]      5 .6[illegible]

    Y=    .292371[illegible]+02  -.183956E+03 X
REGRESSION COEFFICIENT =    .5[illegible]327
VARIATION          DEG OF F        SUM OF SQ       VAR EST        F VALUE
LIN EFFECT            1           .747433E+03    .747433E+03     .399590E+01
OVERALL EFF           1           .747433E+03
DEVIATION            10           .187[illegible]E+04    .187050E+03
TOTAL                11           .261793E+04

    Y=    .642369[illegible]+02  -.931380E+03 X    .336650E+04 XX
REGRESSION COEFFICIENT =    .672[illegible]02
VARIATION          DEG OF F        SUM OF SQ       VAR EST        F VALUE
LIN EFFECT            1           .747433E+03    .747433E+03
QUAD EFFECT           1           .435108E+03    .435108E+03     .272[illegible]16[illegible]+01
OVERALL EFF           2           .118254E+04
DEVIATION             9           .143530E+04    .159[illegible]E+03
TOTAL                11           .261793E+04

    Y=    .768463[illegible]+02  -.137562E+04 X    .79[illegible]666E+04 XX   -.14[illegible]7E+05 XXX
REGRESSION COEFFICIENT =    .674507
VARIATION          DEG OF F        SUM OF SQ       VAR EST        F VALUE
LIN EFFECT            1           .747433E+03    .747433E+03
QUAD EFFECT           1           .435108E+03    .4351[illegible]3E+03
CUB EFFECT            1           .3552[illegible]E+01    .855238E+01     .43119[illegible]-01
OVERALL EFF           3           .119112[illegible]+04
DEVIATION             8           .142551E+04    .178351E+03
TOTAL                11           .261793E+04

    Y=   -.2230[illegible]E+02    .334792E+04 Y   -.694136E+05 XX    .490264E+06 XXY   -.11636[illegible]E+07 XXXY
REGRESSION COEFFICIENT =    6[illegible]725
VARIATION          DEG OF F        SUM OF SQ       VAR EST        F VALUE
LIN EFFECT            1           .747433E+03    .747433E+03
QUAD EFFECT           1           .435108E+03    .435108E+03
CUB EFFECT            1           .552[illegible]E+01    .552[illegible]3[illegible]+01
QUAR EFF              1           .615798E+02    .615798E+02     .315356E+00
OVERALL EFF           4           .125263E+04
DEVIATION             7           .136530E+04    .195043E+03
TOTAL                11           .261793E+04
```

1

2

Exhibition Road, 3. 6. 1975.

X : CO

Y : Total hydrocarbons

Linear regression : F-value : 3.28, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.04, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 2.08, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.12, $P > 0.10$
insignificant correlation.

```
       X                Y
    1.4[illegible]      1.77[illegible]
    1.24[illegible]     1.37[illegible]
    1.14000             1.4[illegible]
     .9[illegible]      1.43[illegible]
    1.44[illegible]     2.53[illegible]
    2.21000             1.79[illegible]
    1.77[illegible]     1.52[illegible]
    1.32[illegible]     1.56[illegible]
    1.44[illegible]     1.57[illegible]
    2.5[illegible]      1.5[illegible]
     .95[illegible]     1.32[illegible]
    3.54000             2.35[illegible]


      Y=      .1342[illegible]E+01     .2552[illegible]9E+00  X
REGRESSION COEFFICIENT  =     .496939
VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
LIN EFFECT             1              .413485E+00     .413485E+00       .327931E+01
OVERALL EFF            1              .413485E+00
DEVIATION             10              .127614E+01     .127614E+00
TOTAL                 11              .169462E+01



      Y=      .144256E+01     .3[illegible]1E-01  X     .364518E-01  XX
REGRESSION COEFFICIENT  =     .5[illegible]1
VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
LIN EFFECT             1              .413485E+00     .413485E+00
QUAD EFFECT            1              .532440E-02     .532440E-02       .377[illegible]78E-01
OVERALL EFF            2              .418[illegible]E+00
DEVIATION              9              .127[illegible]2E+01     .141202E+00
TOTAL                 11              .169462E+01

      Y=     -.179481E+01     .556479E+01  X    -.273210E+01  XX     .421225E+00  XXX
REGRESSION COEFFICIENT  =     .676741
VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
LIN EFFECT             1              .413485E+00     .413485E+00
QUAD EFFECT            1              .532440E-02     .532440E-02
CUB EFFECT             1              .262394E+00     .262394E+00       .2[illegible]8162E+01
OVERALL EFF            3              .6[illegible]62[illegible]4E+00
DEVIATION              8              .10[illegible]42E+01     .126[illegible]53[illegible]E+00
TOTAL                 11              .169462E+01

      Y=     -.5[illegible]7548E+01     .15[illegible]276E+02  X    -.125358E+02  XX     .3[illegible]E+01  XXX    -.316223E+[illegible]  XXXX
REGRESSION COEFF[illegible]  =     .644546
VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
LIN EFFECT             1              .413485E+00     .413485E+00
QUAD EFFECT            1              .532440E-02     .532440E-02
CUB EFFECT             1              .262394E+00     .262394E+00
QUAR EFF               1              .17[illegible]1[illegible]1-01  .17[illegible]1[illegible]E-01     .125[illegible]52[illegible]+[illegible]
OVERALL EFF            4              .[illegible]14[illegible]+00
DEVIATION              7              .[illegible]6111[illegible]+00  .141516E+00
TOTAL                 11              .169462E+01
```

Exhibition Road, 3. 6. 1975.

X : $CH_4 - CH_{4(bg)}$

Y : CO

Linear regression : F-value : 1.59, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.003, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.58, $P > 0.10$
insignificant correlation.

Quartic regression: F-value : 1.34, $P > 0.10$
insignificant correlation.

```
     X              Y
      1[illegible]      [illegible]
     .1[illegible]      [illegible]
     .[illegible]      1.14[illegible]
     .17[illegible]     .98[illegible]
     .1[illegible]      1.44[illegible]
     .11[illegible]     2.21[illegible]
     [illegible]       1.77[illegible]
     .[illegible]      1.32[illegible]
     .[illegible]      1.44[illegible]
     .[illegible]      2.5[illegible]
     .[illegible]       .96[illegible]
     .[illegible]6[illegible]     7.54[illegible]


        Y=    .2295[illegible]+[illegible]1   -.632252[illegible]+[illegible]1 X
REGRESSION COEFFICIENT =   .37[illegible]732
VARIATION          DEG OF F          SUM OF SQ       VAR EST         F VALUE
LIN EFFECT            1               [illegible]+00     [illegible]+00    .159343[illegible]+[illegible]1
OVERALL EFF           1              .[illegible]+[illegible]
DEVIATION            10              .554213[illegible]+[illegible]1    .554213E+00
TOTAL                11              .642523E+[illegible]1

        Y=   [illegible]235[illegible]+[illegible]1   [illegible]+[illegible]1 X    .71[illegible]262[illegible]+[illegible]1 XX
REGRESSION COEFFICIENT =   .37113[illegible]
VARIATION          DEG OF F          SUM OF SQ       VAR EST         F VALUE
LIN EFFECT            1              .[illegible]+00     .883098E+00
QUAD EFFECT           1              1[illegible]676[illegible]-[illegible]2     1[illegible]676[illegible]-[illegible]2     [illegible]314626 -[illegible]2
OVERALL EFF           2              .[illegible]+[illegible]
DEVIATION             [illegible]              .5[illegible]+[illegible]1    .615577E+00
TOTAL                11              .642523E+[illegible]1

        Y=   [illegible]272[illegible]+[illegible]   [illegible]84[illegible]226[illegible]+[illegible]2 X   -.[illegible]48[illegible]7[illegible]+[illegible]3 XX    .2[illegible]4[illegible]23[illegible]+[illegible]4 XXX
REGRESSION COEFFICIENT =   .442644


VARIATION          DEG OF F          SUM OF SQ       VAR EST         F VALUE
LIN EFFECT            1              .[illegible]+[illegible]     .[illegible]+00
QUAD EFFECT           1              1[illegible]3676 -[illegible]2     1[illegible]3676 -[illegible]2
CUB EFFECT            1              .373885[illegible]+0[illegible]     .373885[illegible]+0[illegible]    .57[illegible]+[illegible]
OVERALL EFF           3              .125892[illegible]+[illegible]1
DEVIATION             8              .5[illegible]+[illegible]1    .645768E+0[illegible]
TOTAL                11               642523 +[illegible]1

        Y=  -.1177[illegible]+[illegible]2    .532[illegible]5[illegible]+[illegible]3 X   -.[illegible]925[illegible]+[illegible]4 XX    .614696E+[illegible]5 XXX   -.135[illegible]45[illegible]+[illegible]6 XXXX
REGRESSION COEFFICIENT =   .569961
VARIATION          DEG OF F          SUM OF SQ       VAR EST         F VALUE
LIN EFFECT            1              [illegible]+[illegible]     .[illegible]+[illegible]
QUAD EFFECT           1              .1[illegible]576[illegible]-[illegible]2     .19[illegible]676[illegible]-[illegible]2
CUB EFFECT            1              .[illegible]+[illegible]     .373885E+[illegible]
QUART EFF             1              .[illegible]+[illegible]     .829349[illegible]+[illegible]    .133668E+[illegible]1
OVERALL EFF           4              2[illegible]727[illegible]+[illegible]1
DEVIATION             7              .[illegible]37965[illegible]+[illegible]1    .6197[illegible]E+[illegible]
TOTAL                11              .642523[illegible]+[illegible]1
```

Exhibition Road, 3. 6. 1975.

X : Total hydrocarbons

Y : $CH_4 - CH_{4(bg)}$

Linear regression	: F-value : 0.19,	$P > 0.10$
	insignificant correlation.	
Square regression	: F-value : 0.07,	$P > 0.10$
	insignificant correlation.	
Cubic regression	: F-value : 2.30,	$P > 0.10$
	insignificant correlation.	
Quartic regression	: F-value : 0.02,	$P > 0.10$
	insignificant correlation.	

```
      X                Y
    1.73000          .1[illegible]
    1.37000          .12
    1.24000          .1[illegible]
    1.4[illegible]   .1[illegible]
    2.53000          .14[illegible]
    1.37000          .11[illegible]
    1.52000          .[illegible]
    1.64000          .[illegible]
    1.37000          .[illegible]
    1.5[illegible]   .[illegible]
    1.32[illegible]  .[illegible]
    2.35000          .150[illegible]

      Y=     .741261E-01    .155149E-01 X
   REGRESSION COEFFICIENT  =    .135777
   VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
   LIN EFFECT          1              .407391E-03     .407391E-03      .187874E+00
   OVERALL EFF         1              .407391E-03
   DEVIATION          10              .216843E-01     .216843E-02
   TOTAL              11              .220917E-01

      Y=   -.209517E-01    .119123E+00 X   -.269334E-01 XX
   REGRESSION COEFFICIENT  =    .161557
   VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
   LIN EFFECT          1              .407391E-03     .407391E-03
   QUAD EFFECT         1              .162103E-03     .162103E-03      .677871E-01
   OVERALL EFF         2              .569494E-03
   DEVIATION           9              .215222E-01     .239135E-02
   TOTAL              11              .220917E-01

      Y=   -.321559E+01    .544715E+01 X   -.290916E+01 XX    .507449E+00 XXX
   REGRESSION COEFFICIENT  =    .493233
   VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
   LIN EFFECT          1              .407391E-03     .407391E-03
   QUAD EFFECT         1              .162103E-03     .162103E-03
   CUB EFFECT          1              .482494E-02     .482494E-02      .229947E+01
   OVERALL EFF         3              .537444E-02
   DEVIATION           8              .167172E-01     .208965E-02
   TOTAL              11              .220917E-01

      Y=   -.139151E+01    .146665E+01 X    .284115E+00 XX   -.612672E+00 XXX    .143957E+00 XXXX
   REGRESSION COEFFICIENT  =    .495581
   VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
   LIN EFFECT          1              .407391E-03     .407391E-03
   QUAD EFFECT         1              .162103E-03     .162103E-03
   CUB EFFECT          1              .482494E-02     .482494E-02
   QUART EFF           1              .515147E-04     .515147E-04      .216374E-01
   OVERALL EFF         4              .542595E-02


   DEVIATION           7              .166657E-01     .238082E-02
   TOTAL              11              .220917E-01
```

Exhibition Road, 3. 6. 1975.

X : Spot CH_4

Y : - CO

Linear regression : F-value : 3.86, $P > 0.10$
insignificant correlation.

Square regression : F-value : 1.72, $P > 0.10$
insignificant correlation.

Cube regression : F-value : 0.68, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.96, $P > 0.10$
insignificant correlation.

```
     X           Y
  1.61000     1.14000
  1.37000     1.24000
  1.30000      .76000

  1.31000      .57000
  1.33000      .76000
  1.35000     1.42000
  1.32000      .66000
  1.29000     1.33000
  1.26000      .86000
  1.22000     2.00000
  1.31000     1.04000
  1.23000      .66000
  1.29000      .95000
  1.55000     1.18000
  1.29000     1.04000
  1.37000      .76000
  1.31000     1.24000
  1.32000     1.67000
  1.33000      .38000
  1.34000     2.47000
  1.31000     1.34000
  1.30000      .56000
  1.32000     2.56000
  1.31000     2.26000
  1.29000      .76000
  1.25000     1.42000
  1.35000     1.36000
  1.31000     1.52000
  1.29000     1.71000
  1.29000      .63000
  1.24000     2.47000
  1.32000      .48000
  1.30000      .51000
  1.29000     2.56000
  1.30000     1.71000
  1.23000      .76000
  1.20000      .38000
  1.25000     1.42000
  1.25000     5.13000
  1.27000     2.[illegible]
  1.24000      .36000
  1.23000      .10000
  1.25000      .43000
  1.25000     2.39000
  1.19000      .20000
  1.37000     1.53000
  1.26000     1.52000
  1.28000      .95000
```

```
  Y=   -.743486E+01   .693115E+01 X
REGRESSION COEFFICIENT =   .278238
VARIATION        DEG OF F          SUM OF SQ      VAR EST        F VALUE
LIN EFFECT           1           .119583E+02    .119583E+02    .386179E+01
OVERALL EFF          1           .119583E+02
DEVIATION           46           .142452E+03    .309657E+01
TOTAL               47           .154410E+03

  Y=   -.664769E+02   .971568E+02 X   -.312599E+02 XX
REGRESSION COEFFICIENT =   .333649
VARIATION        DEG OF F          SUM OF SQ      VAR EST        F VALUE
LIN EFFECT           1           .119583E+02    .119583E+02
QUAD EFFECT          1           .525044E+01    .525044E+01    .172219E+01
OVERALL EFF          2           .172087E+02
DEVIATION           45           .137201E+03    .304971E+01
TOTAL               47           .154410E+03

  Y=    .543416E+03  -.125357E+04 X    .959102E+03 XY   -.239[illegible]E+03 XXY
REGRESSION COEFFICIENT =   .353573
VARIATION        DEG OF F          SUM OF SQ      VAR EST        F VALUE
LIN EFFECT           1           .119583E+02    .119583E+02
QUAD EFFECT          1           .525044E+01    .525044E+01
CUB EFFECT           1           .209343E+01    .209343E+01    .681926E+00
OVERALL EFF          3           .193022E+02
DEVIATION           44           .135108E+03    .307042E+01
TOTAL               47           .154410E+03

  Y=    .652595E+04  -.247576E+05 X    .262219E+05 XX   -.128483E+05 XXY    .229677E+04 XX
REGRESSION COEFFICIENT =   .3796[illegible]
VARIATION        DEG OF F          SUM OF SQ      VAR EST        F VALUE
LIN EFFECT           1           .119583E+02    .119583E+02
QUAD EFFECT          1           .525044E+01    .525044E+01
CUB EFFECT           1           .209343E+01    .209343E+01
QUART EFF            1           .294623E+01    .294623E+01    .958652E+00
OVERALL EFF          4           .222484E+02


DEVIATION           43           .132152E+03    .307331E+01
TOTAL               47           .154410E+03
```

Exhibition Road, 19. 6. 1975.

X : CO

Y : Pb

Linear regression : F-value : 0.10, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.47, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.14, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.19, $P > 0.10$
insignificant correlation.

```
   X            Y
3.76000      10.71000
5.92000       5.45000
6.05000       3.44000
1.76000       3.38000
1.57000       3.19000
2.10000       4.74000
1.70000       5.09000
2.81000       2.78000
3.32000       3.69000
7.44000       3.12000
3.36000       4.16000
2.93000       2.81000
3.72000       3.49000
3.10000       3.57000
4.67000       4.11000
2.73000       2.73000
4.56000       2.93000
3.80000       2.82000
3.65000       4.40000
3.02000       3.22000
3.05000       3.99000
5.72000       3.96000
1.50000       3.99000
7.25000       3.87000
2.52000       2.99000
2.89000       2.46000
2.13000       4.44000
3.58000       4.86000
3.68000       4.62000

3.50000       3.00000
4.12000       2.68000
2.35000       2.94000
```

```
     Y=     .357716E+01   .561982E-01 X
REGRESSION COEFFICIENT  =    .058958
VARIATION          DEG OF F        SUM OF SQ       VAR EST         F VALUE
LIN EFFECT             1          .234618E+00    .234618E+00     .104646E+00
OVERALL EFF            1          .234618E+00
DEVIATION             30          .672604E+02    .224201E+01
TOTAL                 31          .674950E+02

     Y=     .258507E+01   .605872E+00 X   -.643687E-01 XX
REGRESSION COEFFICIENT  =    .139340
VARIATION          DEG OF F        SUM OF SQ       VAR EST         F VALUE
LIN EFFECT             1          .234618E+00    .234618E+00
QUAD EFFECT            1          .107584E+01    .107584E+01     .471399E+00
OVERALL EFF            2          .131046E+01
DEVIATION             29          .661845E+02    .228223E+01
TOTAL                 31          .674950E+02

     Y=     .386701E+01  -.549815E+00 X    .240030E+00 XX   -.236657E-01 XXX
REGRESSION COEFFICIENT  =    .155446
VARIATION          DEG OF F        SUM OF SQ       VAR EST         F VALUE
LIN EFFECT             1          .234618E+00    .234618E+00
QUAD EFFECT            1          .107584E+01    .107584E+01
CUB EFFECT             1          .320466E+00    .320466E+00     .136236E+00
OVERALL EFF            3          .163092E+01
DEVIATION             28          .658641E+02    .235229E+01
TOTAL                 31          .674950E+02

     Y=     .820745E+01  -.575880E+01 X    .234519E+01 XX   -.368802E+00 XXX    .196456E-01 XXXX
REGRESSION COEFFICIENT  =    .175834
VARIATION          DEG OF F        SUM OF SQ       VAR EST         F VALUE
LIN EFFECT             1          .234618E+00    .234618E+00
QUAD EFFECT            1          .107584E+01    .107584E+01
CUB EFFECT             1          .320466E+00    .320466E+00
QUART EFF              1          .455852E+00    .455852E+00     .188172E+00
OVERALL EFF            4          .208678E+01
DEVIATION             27          .654082E+02    .242253E+01
TOTAL                 31          .674950E+02
```

Exhibition Road, 19. 6. 1975.

X : Total hydrocarbons

Y : Pb

Linear regression : F-value : 1.69, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.12, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 3.06, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 5.00, $P > 0.10$
insignificant correlation.

```
                                      Y=    .143927E+01    .114283E+01 X
                                  REGRESSION COEFFICIENT =   .231064
    X                  Y          VARIATION       DEG OF F          SUM OF SQ       VAR EST        F VALUE
 2.53000          10.71000        LIN EFFECT          1              .362097E+01    .362097E+01    .169205E+01
 1.91000           5.45000        OVERALL EFF         1              .362097E+01
 2.25000           3.44000        DEVIATION          30              .641997E+02    .213999E+01
 2.10000           3.08000        TOTAL              31              .678207E+02
 1.44000           3.19000
 1.93000           4.74000
 2.01000           5.00000            Y=    .412525E+01   -.147152E+01 X    .623264E+00 XX
 1.73000           2.78000        REGRESSION COEFFICIENT =   .239374
 1.95000           3.69000        VARIATION       DEG OF F          SUM OF SQ       VAR EST        F VALUE
 1.70000           3.12000        LIN EFFECT          1              .362097E+01    .362097E+01
 2.55000           4.16000        QUAD EFFECT         1              .265136E+00    .265136E+00    .120263E+00
 1.86000           2.81000        OVERALL EFF         2              .388611E+01
 2.37000           3.48000        DEVIATION          29              .639346E+02    .220464E+01
 2.07000           3.53000        TOTAL              31              .678207E+02
 2.21000           4.11000
 1.88000           2.73000
 2.24000           2.93000            Y=    .701610E+02   -.990187E+02 X    .482000E+02 XX   -.747969E+01 XXX
 2.06000           2.82000        REGRESSION COEFFICIENT =   .387672
 2.37000           4.48000        VARIATION       DEG OF F          SUM OF SQ       VAR EST        F VALUE
 2.20000           3.22000        LIN EFFECT          1              .362097E+01    .362097E+01
 1.43000           3.99000        QUAD EFFECT         1              .265136E+00    .265136E+00
                                  CUB EFFECT          1              .630661E+01    .630661E+01    .306423E+01
                                  OVERALL EFF         3              .101927E+02
                                  DEVIATION          28              .576280E+02    .205814E+01
 2.02000           3.06000        TOTAL              31              .678207E+02
 2.01000           3.09000
 1.95000           3.87000
 1.90000           2.90000           Y=   -.432748E+03    .896820E+03 X   -.677701E+03 XX    .223040E+03 XXX   -.269463E+02 XXXX
 1.93000           2.46000        REGRESSION COEFFICIENT =   .532078
 1.63000           4.44000        VARIATION       DEG OF F          SUM OF SQ       VAR EST        F VALUE
 1.94000           4.06000        LIN EFFECT          1              .362097E+01    .362097E+01
 2.12000           4.62000        QUAD EFFECT         1              .265136E+00    .265136E+00
 2.88000           3.00000        CUB EFFECT          1              .630661E+01    .630661E+01
 2.07000           2.63000        QUART EFF           1              .900793E+01    .900793E+01    .500228E+01
 2.81000           2.94000        OVERALL EFF         4              .192006E+02
                                  DEVIATION          27              .486201E+02    .180075E+01
                                  TOTAL              31              .678207E+02
```

Exhibition Road, 19. 6. 1975.

X : $CH_4 - CH_{4(bg)}$

Y : Pb

Linear regression : F-value : 4.78, $P > 0.10$
insignificant correlation.

Square regression : F-value : 7.16, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.0009, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.77, $P > 0.10$
insignificant correlation.

```
                                    Y=    .233736E+01   .459684E+01 X
                                 REGRESSION COEFFICIENT =  .370657
   X                Y            VARIATION       DEG OF F         SUM OF SQ        VAR EST          F VALUE
 .57000         10.71000         LIN EFFECT          1             .931767E+01     .931767E+01     .477805E+01
 .26000          5.45000         OVERALL EFF         1             .931767E+01
 .33000          3.44000         DEVIATION          30             .565030E+02     .195010E+01
                                 TOTAL              31             .678207E+02

 .20000          3.08000            Y=    .600887E+01  -.191281E+02 X    .335534E+02 XX
 .28000          3.19000         REGRESSION COEFFICIENT =   .555200
 .30000          4.74000         VARIATION       DEG OF F         SUM OF SQ        VAR EST          F VALUE
 .54000          5.00000         LIN EFFECT          1             .931767E+01     .931767E+01
 .40000          2.73000         QUAD EFFECT         1             .115879E+02     .115879E+02     .716291E+01
 .34000          3.69000         OVERALL EFF         2             .209056E+02
 .24000          3.12000         DEVIATION          29             .469151E+02     .161776E+01
 .61000          4.16000         TOTAL              31             .678207E+02
 .44000          2.81000
 .34000          3.48000
 .42000          3.53000            Y=    .611314E+01  -.202211E+02 X    .369439E+02 XX  -.315151E+01 XXX
 .34000          4.11000         REGRESSION COEFFICIENT =   .555220
 .40000          2.73000         VARIATION       DEG OF F         SUM OF SQ        VAR EST          F VALUE
 .23000          2.93000         LIN EFFECT          1             .931767E+01     .931767E+01
 .39000          2.82000         QUAD EFFECT         1             .115879E+02     .115879E+02
 .32000          4.48000         CUB EFFECT          1             .146321E-02     .146321E-02     .873305E-03
 .23000          3.22000         OVERALL EFF         3             .209070E+02
 .32000          3.99000         DEVIATION          28             .469137E+02     .167549E+01
 .33000          3.06000         TOTAL              31             .678207E+02
 .28000          3.09000
 .21000          3.87000
 .15000          2.90000            Y=   -.149118E+01   .902413E+02 X   -.509703E+03 XX    .110363E+04 XXX   -.780766E+03 XXXX
 .22000          2.46000         REGRESSION COEFFICIENT =   .572160
 .13000          4.44000         VARIATION       DEG OF F         SUM OF SQ        VAR EST          F VALUE
 .17000          4.06000         LIN EFFECT          1             .931767E+01     .931767E+01
 .13000          4.62000         QUAD EFFECT         1             .115879E+02     .115879E+02
 .28000          3.00000         CUB EFFECT          1             .146321E-02     .146321E-02
 .22000          2.68000         QUART EFF           1             .129524E+01     .129524E+01     .766608E+00
 .24000          2.94000         OVERALL EFF         4             .222023E+02
                                 DEVIATION          27             .456184E+02     .168957E+01
                                 TOTAL              31             .678207E+02
```

Exhibition Road, 19. 6. 1975.

X : CO

Y : Total hydrocarbons

Linear regression : F-value : 0.65, $P > 0.10$
insignificant correlation.

Square regression : F-value : 9.32, P : 0.10
slight correlation,

$Y : -0.05X^2 + 0.46X + 1.16$

$r : 0.51$

Y can never take a negative value

Cubic regression : F-value : 0.06, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.88, $P > 0.10$
insignificant correlation.

```
    X                   Y
 3.76000             2.50000
 5.90000             1.91000
 6.05000             2.25000
 1.76000             2.10000
 1 50000             1 44000
 2.10000             1.93000
 1.70000             2.01000
 2.01000             1.73000
 3.92000             1.95000
 7.44000             1.70000
 3 36000             2 56000
 2.99000             1.86000
 3.72000             2.37000
 3.11000             2.07000
 4.67000             2.21000
 2.78000             1.85000
 4 56000             2 24000
 3.80000             2.06000
 3.65000             2.30000
 3.02000             2.20000
 3.05000             1.43000
 5.72000             2.02000
 1 50000             2 01000
 7.25000             1.95000
 2.52000             1.90000
 2.89000             1.99000
 2.13000             1.63000
 3.58000             1.94000
 3 69000             2 12000
 3.50000             2.83000
 4.12000             2.07000
 2.36000             2.01000
```

```
      Y=    .193671E+01    .281821E-01 X
REGRESSION COEFFICIENT =   .145902
VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
LIN EFFECT             1             .590183E-01     .590183E-01       .652514E+00
OVERALL EFF            1             .590183E-01
DEVIATION             30             .271343E+01     .904476E-01
TOTAL                 31             .277245E+01

      Y=    .115961E+01    .458743E+00 X   -.594194E-01 XX
REGRESSION COEFFICIENT =   .509285
VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
LIN EFFECT             1             .590183E-01     .590183E-01
QUAD EFFECT            1             .660075E+00     .660075E+00       .932240E+01
OVERALL EFF            2             .719094E+00
DEVIATION             29             .205335E+01     .708053E-01
TOTAL                 31             .277245E+01

      Y=    .130744E+01    .325476E+00 Y   -.153179E-01 XX   -.272099E-02 XXY
REGRESSION COEFFICIENT =   .510792
VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
LIN EFFECT             1             .590183E-01     .590183E-01
QUAD EFFECT            1             .660075E+00     .660075E+00
CUB EFFECT             1             .426135E-02     .426135E-02       .582296E-01
OVERALL EFF            3             .723355E+00
DEVIATION             28             .204909E+01     .731819E-01
TOTAL                 31             .277245E+01

      Y=    .294286E+01   -.163720E+01 X    .777685E+00 XX   -.132772E+00 XXX    .740221E-02 XXXX
REGRESSION COEFFICIENT =   .533152
VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
LIN EFFECT             1             .590183E-01     .590183E-01
QUAD EFFECT            1             .660075E+00     .660075E+00
CUB EFFECT             1             .426135E-02     .426135E-02

QUART EFF              1             .647166E-01     .647166E-01       .880553E+00
OVERALL EFF            4             .788071E+00
DEVIATION             27             .198438E+01     .734954E-01
TOTAL                 31             .277245E+01
```

Exhibition Road, 19. 6. 1975.

X : $CH_4 - CH_{4(bg)}$

Y : CO

Linear regression : F-value : 0.21, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.51, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 1.88, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.002, $P > 0.10$
insignificant correlation.

```
   X            Y
 .57000      3.76000
 .26000      5.90000
 .35000      6.05000
 .20000      1.76000
 .28000      1.59000
 .30000      2.10000
 .54000      1.73000
 .40000      2.01000
 .34000      3.92000
 .24000      7.44000
 .61000      3.36000
 .44000      2.97000
 .34000      3.72000
 .42000      3.10000
 .34000      4.67000
 .42000      2.78000
 .23000      4.56000
 .35000      5.80000
 .32000      5.65000
 .29000      3.92000
 .32000      3.05000
 .33000      5.72000
 .28000      1.53000
 .21000      7.25000
 .15000      2.52000
 .22000      2.89000
 .13000      2.13000
 .17000      3.59000
 .13000      3.68000
 .2 000      3.50000
 .22000      4.12000
 .24000      2.36000
```

```
      Y=     .390350E+01   -.108655E+01  X
REGRESSION COEFFICIENT =    .083699
VARIATION          DEG OF F          SUM OF SQ      VAR EST          F VALUE
LIN EFFECT            1              .520578E+00    .520578E+00      .211651E+00
OVERALL EFF           1              .520578E+00
DEVIATION            30              .737882E+02    .245961E+01
TOTAL                31              .743088E+02


      Y=     .268093E+01    .691359E+01  X   -.111729E+02  XX
REGRESSION COEFFICIENT =    .155974
VARIATION          DEG OF F          SUM OF SQ      VAR EST          F VALUE
LIN EFFECT            1              .520578E+00    .520578E+00
QUAD EFFECT           1              .128468E+01    .128468E+01      .513927E+00
OVERALL EFF           2              .180546E+01
DEVIATION            29              .725033E+02    .250012E+01
TOTAL                31              .743088E+02


      Y=    -.179411E+01    .537242E+02  X   -.156690E+03  XX     135260E+03  XXX
REGRESSION COEFFICIENT =    .246176
VARIATION          DEG OF F          SUM OF SQ      VAR EST          F VALUE
LIN EFFECT            1              .520578E+00    .520578E+00
QUAD EFFECT           1              .128468E+01    .128468E+01
CUB EFFECT            1              .269529E+01    .269529E+01      .108108E+01
OVERALL EFF           3              .450075E+01
DEVIATION            28              .698080E+02    .249314E+01
TOTAL                31              .743088E+02


      Y=    -.129970E+01    .465437E+02  X   -.121156E+03  XX    .633144E+02  XXX     .507529E+02  XXX
REGRESSION COEFFICIENT =    .246256
VARIATION          DEG OF F          SUM OF SQ      VAR EST          F VALUE
LIN EFFECT            1              .520578E+00    .520578E+00
QUAD EFFECT           1              .128468E+01    .128468E+01
CUB EFFECT            1              .269529E+01    .269529E+01
QUART EFF             1              .547306E-02    .547306E-02      .211701E-02
OVERALL EFF           4              .450622E+01
DEVIATION            27              .698026E+02    .258528E+01
TOTAL                31              .743088E+02
```

Exhibition Road, 19. 6. 1975.

X : Total hydrocarbons

Y : $CH_4 - CH_{4(bg)}$

Linear regression : F-value : 3.08, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.16, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 2.40, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 4.02, $0.10 > P > 0.05$
slight correlation, doubtful application.
Y cannot ever become negative

```
    X              Y
 2.50000        .57000
 1.91000        .26000
 2.25000        .33000
 2.10000        .20000
 1.44000        .28000
 1.90000        .35000
 2.01000        .54000
 1.73000        .40000
 1.95000        .34000
 1.70000        .24000
 2.56000        .61000
 1.86000        .44000
 2.37000        .34000
 2.07000        .42000
 2.21000        .34000
 1.88000        .40000
 2.24000        .23000
 2.06000        .39000
 2.32000        .32000
 2.20000        .28000
 1.43000        .32000
 2.02000        .33000
 2.11000        .22000
 1.95000        .21000
 1.90000        .15000
 1.99000        .22000
 1.63000        .17000
 1.94000        .17000
 2.12000        .13000
 2.88000        .23000
 2.07000        .22000
 2.01000        .24000
```

```
     Y=    .630262E-01    .121846E+00  X
REGRESSION COEFFICIENT =   .305527
VARIATION       DEG OF F         SUM OF SQ      VAR EST          F VALUE
LIN EFFECT         1            .411612E-01    .411612E-01     .308872E+01
OVERALL EFF        1            .411612E-01
DEVIATION         30            .399789E+00    .133263E-01
TOTAL             31            .440950E+00

     Y=    .307379E+00   -.116351E+00  X    .567159E-01  XX
REGRESSION COEFFICIENT =   .313569
VARIATION       DEG OF F         SUM OF SQ      VAR EST          F VALUE
LIN EFFECT         1            .411612E-01    .411612E-01
QUAD EFFECT        1            .219544E-02    .219544E-02     .160137E+00
OVERALL EFF        2            .433567E-01
DEVIATION         29            .397593E+00    .137101E-01
TOTAL             31            .440950E+00

     Y=    .496678E+01   -.795320E+01  X    .341266E+01  XX   -.527598E+00  XXX
REGRESSION COEFFICIENT =   .411688
VARIATION       DEG OF F         SUM OF SQ      VAR EST          F VALUE
LIN EFFECT         1            .411612E-01    .411612E-01
QUAD EFFECT        1            .219544E-02    .219544E-02
CUB EFFECT         1            .313787E-01    .313787E-01     .239915E+01

OVERALL EFF        3            .747354E-01
DEVIATION         28            .366215E+00    .130791E-01
TOTAL             31            .440950E+00

     Y=   -.315609E+02    .653325E+02  X   -.49[illegible]4E+02  XX    .162158E+02  XXX   -.195711E+01  XXXX
REGRESSION COEFFICIENT =   .526543
VARIATION       DEG OF F         SUM OF SQ      VAR EST          F VALUE
LIN EFFECT         1            .411612E-01    .411612E-01
QUAD EFFECT        1            .219544E-02    .219544E-02
CUB EFFECT         1            .313787E-01    .313787E-01
QUART EFF          1            .475171E-01    .475171E-01     .402564E+01
OVERALL EFF        4            .122252E+00
DEVIATION         27            .318698E+00    .118036E-01
TOTAL             31            .440950E+00
```

Exhibition Road, 19. 6. 1975.

X : Spot CH_4

Y : - CO

Linear regression : F-value : 0.13, $P > 0.10$
insignificant correlation.

Square regression : F-value : 3.82, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.91, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.28, $P > 0.10$
insignificant correlation.

```
        Y=     .269715E+01     .565180E+00  X
REGRESSION COEFFICIENT =    .039907
VARIATION        DEG OF F          SUM OF SQ        VAR EST          F VALUE
LIN EFFECT           1             .767870E+00      .767870E+00      .126016E+00
OVERALL EFF          1             .767870E+00
DEVIATION           79             .481382E+03      .609344E+01
TOTAL               80             .482149E+03

        Y=    -.581351E+02     .796837E+02  X   -.254060E+02  XX
REGRESSION COEFFICIENT =    .320958
VARIATION        DEG OF F          SUM OF SQ        VAR EST          F VALUE
LIN EFFECT           1             .767870E+00      .767870E+00
QUAD EFFECT          1             .489003E+02      .489003E+02      .881939E+01
OVERALL EFF          2             .496681E+02
DEVIATION           78             .432481E+03      .554463E+01
TOTAL               80             .482149E+03

        Y=    -.228139E+03     .412019E+03  X   -.240158E+03  XX     .458666E+02  XXX
REGRESSION COEFFICIENT =    .336823
VARIATION        DEG OF F          SUM OF SQ        VAR EST          F VALUE
LIN EFFECT           1             .767870E+00      .767870E+00
QUAD EFFECT          1             .489003E+02      .489003E+02
CUB EFFECT           1             .503145E+01      .503145E+01      .906356E+00
OVERALL EFF          3             .546998E+02
DEVIATION           77             .427450E+03      .555130E+01
TOTAL               80             .482149E+03

        Y=     .616096E+03   -.100032E+04  X     .192102E+04  XX   -.886112E+03  XXX     .149744E+03  XXXX
REGRESSION COEFFICIENT =    .341675
VARIATION        DEG OF F          SUM OF SQ        VAR EST          F VALUE
LIN EFFECT           1             .767870E+00      .767870E+00
QUAD EFFECT          1             .489003E+02      .489003E+02
CUB EFFECT           1             .503145E+01      .503145E+01
QUART EFF            1             .158750E+01      .158750E+01      .283307E+00
OVERALL EFF          4             .562871E+02
DEVIATION           76             .425862E+03      .560345E+01
TOTAL               80             .482149E+03
```

Teeside, July, 1975.

X : CO

Y : Pb

Linear regression : F-value : 0.40, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.18, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.46, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.41, $P > 0.10$
insignificant correlation.

```
              X            Y
           .55000       .57000
           .44000      1.04000
           .43000       .36000
           .34000       .43000
           .38000       .92000
           .37000        74000
          1.01000       .47000
           .85000       .47000
           .39000       .45000
           .34000       .25000
           .39000      1.99000
           .31000        73000
           .33000       .57000


        Y=     .877199E+00  -.393733E+00  X
REGRESSION COEFFICIENT  =    .188409
VARIATION       DEG OF F         SUM OF SQ       VAR EST        F VALUE
LIN EFFECT          1             .860033E-01     .860033E-01    .404849E+00
OVERALL EFF         1             .860033E-01
DEVIATION          11             .233677E+01     .212433E+00
TOTAL              12             .242277E+01

        Y=     .265405E+00   .189622E+01  X   -.176591E+01  XX
REGRESSION COEFFICIENT  =    .229943
VARIATION       DEG OF F         SJM OF SQ       VAR EST        F VALUE
LIN EFFECT          1             .860033E-01     .860033E-01
QUAD EFFECT         1             .420982E-01     .420982E-01    .183461E+00
OVERALL EFF         2             .128101E+00
DEVIATION          10             .229467E+01     .229467E+00
TOTAL              12             .242277E+01

        Y=   -.248999E+01   .172072E+02  X   -.279245E+02  XX     .136895E+02  XXX
REGRESSION COEFFICIENT  =    .314355
VARIATION       DEG OF F         SJM OF SQ       VAR EST        F VALUE
LIN EFFECT          1             .860033E-01     .860033E-01
QUAD EFFECT         1             .420982E-01     .420982E-01
CUB EFFECT          1             .111314E+00     .111314E+00    .458848E+00
OVERALL EFF         3             .239416E+00
DEVIATION           9             .218335E+01     .242595E+00
TOTAL              12             .242277E+01

        Y=   -.140759E+02   .102642E+03  X   -.250049E+03  XX     .253967E+03  XXX   -.919746E+02  XXXX
REGRESSION COEFFICIENT  =    .377727
VARIATION       DEG OF F         SUM OF SQ       VAR EST        F VALUE
LIN EFFECT          1             .860033E-01     .860033E-01
QUAD EFFECT         1             .420982E-01     .420982E-01
CUB EFFECT          1             .111314E+00     111314E+00
QUART EFF           1             .106259E+00     .106259E+00    .409261E+00
OVERALL EFF         4             .345675E+00
DEVIATION           8             .207709E+01     .259637E+00
TOTAL              12             .242277E+01
```

Teeside, July, 1975.

X : Total hydrocarbons

Y : Pb

Linear regression	: F-value : 0.56, $P > 0.10$	insignificant correlation.
Square regression	: F-value : 0.02, $P > 0.10$	insignificant correlation.
Cubic regression	: F-value : 0.05, $P > 0.10$	insignificant correlation.
Quartic regression	: F-value : 0.36, $P > 0.10$	insignificant correlation.

```
        X               Y
    1.40000          .57000
    1.36000         1.04000
    1.46000          .36000



    1.40000          .43000
    1.54000          .92000
    1.42000          .74000
    2.05000          .47000
    2.48000          .47000
    1.58000          .45000
    1.55000          .25000
    1.48000         1.99000
    1.39000          .73000
    1.37000          .57000

        Y=    .116878E+01   -.302938E+00  X
REGRESSION COEFFICIENT  =   .219894
VARIATION         DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT            1              .117149E+00     .117149E+00      .558910E+00
OVERALL EFF           1              .117149E+00
DEVIATION            11              .230562E+01     .209602E+00
TOTAL                12              .242277E+01

        Y=    .194535E+01   -.117245E+01  X     .229939E+00  XX
REGRESSION COEFFICIENT  =   .224561
VARIATION         DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT            1              .117149E+00     .117149E+00
QUAD EFFECT           1              .502634E-02     .502634E-02      .218480E-01
OVERALL EFF           2              .122175E+00
DEVIATION            10              .230059E+01     .230059E+00
TOTAL                12              .242277E+01

        Y=   -.540554E+01    .110849E+02  X   -.642124E+01  XX     .117252E+01  XXX
REGRESSION COEFFICIENT  =   .235948
VARIATION         DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT            1              .117149E+00     .117149E+00
QUAD EFFECT           1              .502634E-02     .502634E-02
CUB EFFECT            1              .127037E-01     .127037E-01      .499734E-01
OVERALL EFF           3              .134879E+00
DEVIATION             9              .228789E+01     .254210E+00
TOTAL                12              .242277E+01

        Y=   -.439329E+03    .994263E+03  X   -.827932E+03  XX     .300858E+03  XXX   -.402575E+02  XXXX
REGRESSION COEFFICIENT  =   .310513
VARIATION         DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT            1              .117149E+00     .117149E+00
QUAD EFFECT           1              .502634E-02     .502634E-02
CUB EFFECT            1              .127037E-01     .127037E-01
QUART EFF             1              .987207E-01     .987207E-01      .360760E+00
OVERALL EFF           4              .233599E+00
DEVIATION             8              .218917E+01     .273646E+00
TOTAL                12              .242277E+01
```

Teeside, July, 1975.

X : CH_4

Y : Pb

Linear regression :: F-value : 0.20, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.14, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.82, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 1.71, $P > 0.10$
insignificant correlation.

```
        X              Y
    1.16000         .57000
    1.14000        1.04000
    1.25000         .36000
    1.21000         .43000
    1.44000         .92000
    1.30000         .74000
    1.33000         .47000
    1.38000         .47000
    1.43000         .45000
    1.44000         .25000
    1.31000        1.99000
    1.25000         .73000
    1.29000         .57000


     Y=     .146061E+01   -.590542E+00  X
REGRESSION COEFFICIENT  =    .132426
VARIATION          DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT             1              .424872E-01     .424872E-01      .196346E+00
OVERALL EFF            1              .424872E-01
DEVIATION             11              .230028E+01     .216389E+00
TOTAL                 12              .242277E+01

     Y=   -.796536E+01     .139861E+02  X   -.560420E+01  XX
REGRESSION COEFFICIENT  =    .177228
VARIATION          DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT             1              .424872E-01     .424872E-01
QUAD EFFECT            1              .336112E-01     .336112E-01      .143229E+00
OVERALL EFF            2              .760984E-01
DEVIATION             10              .234667E+01     .234667E+00
TOTAL                 12              .242277E+01


     Y=     .448289E+03   -.105260E+04  X     .822465E+03  XX    -.213513E+03  XXX
REGRESSION COEFFICIENT  =    .375842
VARIATION          DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT             1              .424872E-01     .424872E-01
QUAD EFFECT            1              .336112E-01     .336112E-01
CUB EFFECT             1              .197165E+00     .197165E+00      .825531E+00
OVERALL EFF            3              .273263E+00
DEVIATION              9              .214951E+01     .238834E+00
TOTAL                 12              .242277E+01

     Y=     .119920E+05   -.370827E+05  X     .423984E+05  XX    -.220027E+05  XXX      .422187E+04  XXXX
REGRESSION COEFFICIENT  =    .518528
VARIATION          DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT             1              .424872E-01     .424872E-01
QUAD EFFECT            1              .336112E-01     .336112E-01
CUB EFFECT             1              .197165E+00     .197165E+00
QUART EFF              1              .378498E+00     .378498E+00      .170975E+01
OVERALL EFF            4              .651761E+00
DEVIATION              8              .177101E+01     .221376E+00
TOTAL                 12              .242277E+01
```

Teeside, July, 1975.

X : THC - CH_4

Y : Pb

Linear regression : F-value : 0.44, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.006, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.21, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.34, $P > 0.10$
insignificant correlation.

```
       X              Y
     .24000         .57000
     .22000        1.04000
     .21000         .36000
     .19000         .43000
     .10000         .92000
     .12000         .74000
     .72000         .47000
    1.10000         .47000
     .15000         .45000
     .11000         .25000
     .17000        1.99000
     .14000         .73000
     .08000         .57000


    Y=     .772698E+00   -.297204E+00  X
REGRESSION COEFFICIENT =   .196500
VARIATION        DEG OF F         SUM OF SQ       VAR EST        F VALUE
LIN EFFECT           1             .935483E-01    .935483E-01    .441792E+00
OVERALL EFF          1             .935483E-01
DEVIATION           11             .232922E+01    .211747E+00
TOTAL               12             .242277E+01

    Y=     .746838E+00   -.107574E+00  X   -.166458E+00  XX
REGRESSION COEFFICIENT =   .198036
VARIATION        DEG OF F         SUM OF SQ       VAR EST        F VALUE
LIN EFFECT           1             .935483E-01    .935483E-01
QUAD EFFECT          1             .146810E-02    .146810E-02    .630693E-02
OVERALL EFF          2             .950164E-01
DEVIATION           10             .232775E+01    .232775E+00
TOTAL               12             .242277E+01

    Y=     .475279E+00    .258147E+01  X   -.606187E+01  XX    .337622E+01  XXX
REGRESSION COEFFICIENT =   .247399
VARIATION        DEG OF F         SUM OF SQ       VAR EST        F VALUE
LIN EFFECT           1             .935483E-01    .935483E-01
QUAD EFFECT          1             .146810E-02    .146810E-02
CUB EFFECT           1             .532728E-01    .532728E-01    .210798E+00
OVERALL EFF          3             .148289E+00
DEVIATION            9             .227448E+01    .252720E+00
TOTAL               12             .242277E+01

    Y=    -.897757E+00    .254588E+02  X   -.116747E+03  XX    .174640E+03  XXX   -.804713E+02  XXXX
REGRESSION COEFFICIENT =   .315354
VARIATION        DEG OF F         SUM OF SQ       VAR EST        F VALUE
LIN EFFECT           1             .935483E-01    .935483E-01
QUAD EFFECT          1             .146810E-02    .146810E-02
CUB EFFECT           1             .532728E-01    .532728E-01
QUART EFF            1             .934148E-01    .934148E-01    .342639E+00
OVERALL EFF          4             .241704E+00
DEVIATION            8             .218107E+01    .272633E+00
TOTAL               12             .242277E+01
```

Teeside, July, 1975.

X : CO

Y : THC

Linear regression : F-value : 26.54, $P > 0.10$

insignificant correlation.

Square regression : F-value : 0.0005, $P > 0.10$

insignificant correlation.

Cubic regression : F-value : 10.98, $0.050 > P > 0.025$

significant correlation, doubtful application.

Y cannot ever take a negative value, cf. eq'n.

Quartic regression : F-value : 25.39, $P < 0.01$

Highly significant, but doubtful because of scant data points, worth comparing with other sites, pooling together.

$Y : -100.98\,x^4 + 245.22\,x^3 - 208.31\,x^2 + 74.23x - 7.9$

Y cannot ever take a negative value

```
      X             Y
     .55000        1.40000
     .44000        1.36000
     .43000        1.46000
     .34000        1.40000
     .38000        1.54000


     .37000        1.42000
    1.01000        2.05000
     .85000        2.48000
     .39000        1.58000
     .34000        1.55000
     .39000        1.48000
     .31000        1.39000
     .33000        1.37000


      Y=     .973951E+00    .127547E+01 X
 REGRESSION COEFFICIENT =   .840838
 VARIATION         DEG OF F         SUM OF SQ         VAR EST          F VALUE
 LIN EFFECT            1            .902514E+00       .902514E+00      .265439E+02
 OVERALL EFF           1            .902514E+00
 DEVIATION            11            .374009E+00       .340008E-01
 TOTAL                12            .127652E+01

      Y=     .986803E+00    .122736E+01 X     .370986E-01 XX
 REGRESSION COEFFICIENT =   .840847
 VARIATION         DEG OF F         SUM OF SQ         VAR EST          F VALUE
 LIN EFFECT            1            .902514E+00       .902514E+00
 QUAD EFFECT           1            .185798E-04       .185798E-04      .496798E-03
 OVERALL EFF           2            .902532E+00
 DEVIATION            10            .373991E+00       .373991E-01
 TOTAL                12            .127652E+01

      Y=     .473084E+01   -.195773E+02 X     .355815E+02 XX   -.186013E+02 XXX
 REGRESSION COEFFICIENT =   .931680
 VARIATION         DEG OF F         SUM OF SQ         VAR EST          F VALUE
 LIN EFFECT            1            .902514E+00       .902514E+00
 QUAD EFFECT           1            .185798E-04       .185798E-04
 CUB EFFECT            1            .205525E+00       .205525E+00      .109798E+02
 OVERALL EFF           3            .110806E+01
 DEVIATION             9            .168466E+00       .187184E-01
 TOTAL                12            .127652E+01

      Y=    -.799055E+01    .742309E+02 X    -.208312E+03 XX     .245224E+03 XXX    -.100988E+03 XXXX
 REGRESSION COEFFICIENT =   .984065
 VARIATION         DEG OF F         SUM OF SQ         VAR EST          F VALUE
 LIN EFFECT            1            .902514E+00       .902514E+00
 QUAD EFFECT           1            .185798E-04       .185798E-04
 CUB EFFECT            1            .205525E+00       .205525E+00
 QUART EFF             1            .128107E+00       .128107E+00      .253938E+02
 OVERALL EFF           4            .123616E+01
 DEVIATION             8            .403585E-01       .504462E-02
 TOTAL                12            .127652E+01
```

Teeside, July, 1975.

X : CH_4

Y : CO

Linear regression : F-value : 0.07, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.24, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 7.14, $0.10 > P > 0.05$
slight correlation, doubtful application.
Y cannot become negative

Quartic regression : F-value : 3.61, $P > 0.10$
insignificant correlation.

```
     X                 Y
  1.16000          .55000
  1.14000          .44000
  1.25000          .43000
  1.21000          .34000
  1.44000          .38000
  1.30000          .37000
  1.33000         1.01000
  1.38000          .95000
  1.43000          .33000
  1.44000          .34000
  1.31000          .39000
  1.25000          .31000
  1.29000          .33000


      Y=    .244346E+00    .174454E+00  X
REGRESSION COEFFICIENT  =    .081753
VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1              .370782E-02     .370782E-02      .740135E-01
OVERALL EFF          1              .370782E-02
DEVIATION           11              .551061E+00     .500965E-01
TOTAL               12              .554769E+00

      Y=   -.561810E+01    .924033E+01  X   -.348551E+01  XX
REGRESSION COEFFICIENT  =    .173549
VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1              .370782E-02     .370782E-02
QUAD EFFECT          1              .130014E-01     .130014E-01      .241634E+00
OVERALL EFF          2              .167092E-01
DEVIATION           10              .538060E+00     .538060E-01
TOTAL               12              .554769E+00



      Y=    .495695E+03   -.116268E+04  X    .906361E+03  XX   -.234599E+03  XXX
REGRESSION COEFFICIENT  =    .677629
VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1              .370782E-02     .370782E-02
QUAD EFFECT          1              .130014E-01     .130014E-01
CUB EFFECT           1              .238031E+00     .238031E+00      .714022E+01
OVERALL EFF          3              .254740E+00
DEVIATION            9              .300029E+00     .333366E-01
TOTAL               12              .554769E+00

      Y=   -.523615E+04    .167275E+05  X   -.199858E+05  XX    .105845E+05  XXX   -.209631E+04  XXXX
REGRESSION COEFFICIENT  =    .791979
VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1              .370782E-02     .370782E-02
QUAD EFFECT          1              .130014E-01     .130014E-01
CUB EFFECT           1              .238031E+00     .238031E+00
QUART EFF            1              .933071E-01     .933071E-01      .361092E+01
OVERALL EFF          4              .348047E+00
DEVIATION            8              .206722E+00     .258403E-01
TOTAL               12              .554769E+00
```

Teeside, July, 1975.

X : THC - CH_4

Y : CO

Linear regression : F-value : 44.48, $P > 0.10$

insignificant correlation.

Square regression : F-value : 17.07, $0.10 > P > 0.05$

slight correlation,

$Y : -1.14X^2 + 1.95X + 0.12$

r : 0.96

regression of doubtful application, Y cannot ever take a negative value.

Cubic regression : F-value : 11.12, $0.050 > P > 0.025$

significant correlation,

$Y : -2.19X^3 + 2.63X^2 + 0.20X + 0.29$

r : 0.98

Y cannot become negative.

Quartic regression : F-value : 3.29, $P > 0.10$

insignificant correlation.

```
        X             Y
     .24000        .55000
     .22000        .44000
     .21000        .43000
     .19000        .34000
     .10000        .38000
     .12000        .37000
     .72000       1.01000
    1.10000        .85000
     .15000        .39000
     .11000        .34000
     .17000        .39000
     .14000        .31000
     .08000        .33000


    Y=    .294570E+00    .648053E+00  X
REGRESSION COEFFICIENT  =    .895403
VARIATION        DEG OF F         SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1           .444784E+00     .444784E+00      .444844E+02
OVERALL  EFF         1           .444784E+00
DEVIATION           11           .109985E+00     .999866E-02
TOTAL               12           .554769E+00

    Y=    .117162E+00    .195151E+01  X   -.114418E+01  XX
REGRESSION COEFFICIENT  =    .962693
VARIATION        DEG OF F         SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1           .444784E+00     .444784E+00
QUAD  EFFECT         1           .693641E-01     .693641E-01      .170759E+02
OVERALL  EFF         2           .514148E+00
DEVIATION           10           .406211E-01     .406211E-02
TOTAL               12           .554769E+00

    Y=    .293476E+00    .205926E+00  X    .268280E+01  XX   -.219166E+01  XXX
REGRESSION COEFFICIENT  =    .983485
VARIATION        DEG OF F         SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1           .444784E+00     .444784E+00
QUAD  EFFECT         1           .693641E-01     .693641E-01
CUB  EFFECT          1           .224486E-01     .224486E-01      .111178E+02
OVERALL  EFF         3           .536597E+00
DEVIATION            9           .181725E-01     .201916E-02
TOTAL               12           .554769E+00

    Y=    .620485E+00   -.524266E+01  X    .290442E+02  XX   -.429807E+02  XXX    .191655E+02  XXXX
REGRESSION COEFFICIENT  =    .988329
VARIATION        DEG OF F         SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1           .444784E+00     .444784E+00
QUAD  EFFECT         1           .693641E-01     .693641E-01
CUB  EFFECT          1           .224486E-01     .224486E-01
QUART  EFF           1           .529873E-02     .529873E-02      .329275E+01
OVERALL  EFF         4           .541896E+00
DEVIATION            8           .128737E-01     .160921E-02
TOTAL               12           .554769E+00
```

Teeside , July, 1975.

X : THC

Y : CH_4

Linear regression : F-value : 2.50, $P > 0.10$
insignificant correlation

Square regression : F-value : 4.63, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 11.71, $0.050 > P > 0.025$
significant correlation,
$Y : 2.04X^3 - 12.13X^2 + 23.61X - 13.62$
$r : 0.87$
regression of doubtful application, Y cannot ever take a negative value.

Quartic regression : F-value : 1.81, $P > 0.10$
insignificant correlation.

```
        X                 Y
     1.40000           1.16000
     1.36000           1.14000
     1.46000           1.25000
     1.40000           1.21000
     1.54000           1.44000
     1.42000           1.30000
     2.05000           1.33000


     2.48000           1.38000
     1.58000           1.43000
     1.55000           1.44000
     1.48000           1.31000
     1.39000           1.25000
     1.37000           1.29000

       Y=     .109295E+01    .132891E+00  X
 REGRESSION COEFFICIENT  =    .430161
 VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
 LIN EFFECT             1             .225434E-01     .225434E-01      .249758E+01
 OVERALL EFF            1             .225434E-01
 DEVIATION             11             .992873E-01     .902612E-02
 TOTAL                 12             .121831E+00

       Y=    -.848903E+00    .230725E+01  X   -.574997E+00  XX
 REGRESSION COEFFICIENT  =    .665604
 VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
 LIN EFFECT             1             .225434E-01     .225434E-01
 QUAD EFFECT            1             .314311E-01     .314311E-01      .463201E+01
 OVERALL EFF            2             .539745E-01
 DEVIATION             10             .678562E-01     .678562E-02
 TOTAL                 12             .121831E+00

       Y=    -.136249E+02    .236176E+02  X   -.121348E+02  XX    .203784E+01  XXX
 REGRESSION COEFFICIENT  =    .870635
 VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
 LIN EFFECT             1             .225434E-01     .225434E-01
 QUAD EFFECT            1             .314311E-01     .314311E-01
 CUB EFFECT             1             .383738E-01     .383738E-01      .117142E+02
 OVERALL EFF            3             .923483E-01
 DEVIATION              9             .294825E-01     .327583E-02
 TOTAL                 12             .121831E+00

       Y=     .881902E+02   -.207080E+03  X    .180623E+03  XX   -.682797E+02  XXX    .344595E+01  XXXX
 REGRESSION COEFFICIENT  =    .895889
 VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
 LIN EFFECT             1             .225434E-01     .225434E-01
 QUAD EFFECT            1             .314311E-01     .314311E-01
 CUB EFFECT             1             .383738E-01     .383738E-01
 QUART EFF              1             .543507E-02     .543507E-02      .180812E+01
 OVERALL EFF            4             .977834E-01
 DEVIATION              8             .240474E-01     .300592E-02
 TOTAL                 12             .121831E+00
```

Teeside, July, 1975.

X : Spot CH_4
Y : – CO

Linear regression : F-value : 3.46, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.30, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 2.04, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.04, $P > 0.10$
insignificant correlation.

2 E 2238 1

```
    X              Y            Y=   -.419329E-01    .400553E+00  X
 1.27000         .70000
 1.17000         .70000
 1.12500         .63000
 1.12000         .46000     REGRESSION COEFFICIENT =    .165379
 1.15000         .43000     VARIATION        DEG OF F       SUM OF SQ       VAR EST           F VALUE
 1.18000         .75000     LIN EFFECT           1          .258310E+00     .258310E+00      .345866E+01
 1.16500         .53000     OVERALL EFF          1          .258310E+00
 1.16000         .42000     DEVIATION          123          .918626E+01     .746851E-01
 1.14000         .40000     TOTAL              124          .944457E+01
 1.15000         .54000
 1.17000         .52000
 1.17000         .70000       Y=   -.150479E+01    .264149E+01  X    -.851721E+00  XX
 1.15000         .80000     REGRESSION COEFFICIENT =    .172342
 1.12000         .41000     VARIATION        DEG OF F       SUM OF SQ       VAR EST           F VALUE
 1.10000         .42000     LIN EFFECT           1          .258310E+00     .258310E+00
 1.14000         .39000     QUAD EFFECT          1          .222113E-01     .222113E-01     .295697E+00
 1.13000         .37000     OVERALL EFF          2          .280521E+00
 1.13000         .37000     DEVIATION          122          .916405E+01     .751152E-01
 1.11000         .34000     TOTAL              124          .944457E+01
 1.10000         .39000
 1.11000         .22000
 1.19000         .24000       Y=    .342935E+02   -.790931E+02  X     .609731E+02  XX   -.154918E+02  XXX
 1.17000         .61000     REGRESSION COEFFICIENT =    .213897
 1.20000         .29000     VARIATION        DEG OF F       SUM OF SQ       VAR EST           F VALUE
 1.26000         .61000     LIN EFFECT           1          .258310E+00     .258310E+00
 1.23000         .36000     QUAD EFFECT          1          .222113E-01     .222113E-01
 1.28000         .36000     CUB EFFECT           1          .151586E+00     .151586E+00     .203518E+01
 1.21500         .34000     OVERALL EFF          3          .432108E+00
 1.24000         .38000     DEVIATION          121          .901246E+01     .744832E-01
 1.28000         .43000     TOTAL              124          .944457E+01
 1.25000         .49000
 1.29000         .56000
 1.26000         .55000       Y=    .813675E+02   -.221270E+03  X     .221105E+03  XX   -.952425E+02  XXX     .148191E+02  XX
 1.24000         .38000     REGRESSION COEFFICIENT =    .214577
 1.23000         .42000     VARIATION        DEG OF F       SUM OF SQ       VAR EST           F VALUE
 1.24000         .47000     LIN EFFECT           1          .258310E+00     .258310E+00
 1.26000         .31000     QUAD EFFECT          1          .222113E-01     .222113E-01
 1.21000         .38000     CUB EFFECT           1          .151586E+00     .151586E+00
 1.18000         .29000     QUART EFF            1          .275155E-02     .275155E-02     .366477E-01
 1.18000         .26000     OVERALL EFF          4          .434859E+00
 1.22000         .34000     DEVIATION          120          .900971E+01     .750809E-01
 1.22000         .30000     TOTAL              124          .944457E+01
 1.20000         .35000
```

Teeside, September, 1975.

X : CO

Y : Pb

Linear regression : F-value : 18.61, $P > 0.10$
insignificant correlation.

Square regression : F-value : 3.76, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 10.46, $0.050 > P > 0.025$
significant correlation,
Y : $57.9X^3 - 80.0X^2 + 35.6X - 4.35$
r : 0.96
regression of doubtful application, Y cannot ever take a negative value.

Quartic regression : F-value : 0.22, $P > 0.10$
insignificant correlation.

```
      X                   Y
   .43000             .97000
   .29000            1.05000
   .42000             .76000


   .59000             .73000
   .40000             .64000
   .22000             .19000
   .30000             .51000
   .25000             .37000
   .43000             .64000
   .80000            2.57000

        Y=   -.461782E+00    .315928E+01  X
REGRESSION COEFFICIENT  =    .836306
VARIATION         DEG OF F         SUM OF SQ       VAR EST         F VALUE
LIN EFFECT            1             .273091E+01    .273091E+01     .186141E+02
OVERALL EFF           1             .273091E+01
DEVIATION             8             .117370E+01    .146712E+00
TOTAL                 9             .390461E+01

        Y=    .943649E+00   -.335183E+01  X    .648550E+01  XX
REGRESSION COEFFICIENT  =    .896886
VARIATION         DEG OF F         SUM OF SQ       VAR EST         F VALUE
LIN EFFECT            1             .273091E+01    .273091E+01
QUAD EFFECT           1             .409971E+00    .409971E+00     .375762E+01
OVERALL EFF           2             .314088E+01
DEVIATION             7             .763728E+00    .109104E+00
TOTAL                 9             .390461E+01

        Y=   -.435357E+01    .356261E+02  X   -.800435E+02  XX    .579229E+02  XXX
REGRESSION COEFFICIENT  =    .963702
VARIATION         DEG OF F         SUM OF SQ       VAR EST         F VALUE
LIN EFFECT            1             .273091E+01    .273091E+01
QUAD EFFECT           1             .409971E+00    .409971E+00
CUB EFFECT            1             .485410E+00    .485410E+00     .104645E+02
OVERALL EFF           3             .362629E+01
DEVIATION             6             .278318E+00    .463863E-01
TOTAL                 9             .390461E+01

        Y=   -.755718E+01    .669655E+02  X   -.187445E+03  XX    .211449E+03  XXX   -.774968E+02  XXXX
REGRESSION COEFFICIENT  =    .965298
VARIATION         DEG OF F         SUM OF SQ       VAR EST         F VALUE
LIN EFFECT            1             .273091E+01    .273091E+01
QUAD EFFECT           1             .409971E+00    .409971E+00
CUB EFFECT            1             .485410E+00    .485410E+00
QUART EFF             1             .120210E-01    .120210E-01     .225707E+00
OVERALL EFF           4             .363831E+01
DEVIATION             5             .266297E+00    .532593E-01
TOTAL                 9             .390461E+01
```

Teeside, September, 1975.

X : Total hydrocarbons

Y : Pb

Linear regression : F-value : 1.75, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.10, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.04, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 3.07, $P > 0.10$
insignificant correlation.

```
       X                  Y
    1.48000            .97000
    1.38000           1.05000
    1.55000            .76000
    1.49000            .73000
    1.50000            .64000
    1.39000            .19000
    1.45000            .51000
    1.33000            .37000
    1.49000            .64000
    1.52000           2.57000


      Y=   -.498967E+01    .400046E+01 X
REGRESSION COEFFICIENT =   .423506
VARIATION        DEG OF F        SUM OF SQ      VAR EST          F VALUE
LIN EFFECT           1          .700320E+00    .700320E+00    .174846E+01
OVERALL EFF          1          .700320E+00
DEVIATION            8          .320429E+01    .400536E+00
TOTAL                9          .390461E+01

      Y=    .294417E+02  -.438861E+02 X    .166811E+02 XX
REGRESSION COEFFICIENT =   .436731
VARIATION        DEG OF F        SUM OF SQ      VAR EST          F VALUE
LIN EFFECT           1          .700320E+00    .700320E+00
QUAD EFFECT          1          .444227E-01    .444227E-01    .984089E-01
OVERALL EFF          2          .744743E+00
DEVIATION            7          .315987E+01    .451410E+00
TOTAL                9          .390461E+01

      Y=    .548000E+03  -.112645E+04 X    .767667E+03 XX  -.173436E+03 XXX
REGRESSION COEFFICIENT =   .443583
VARIATION        DEG OF F        SUM OF SQ      VAR EST          F VALUE
LIN EFFECT           1          .700320E+00    .700320E+00


QUAD EFFECT          1          .444227E-01    .444227E-01
CUB EFFECT           1          .235520E-01    .235520E-01    .459567E-01
OVERALL EFF          3          .768295E+00
DEVIATION            6          .313632E+01    .522719E+00
TOTAL                9          .390461E+01

      Y=   -.126406E+06    .352660E+06 X   -.368541E+06 XX    .170979E+06 XXX   -.297124E+05 XXXX
REGRESSION COEFFICIENT =   .705109
VARIATION        DEG OF F        SUM OF SQ      VAR EST          F VALUE
LIN EFFECT           1          .700320E+00    .700320E+00
QUAD EFFECT          1          .444227E-01    .444227E-01
CUB EFFECT           1          .235520E-01    .235520E-01
QUART EFF            1          .119396E+01    .119396E+01    .307350E+01
OVERALL EFF          4          .196226E+01
DEVIATION            5          .194235E+01    .388470E+00
TOTAL                9          .390461E+01
```

Teeside, September, 1975.

X : CH_4

Y : Pb

Linear regression : F-value : 0.37, $P > 0.10$
insignificant correlation.

Square regression : F-value : 3.17, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 1.13, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 6.32, $0.050 > P > 0.025$
significant correlation, but of doubtful application.
Y annot ever become negative

```
       X              Y
   1.60000         .97000
   1.39000        1.05000
   1.41000         .76000
   1.39000         .73000
   1.55000         .64000
   1.38000         .19000
   1.42000         .51000
   1.38000         .37000
   1.40000         .64000
   1.45000        2.57000

      Y=   -.175263E+01    .180623E+01 X
REGRESSION COEFFICIENT =    .210066
VARIATION        DEG OF F        SUM OF SQ        VAR EST          F VALUE
LIN EFFECT           1           .172302E+00    .172302E+00    .369319E+00
OVERALL EFF          1           .172302E+00
DEVIATION            8           .373231E+01    .466539E+00
TOTAL                9           .390461E+01

      Y=   -.211358E+03    .284968E+03 X   -.953153E+02 XX
REGRESSION COEFFICIENT =    .531916
VARIATION        DEG OF F        SUM OF SQ        VAR EST          F VALUE
LIN EFFECT           1           .172302E+00    .172302E+00
QUAD EFFECT          1           .114990E+01    .114990E+01    .311697E+01
OVERALL EFF          2           .132220E+01
DEVIATION            7           .258241E+01    .368915E+00
TOTAL                9           .390461E+01

      Y=   -.297732E+04    .590025E+04 X   -.388959E+04 XX    .853300E+03 XXX
REGRESSION COEFFICIENT =    .665819
VARIATION        DEG OF F        SUM OF SQ        VAR EST          F VALUE
LIN EFFECT           1           .172302E+00    .172302E+00
QUAD EFFECT          1           .114990E+01    .114990E+01
CUB EFFECT           1           .408775E+00    .408775E+00    .112836E+01
OVERALL EFF          3           .173098E+01
DEVIATION            6           .217363E+01    .362272E+00
TOTAL                9           .390461E+01

      Y=    .170268E+06   -.461294E+06 X    .468051E+06 XX   -.210794E+06 XXX    .355541E+05 XXXX
REGRESSION COEFFICIENT =    .853959
VARIATION        DEG OF F        SUM OF SQ        VAR EST          F VALUE
LIN EFFECT           1           .172302E+00    .172302E+00
QUAD EFFECT          1           .114990E+01    .114990E+01
CUB EFFECT           1           .408775E+00    .408775E+00
QUART EFF            1           .121341E+01    .121341E+01    .631837E+01
OVERALL EFF          4           .294439E+01
DEVIATION            5           .960224E+00    .192045E+00
TOTAL                9           .390461E+01
```

Teeside, September, 1975.

X : CO

Y : Total hydrocarbons

Linear regression : F-value : 7.48, $P > 0.10$
insignificant correlation.

Square regression : F-value : 6.08, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.75, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 1.76, $P > 0.10$
insignificant correlation.

```
          X                 Y
        .43000          1.48000
        .29000          1.38000
        .42000          1.55000
        .59000          1.49000
        .40000          1.50000
        .22000          1.39000
        .30000          1.45000
        .25000          1.33000
        .43000          1.49000
        .78000          1.52000


       Y=     .134047E+01     .285969E+00  X
    REGRESSION COEFFICIENT =    .695027


    VARIATION          DEG OF F         SUM OF SQ       VAR EST         F VALUE
    LIN EFFECT             1             .211388E-01    .211388E-01     .747574E+01
    OVERALL  EFF           1             .211388E-01
    DEVIATION              8             .226212E-01    .282765E-02
    TOTAL                  9             .437600E-01

       Y=     .110706E+01     .137835E+01  X   -.111086E+01  XX
    REGRESSION COEFFICIENT =    .858536
    VARIATION          DEG OF F         SUM OF SQ       VAR EST         F VALUE
    LIN EFFECT             1             .211388E-01    .211388E-01
    QUAD EFFECT            1             .105177E-01    .105177E-01     .608283E+01
    OVERALL  EFF           2             .316565E-01
    DEVIATION              7             .121035E-01    .172908E-02
    TOTAL                  9             .437600E-01

       Y=     .815957E+00     .354639E+01  X   -.598532E+01  XX    .332074E+01  XXX
    REGRESSION COEFFICIENT =    .868506
    VARIATION          DEG OF F         SUM OF SQ       VAR EST         F VALUE
    LIN EFFECT             1             .211388E-01    .211388E-01
    QUAD EFFECT            1             .105177E-01    .105177E-01
    CUB EFFECT             1             .135184E-02    .135184E-02     .754397E+00
    OVERALL  EFF           3             .330083E-01
    DEVIATION              6             .107517E-01    .179195E-02
    TOTAL                  9             .437600E-01

       Y=     .238467E+01    -.118866E+02  X     .473081E+02  XX   -.736211E+02  XXX     .393410E+02  XXXX
    REGRESSION COEFFICIENT =    .904535
    VARIATION          DEG OF F         SUM OF SQ       VAR EST         F VALUE
    LIN EFFECT             1             .211388E-01    .211388E-01
    QUAD EFFECT            1             .105177E-01    .105177E-01
    CUB EFFECT             1             .135184E-02    .135184E-02
    QUART EFF              1             .279540E-02    .279540E-02     .175672E+01
    OVERALL  EFF           4             .358037E-01
    DEVIATION              5             .795629E-02    .159126E-02
    TOTAL                  9             .437600E-01
```

Teeside, September, 1975.

X : CH_4

Y : CO

Linear regression : F-value : 0.38, $P > 0.10$
insignificant correlation.

Square regression : F-value : 3.00, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.82, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 1.04, $P > 0.10$
insignificant correlation.

```
         X                     Y
     1.60000              .43000
     1.39000              .29000
     1.41000              .42000
     1.39000              .59000
     1.55000              .40000
     1.38000              .22000
     1.42000              .30000
     1.38000              .24000
     1.40000              .43000
     1.45000              .80000


        Y=   -.288949E+00     .467786E+00  X
REGRESSION COEFFICIENT =    .213000
VARIATION          DEG OF F         SUM OF SQ         VAR EST           F  VALUE
LIN EFFECT               1           .125654E-01       .125654E-01       .380201E+00
OVERALL EFF              1           .125654E-01
DEVIATION                8           .264395E+00       .330493E-01
TOTAL                    9           .276960E+00


        Y=   -.553471E+02     .748725E+02  X    -.250369E+02  XX
REGRESSION COEFFICIENT =    .576055
VARIATION          DEG OF F         SUM OF SQ         VAR EST           F  VALUE
LIN EFFECT               1           .125654E-01       .125654E-01
QUAD EFFECT              1           .793409E-01       .793409E-01       .300122E+01
OVERALL EFF              2           .919063E-01
DEVIATION                7           .165054E+00       .264362E-01
TOTAL                    9           .276960E+00


        Y=   -.702493E+03     .138867E+04  X    -.912776E+03  XX     .199645E+03  XXX
REGRESSION COEFFICIENT =    .642365
VARIATION          DEG OF F         SUM OF SQ         VAR EST           F  VALUE
LIN EFFECT               1           .125654E-01       .125654E-01
QUAD EFFECT              1           .793409E-01       .793409E-01
CUB EFFECT               1           .223768E-01       .223768E-01       .825320E+00
OVERALL EFF              3           .114283E+00
DEVIATION                6           .162677E+00       .271128E-01
TOTAL                    9           .276960E+00


        Y=    .256936E+05   -.697862E+05  X     .709851E+05  XX    -.320439E+05  XXX     .541650E+04  XXXX
REGRESSION COEFFICIENT =    .711460
VARIATION          DEG OF F         SUM OF SQ         VAR EST           F  VALUE
LIN EFFECT               1           .125654E-01       .125654E-01


QUAD EFFECT              1           .793409E-01       .793409E-01
CUB EFFECT               1           .223768E-01       .223768E-01
QUART EFF                1           .281422E-01       .281422E-01       .104591E+01
OVERALL EFF              4           .142425E+00
DEVIATION                5           .134535E+00       .269069E-01
TOTAL                    9           .276960E+00
```

Teeside, September, 1975.

X : Total hydrocarbons

Y : CH_4

Linear regression	: F-value : 1.67, $P > 0.10$ insignificant correlation.
Square regression	: F-value : 0.68, $P > 0.10$ insignificant correlation.
Cubic regression	: F-value : 0.76, $P > 0.10$ insignificant correlation.
Oartic regression	: F-value : 0.007, $P > 0.10$ insignificant correlation.

```
      X              Y
   1.48000        1.60000
   1.38000        1.39000
   1.55000        1.41000
   1.49000        1.39000
   1.50000        1.55000
   1.39000        1.38000
   1.45000        1.42000
   1.33000        1.37000
   1.49000        1.40000
   1.52000        1.45000


    Y=     .762308E+00    .462066E+00  X
REGRESSION COEFFICIENT =    .415800
VARIATION       DEG OF F        SUM OF SQ      VAR EST         F VALUE
LIN EFFECT          1            .934297E-02   .934297E-02     .167223E+01
OVERALL EFF         1            .934297E-02
DEVIATION           8            .446970E-01   .558713E-02
TOTAL               9            .540400E-01

    Y=   -.953534E+01    .148138E+02  X   -.498892E+01  XX
REGRESSION COEFFICIENT =    .496406
VARIATION       DEG OF F        SUM OF SQ      VAR EST         F VALUE
LIN EFFECT          1            .934297E-02   .934297E-02
QUAD EFFECT         1            .397349E-02   .397349E-02     .683006E+00
OVERALL EFF         2            .133165E-01
DEVIATION           7            .407235E-01   .581765E-02
TOTAL               9            .540400E-01

    Y=     .219990E+03  -.463570E+03  X    .326902E+03  XX    -.766482E+02  XXX
REGRESSION COEFFICIENT =    .575796
VARIATION       DEG OF F        SUM OF SQ      VAR EST         F VALUE
LIN EFFECT          1            .934297E-02   .934297E-02
QUAD EFFECT         1            .397349E-02   .397349E-02
CUB EFFECT          1            .459997E-02   .459997E-02     .764040E+00
OVERALL EFF         3            .179164E-01
DEVIATION           6            .361236E-01   .602059E-02
TOTAL               9            .540400E-01

    Y=   -.610855E+03    .185175E+04  X   -.209000E+04  XX    .104344E+04  XXX   -.194450E+03  XXXX
REGRESSION COEFFICIENT =    .576603
VARIATION       DEG OF F        SUM OF SQ      VAR EST         F VALUE
LIN EFFECT          1            .934297E-02   .934297E-02
QUAD EFFECT         1            .397349E-02   .397349E-02
CUB EFFECT          1            .459997E-02   .459997E-02
QUART EFF           1            .510692E-04   .510692E-04     .707869E-02
OVERALL EFF         4            .179675E-01
DEVIATION           5            .360725E-01   .721450E-02
TOTAL               9            .540400E-01
```

Teeside, September, 1975.

X : Spot CH_4

Y : – CO

Linear regression : F-value : 1.87, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.04, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 2.34, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 1.20, $P > 0.10$
insignificant correlation.

X	Y
1.64000	.33000
1.60000	.32000
1.65000	.39000
1.62000	.44000
1.62000	.53000
1.58000	.50000
1.67000	.57000
1.61000	.58000
1.48000	.43000
1.49000	.18000
1.39000	.12000
1.40000	.12000
1.40000	.37000
1.38000	.46000
1.40000	.39000
1.40000	.28000
1.36000	.16000
1.38000	.31000

1.38000	.24000
1.46000	.42000
1.35000	.22000
1.37000	.20000
1.35000	.29000
1.38000	.61000
1.36000	.29000
1.37000	.30000
1.41000	.56000
1.49000	.58000
1.51000	.70000
1.51000	.59000
1.45000	.53000
1.45000	.28000
1.36000	.23000
1.39000	.33000
1.42000	.39000
1.42000	.51000
1.40000	.59000
1.42000	.26000
1.43000	.39000
1.37000	.32000
1.40000	.29000
1.40000	.42000
1.41000	.42000
1.40000	.34000
1.40000	.32000
1.27000	1.47000
1.40000	.32000
1.40000	.36000
1.40000	.32000
1.42000	1.15000
1.38000	2.10000
1.37000	.32000
1.56000	.35000
1.53000	.35000
1.54000	.35000
1.57000	.41000
1.58000	.42000
1.53000	.38000
1.56000	.42000
1.57000	.41000
1.56000	.44000
1.55000	.44000
1.53000	.41000
1.50000	.39000
1.56000	.44000
1.51000	.39000
1.39000	.20000
1.49000	.41000
1.38000	.17000
1.40000	.19000
1.42000	.20000
1.37000	.19000
1.39000	.22000
1.37000	.20000
1.35000	.18000
1.37000	.21000
1.35000	.19000
1.36000	.26000

1.35000	.23000
1.32000	.21000
1.43000	.40000
1.40000	.33000
1.38000	.20000
1.42000	.26000
1.41000	.32000
1.46000	.36000
1.41000	.27000
1.44000	.31000
1.60000	.38000
1.35000	.24000
1.44000	.29000
1.40000	.27000
1.39000	.22000
1.41000	.23000
1.41000	.15000
1.40000	.20000
1.22000	.24000
1.37000	.22000
1.37000	.26000
1.38000	.27000
1.38000	.31000
1.40000	.27000
1.38000	.27000

1.41000	.29000
1.42000	.59000
1.42000	.29000
1.38000	.27000
1.38000	.39000
1.39000	.21000
1.40000	.32000
1.33000	.32000
1.42000	.41000
1.40000	.29000
1.38000	.25000
1.38000	.26000
1.40000	.50000
1.40000	.56000
1.42000	.32000
1.41000	.51000
1.39000	1.58000
1.36000	.24000
1.44000	.36000
1.50000	.29000
1.50000	1.05000
1.44000	.99000
1.40000	.29000
1.44000	1.17000
1.41000	.72000
1.48000	1.95000
1.43000	.35000

```
        Y=   -.249967E+00    .458507E+00  X
    REGRESSION COEFFICIENT =   .119902
    VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
    LIN EFFECT            1            .173077E+00    .173077E+00     .186703E+01
    OVERALL EFF           1            .173077E+00
    DEVIATION           128            .118658E+02    .927018E-01
    TOTAL               129            .120389E+02

        Y=   -.165464E+01    .237517E+01  X   -.651441E+00  XX
    REGRESSION COEFFICIENT =   .121267
    VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
    LIN EFFECT            1            .173077E+00    .173077E+00
    QUAD EFFECT           1            .396161E-02    .396161E-02     .424152E-01
    OVERALL EFF           2            .177039E+00
    DEVIATION           127            .118619E+02    .934006E-01
    TOTAL               129            .120389E+02

        Y=    .100659E+03   -.210815E+03  X    .146958E+03  XX   -.339556E+02  XXX
    REGRESSION COEFFICIENT =   .180802
    VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
    LIN EFFECT            1            .173077E+00    .173077E+00
    QUAD EFFECT           1            .396161E-02    .396161E-02
    CUB EFFECT            1            .216506E+00    .216506E+00     .234254E+01
    OVERALL EFF           3            .393545E+00
    DEVIATION           126            .116454E+02    .924235E-01
    TOTAL               129            .120389E+02

        Y=    .102687E+04   -.279666E+04  X    .284507E+04  XX   -.128104E+04  XXX    .215452E+03  XXXX
    REGRESSION COEFFICIENT =   .204786
    VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
    LIN EFFECT            1            .173077E+00    .173077E+00
    QUAD EFFECT           1            .396161E-02    .396161E-02
    CUB EFFECT            1            .216506E+00    .216506E+00
    QUART EFF             1            .111279E+00    .111279E+00     .120598E+01
    OVERALL EFF           4            .504824E+00
    DEVIATION           125            .115341E+02    .922727E-01
    TOTAL               129            .120389E+02
```

Olympia Car Park, October 22nd, 1975.

X : CO

Y : Pb

Linear regression : F-value : 33.18, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.39, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.06, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 1.49, $P > 0.10$
insignificant correlation.

```
         X              Y
     7.65000        5.13000
     7.55000        4.59000
     7.12000        5.33000


     8.77000        4.97000
     6.35000        5.24000
     9.67000        4.92000
    10.46000        6.50000
    12.28000        8.41000
     8.79000        4.49000
    11.69000        4.45000
    26.78000       11.27000
    15.36000        6.62000

      Y=     .248636E+01    .317685E+00  X
  REGRESSION COEFFICIENT =    .876594
  VARIATION      DEG OF F          SUM OF SQ       VAR EST          F VALUE
  LIN EFFECT         1              .344990E+02    .344990E+02    .331810E+02
  OVERALL EFF        1              .344990E+02
  DEVIATION         10              .103972E+02    .103972E+01
  TOTAL             11              .448963E+02

      Y=     .373029E+01    .125561E+00  X     .583273E-02  XX
  REGRESSION COEFFICIENT =    .882084
  VARIATION      DEG OF F          SUM OF SQ       VAR EST          F VALUE
  LIN EFFECT         1              .344990E+02    .344990E+02
  QUAD EFFECT        1              .433467E+00    .433467E+00    .391539E+00
  OVERALL EFF        2              .349325E+02
  DEVIATION          9              .996377E+01    .110709E+01
  TOTAL             11              .448963E+02

      Y=     .576156E+01   -.377533E+00  X     .429218E-01  XX    -.790537E-03  XXX
  REGRESSION COEFFICIENT =    .883065
  VARIATION      DEG OF F          SUM OF SQ       VAR EST          F VALUE
  LIN EFFECT         1              .344990E+02    .344990E+02
  QUAD EFFECT        1              .433467E+00    .433467E+00
  CUB EFFECT         1              .777513E-01    .777513E-01    .629182E-01
  OVERALL EFF        3              .350103E+02
  DEVIATION          8              .988602E+01    .123575E+01
  TOTAL             11              .448963E+02

      Y=     .472464E+02   -.147546E+02  X     .178702E+01  XX    -.877817E-01  XXX    .148441E-02  XXXX
  REGRESSION COEFFICIENT =    .904670
  VARIATION      DEG OF F          SUM OF SQ       VAR EST          F VALUE
  LIN EFFECT         1              .344990E+02    .344990E+02
  QUAD EFFECT        1              .433467E+00    .433467E+00
  CUB EFFECT         1              .777513E-01    .777513E-01
  QUART EFF          1              .173408E+01    .173408E+01    .148904E+01
  OVERALL EFF        4              .367443E+02
  DEVIATION          7              .815194E+01    .116456E+01
  TOTAL             11              .448963E+02
```

Olympia Car Park, October 22nd, 1975.

X : Total hydrocarbons

Y : Pb

Linear regression : F-value : 36.75, $P > 0.10$
insignificant correlation.

Square regression : F-value : 2.08, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 1.01, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 1.00, $P > 0.10$
insignificant correlation.

```
        X                  Y
    4.43000            5.13000
    4.02000            4.59000
    4.23000            5.33000
    4.30000            4.97000
    4.06000            5.24000
    5.00000            4.92000
    4.63000            6.50000
    6.07000            8.41000
    4.84000            4.49000
    5.24000            4.45000
    8.55000           11.27000
    6.24000            6.62000

     Y=   -.109013E+01    .137967E+01 X
REGRESSION COEFFICIENT =   .886616
VARIATION         DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT            1             .352924E+02    .352924E+02     .367483E+02
OVERALL EFF           1             .352924E+02
DEVIATION            10             .960382E+01    .960382E+00
TOTAL                11             .448963E+02

     Y=    .658960E+01   -.130122E+01 X    .219042E+00 XX
REGRESSION COEFFICIENT =   .908981
VARIATION         DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT            1             .352924E+02    .352924E+02
QUAD EFFECT           1             .180297E+01    .180297E+01     .208012E+01
OVERALL EFF           2             .370954E+02
DEVIATION             9             .780085E+01    .866761E+00
TOTAL                11             .448963E+02



     Y=    .443710E+02   -.212362E+02 X    .359666E+01 XX   -.183106E+00 XXX
REGRESSION COEFFICIENT =   .919661
VARIATION         DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT            1             .352924E+02    .352924E+02
QUAD EFFECT           1             .180297E+01    .180297E+01
CUB EFFECT            1             .876794E+00    .876794E+00     .101304E+01
OVERALL EFF           3             .379722E+02
DEVIATION             8             .692406E+01    .865507E+00
TOTAL                11             .448963E+02

     Y=   -.368689E+03    .279670E+03 X   -.767968E+02 XX    .913111E+01 XXX   -.393784E+00 XXXX
REGRESSION COEFFICIENT =   .930084
VARIATION         DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT            1             .352924E+02    .352924E+02
QUAD EFFECT           1             .180297E+01    .180297E+01
CUB EFFECT            1             .876794E+00    .876794E+00
QUART EFF             1             .865553E+00    .865553E+00     .100006E+01
OVERALL EFF           4             .388378E+02
DEVIATION             7             .605850E+01    .865501E+00
TOTAL                11             .448963E+02
```

Olympia Car Park, October 22nd, 1975.

X : CH_4

Y : Pb

Linear regression : F-value : 6.86, $P > 0.10$
insignificant correlation.

Square regression : F-value : 6.48, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 1.06, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.54, $P > 0.10$
insignificant correlation.

```
          X                Y
       2.23000          5.13000
       2.24000          4.59000
       2.19000          5.33000
       2.26000          4.97000
       2.22000          5.24000
       2.34000          4.92000
       2.26000          6.50000
       2.61000          8.41000
       2.60000          4.49000
       2.64000          4.45000
       2.92000         11.27000
       2.78000          6.62000

      Y=   -.638234E+01    .507026E+01 X
 REGRESSION COEFFICIENT =    .637740
 VARIATION           DEG OF F           SUM OF SQ        VAR EST           F VALUE
 LIN EFFECT              1                .182599E+02     .182599E+02      .685524E+01
 OVERALL  EFF            1                .182599E+02
 DEVIATION              10                .266364E+02     .266364E+01
 TOTAL                  11                .448963E+02

      Y=    .133504E+03  -.107213E+03 X    .223005E+02 XX
 REGRESSION COEFFICIENT =    .803331
 VARIATION           DEG OF F           SUM OF SQ        VAR EST           F VALUE
 LIN EFFECT              1                .182599E+02     .182599E+02
 QUAD EFFECT             1                .111480E+02     .111480E+02      .647784E+01
 OVERALL  EFF            2                .294078E+02
 DEVIATION               9                .154884E+02     .172094E+01
 TOTAL                  11                .448963E+02

      Y=   -.754757E+03    .940631E+03 X  -.387449E+03 XX    .531261E+02 XXX
 REGRESSION COEFFICIENT =    .833812
 VARIATION           DEG OF F           SUM OF SQ        VAR EST           F VALUE
 LIN EFFECT              1                .182599E+02     .182599E+02
 QUAD EFFECT             1                .111480E+02     .111480E+02
 CUB EFFECT              1                .180598E+01     .180598E+01      .105594E+01
 OVERALL  EFF            3                .312138E+02
 DEVIATION               8                .136824E+02     .171031E+01
 TOTAL                  11                .448963E+02

      Y=    .715187E+04  -.116554E+05 X    .711111E+04 XX  -.192374E+04 XXX    .194728E+03 XXXX
 REGRESSION COEFFICIENT =    .846708
 VARIATION           DEG OF F           SUM OF SQ        VAR EST           F VALUE
 LIN EFFECT              1                .182599E+02     .182599E+02
 QUAD EFFECT             1                .111480E+02     .111480E+02
 CUB EFFECT              1                .180598E+01     .180598E+01
 QUART EFF               1                .972571E+00     .972571E+00      .535646E+00
 OVERALL  EFF            4                .321864E+02
 DEVIATION               7                .127099E+02     .181570E+01
 TOTAL                  11                .448963E+02
```

Olympia Car Park, October 22nd, 1975.

X : Total petrol vehicles in area
Y : Pb

Linear regression : F-value : 2.90, $P > 0.10$
insignificant correlation.

Square regression : F-value : 6.29, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.44, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.28, $P > 0.10$
insignificant correlation.

```
        X                    Y
   245.00000            5.13000
   197.00000            5.33000
   222.00000            4.97000
   162.00000            6.50000
   213.00000            8.41000
   207.00000            4.49000
   213.00000            4.45000
   286.00000           11.27000
   240.00000            6.62000


      Y=    -.138320E+01    .350724E-01  X
REGRESSION COEFFICIENT  =    .541376
VARIATION          DEG  OF  F          SUM  OF  SQ        VAR  EST           F  VALUE
LIN  EFFECT             1               .117377E+02     .117377E+02       .290223E+01
OVERALL  EFF            1               .117377E+02
DEVIATION               7               .283105E+02     .404436E+01
TOTAL                   8               .400482E+02


      Y=     .407140E+02  -.347260E+00  X     .849580E-03  XX


REGRESSION COEFFICIENT  =    .803236
VARIATION          DEG  OF  F          SUM  OF  SQ        VAR  EST           F  VALUE
LIN  EFFECT             1               .117377E+02     .117377E+02
QUAD  EFFECT            1               .144884E+02     .144884E+02       .628926E+01
OVERALL  EFF            2               .262261E+02
DEVIATION               6               .138221E+02     .230368E+01
TOTAL                   8               .400482E+02

      Y=    -.436069E+02    .837701E+00  X    -.457936E-02  XX     .811345E-05  XXX
REGRESSION COEFFICIENT  =    .826345
VARIATION          DEG  OF  F          SUM  OF  SQ        VAR  EST           F  VALUE
LIN  EFFECT             1               .117377E+02     .117377E+02
QUAD  EFFECT            1               .144884E+02     .144884E+02
CUB  EFFECT             1               .112065E+01     .112065E+01       .441153E+00
OVERALL  EFF            3               .273467E+02
DEVIATION               5               .127014E+02     .254028E+01
TOTAL                   8               .400482E+02

      Y=     .102743E+04  -.191530E+02  X     .133290E+00  XX    -.408581E-03  XXX     .465910E-06  XXXX
REGRESSION COEFFICIENT  =    .839024
VARIATION          DEG  OF  F          SUM  OF  SQ        VAR  EST           F  VALUE
LIN  EFFECT             1               .117377E+02     .117377E+02
QUAD  EFFECT            1               .144884E+02     .144884E+02
CUB  EFFECT             1               .112065E+01     .112065E+01
QUART  EFF              1               .845587E+00     .845587E+00       .285290E+00
OVERALL  EFF            4               .281923E+02
DEVIATION               4               .118558E+02     .296396E+01
TOTAL                   8               .400482E+02
```

Olympia Car Park, October 22nd, 1975.

X : Petrol vehicles from car park exit

Y : Pb

Linear regression : F-value : 25.36, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.005, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 2.81, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.50, $P > 0.10$
insignificant correlation.

```
        X             Y
     20.00000       5.13000
      5.00000       5.33000
     13.00000       4.97000
     28.00000       6.50000
     35.00000       8.41000
     20.00000       4.49000
     30.00000       4.45000
    105.00000      11.27000
     35.00000       6.62000

    Y=     .414650E+01    .682182E-01  X
REGRESSION COEFFICIENT =   .885253
VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1            .313847E+02    .313847E+02     .253585E+02
OVERALL EFF          1            .313847E+02
DEVIATION            7            .866348E+01    .123764E+01
TOTAL                8            .400482E+02

    Y=     .422213E+01    .637643E-01  X    .381003E-04  XX
REGRESSION COEFFICIENT =   .885359
VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1            .313847E+02    .313847E+02
QUAD EFFECT          1            .751214E-02    .751214E-02     .520714E-02
OVERALL EFF          2            .313922E+02
DEVIATION            6            .865597E+01    .144266E+01
TOTAL                8            .400482E+02

    Y=     .671638E+01  -.298924E+00  X    .117187E-01  XX   -.805572E-04  XXX
REGRESSION COEFFICIENT =   .928257
VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1            .313847E+02    .313847E+02
QUAD EFFECT          1            .751214E-02    .751214E-02
CUB EFFECT           1            .311575E+01    .311575E+01     .281193E+01
OVERALL EFF          3            .345079E+02
DEVIATION            5            .554022E+01    .110804E+01
TOTAL                8            .400482E+02

    Y=     .457032E+01    .249574E+00  X   -.250045E-01  XX    .753277E-03  XXX   -.506662E-05  XXXX
REGRESSION COEFFICIENT =   .935525
VARIATION        DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1            .313847E+02    .313847E+02
QUAD EFFECT          1            .751214E-02    .751214E-02
CUB EFFECT           1            .311575E+01    .311575E+01
QUART EFF            1            .617442E+00    .617442E+00     .501702E+00
OVERALL EFF          4            .351254E+02
DEVIATION            4            .492278E+01    .123069E+01
TOTAL                8            .400482E+02
```

Olympia Car Park, October 22nd, 1975.

X : Total hydrocarbons

Y : CO

Linear regression : F-value : 196.68, $0.10 > P > 0.05$

slight correlation,

$Y : 4.19X - 10.47$, Y cannot ever become negative.

$r : 0.98$

Square regression : F-value : 6.28, $P > 0.10$

insignificant correlation.

Cubic regression : F-value : 0.41, $P > 0.10$

insignificant correlation.

Quartic regression : F-value : 0.16, $P > 0.10$

insignificant correlation.

```
       X              Y
    4.43000        7.65000
    4.02000        7.55000
    4.23000        7.12000
    4.30000        8.77000
    4.06000        6.35000
    5.00000        9.67000
    4.63000       10.46000
    6.07000       12.28000
    4.84000        8.79000
    5.24000       11.69000
    8.55000       25.78000
    6.24000       15.36000


    Y=   -.104660E+02    .418864E+01  X
REGRESSION COEFFICIENT =   .975507
VARIATION      DEG OF F        SUM OF SQ      VAR EST          F VALUE
LIN EFFECT        1            .325294E+03   .325294E+03    .196675E+03
OVERALL EFF       1            .325294E+03
DEVIATION        10            .165397E+02   .165397E+01
TOTAL            11            .341833E+03


    Y=    .444400E+01  -.101624E+01  X    .423323E+00  XX
REGRESSION COEFFICIENT =   .985645
VARIATION      DEG OF F        SUM OF SQ      VAR EST          F VALUE
LIN EFFECT        1            .325294E+03   .325294E+03
QUAD EFFECT       1            .679596E+01   .679596E+01    .627724E+01
OVERALL EFF       2            .332090E+03
DEVIATION         9            .974372E+01   .108264E+01
TOTAL            11            .341833E+03


    Y=   -.234049E+02    .136779E+02  X   -.206708E+01  XX    .134969E+00  XXX
REGRESSION COEFFICIENT =   .986352
VARIATION      DEG OF F        SUM OF SQ      VAR EST          F VALUE
LIN EFFECT        1            .325294E+03   .325294E+03
QUAD EFFECT       1            .679596E+01   .679596E+01
CUB EFFECT        1            .476386E+00   .476386E+00    .411239E+00
OVERALL EFF       3            .332566E+03
DEVIATION         8            .926733E+01   .115842E+01
TOTAL            11            .341833E+03


    Y=   -.224402E+03    .160159E+03  X   -.412024E+02  XX    .466910E+01  XXX   -.191693E+00  XXXX
REGRESSION COEFFICIENT =   .986656
VARIATION      DEG OF F        SUM OF SQ      VAR EST          F VALUE
LIN EFFECT        1            .325294E+03   .325294E+03
QUAD EFFECT       1            .679596E+01   .679596E+01
CUB EFFECT        1            .476386E+00   .476386E+00
QUART EFF         1            .205111E+00   .205111E+00    .158436E+00
OVERALL EFF       4            .332771E+03


DEVIATION         7            .906222E+01   .129460E+01
TOTAL            11            .341833E+03
```

Olympia Car Park, October 22nd, 1975.

X : CH_4

Y : CO

Linear regression : F-value : 23.69, $P > 0.10$
insignificant correlation.

Square regression : F-value : 18.90, $0.10 > P > 0.05$
slight correlation,
$Y : 55.36X^2 - 260.33X + 313.38$
$r : 0.95$

Cubic regression : F-value : 14.69, $P \simeq 0.025$
significant correlation,
$Y : 181.92X^3 - 1347.78X^2 + 3327.88X - 2728.36$
$r : 0.98$
regression of doubtful application, Y cannot ever take a negative value.

Quartic regression : F-value : 0.002, $P > 0.10$
insignificant correlation.

```
         X               Y
      2.23000         7.65000
      2.24000         7.55000
      2.19000         7.12000
      2.26000         8.77000
      2.22000         6.35000
      2.34000         9.67000
      2.26000        10.46000
      2.61000        12.20000
      2.60000         8.79000
      2.64000        11.69000
      2.92000        25.78000
      2.78000        15.36000


    Y=   -.338569E+02    .183910E+02  X
REGRESSION COEFFICIENT =    .838569
VARIATION        DEG OF F          SUM OF SQ      VAR EST        F VALUE
LIN EFFECT           1            .240241E+03    .240241E+03    .236925E+02
OVERALL  EFF         1            .240241E+03
DEVIATION           10            .101400E+03    .101400E+02
TOTAL               11            .341641E+03


    Y=    .313378E+03   -.260326E+03  X    .553556E+02  XX
REGRESSION COEFFICIENT =    .950924
VARIATION        DEG OF F          SUM OF SQ      VAR EST        F VALUE
LIN EFFECT           1            .240241E+03    .240241E+03
QUAD EFFECT          1            .686895E+02    .686895E+02    .188996E+02
OVERALL  EFF         2            .308931E+03
DEVIATION            9            .327101E+02    .363445E+01
TOTAL               11            .341641E+03


    Y=   -.272836E+04    .332788E+04  X  -.134778E+04  XX    .181924E+03  XXX
REGRESSION COEFFICIENT =    .982977
VARIATION        DEG OF F          SUM OF SQ      VAR EST        F VALUE
LIN EFFECT           1            .240241E+03    .240241E+03
QUAD EFFECT          1            .686895E+02    .686895E+02
CUB EFFECT           1            .211776E+02    .211776E+02    .146987E+02
OVERALL  EFF         3            .330108E+03
DEVIATION            8            .115325E+02    .144156E+01
TOTAL               11            .341641E+03


    Y=   -.232051E+04    .267814E+04  X  -.960978E+03  XX    .799504E+02  XXX    .100447E+02  XXXX
REGRESSION COEFFICIENT =    .982981
VARIATION        DEG OF F          SUM OF SQ      VAR EST        F VALUE
LIN EFFECT           1            .240241E+03    .240241E+03
QUAD EFFECT          1            .686895E+02    .686895E+02
CUB EFFECT           1            .211776E+02    .211776E+02
QUART EFF            1            .260301E-02    .260301E-02    .158033E-02
OVERALL  EFF         4            .330111E+03
DEVIATION            7            .115299E+02    .164713E+01
TOTAL               11            .341641E+03
```

Olympia Car Park, October 22nd, 1975.

X : Number of petrol vehicles in area

Y : CO

Linear regression : F-value : 6.61, $P > 0.10$
insignificant correlation.

Square regression : F-value : 8.21, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.70, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 1.72, $P > 0.10$
insignificant correlation.

```
      X                      Y
  245.00000              7.65000
  197.00000              7.12000
  222.00000              8.77000
  162.00000             11.46000
  213.00000             12.28000
  207.00000              8.79000
  213.00000             11.69000
  266.00000             26.78000
  240.00000             15.36000


      Y=    -.149538E+02    .122662E+00  X
REGRESSION COEFFICIENT  =   .696840
VARIATION         DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT            1            .143572E+03    .143572E+03    .660773E+01
OVERALL EFF           1            .143572E+03
DEVIATION             7            .152096E+03    .217279E+02
TOTAL                 8            .295668E+03

      Y=    .887217E+02  -.818933E+00  X    .209232E-02  XX
REGRESSION COEFFICIENT  =   .884758
VARIATION         DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT            1            .143572E+03    .143572E+03
QUAD EFFECT           1            .878754E+02    .878754E+02    .821007E+01
OVERALL EFF           2            .231448E+03
DEVIATION             6            .642202E+02    .107034E+02


TOTAL                 8            .295668E+03

      Y=   -.135215E+03    .232805E+01  X   -.123257E-01  XX    .215474E-04  XXX
REGRESSION COEFFICIENT  =   .899738
VARIATION         DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT            1            .143572E+03    .143572E+03
QUAD EFFECT           1            .878754E+02    .878754E+02
CUB EFFECT            1            .790408E+01    .790408E+01    .701760E+00
OVERALL EFF           3            .239352E+03
DEVIATION             5            .563161E+02    .112632E+02
TOTAL                 8            .295668E+03

      Y=    .466141E+04  -.871998E+02  X    .605117E+00  XX  -.184460E-02  XXX    .208656E-05  XXXX
REGRESSION COEFFICIENT  =   .931069
VARIATION         DEG OF F          SUM OF SQ       VAR EST          F VALUE
LIN EFFECT            1            .143572E+03    .143572E+03
QUAD EFFECT           1            .878754E+02    .878754E+02
CUB EFFECT            1            .790408E+01    .790408E+01
QUART EFF             1            .169597E+02    .169597E+02    .172370E+01
OVERALL EFF           4            .256312E+03
DEVIATION             4            .393564E+02    .983911E+01
TOTAL                 8            .295668E+03
```

Olympia Car Park, October 22nd, 1975.

X : Number of petrol vehicles from car park exit

Y : CO

Linear regression : F-value : 149.72, $0.10 > P > 0.05$

slight correlation,

$Y : 0.20X - 5.48$

$r : 0.98$

Y cannot ever become negative.

Square regression : F-value : 0.05, $P > 0.10$

insignificant correlation.

Cubic regression : F-value : 3.39, $P > 0.10$

insignificant correlation.

Quartic regression : F-value : 0.90, $P > 0.10$

insignificant correlation.

```
    X           Y
  20.00000     7.65000
   5.00000     7.12000
  13.00000     8.77000
  28.00000    10.46000
  35.00000    12.28000
  20.00000     8.79000
  30.00000    11.69000
 105.00000    26.78000
  35.00000    15.36000


    Y=   .548284E+01   .204655E+00 X
REGRESSION COEFFICIENT =  .977413
VARIATION     DEG OF F      SUM OF SQ     VAR EST      F VALUE
LIN EFFECT        1         .282462E+03   .282462E+03  .149724E+03
OVERALL EFF       1         .282462E+03
DEVIATION         7         .132059E+02   .188656E+01
TOTAL             8         .295668E+03


    Y=   .520351E+01   .221105E+00 X  -.140722E-03 XX
REGRESSION COEFFICIENT =  .977590
VARIATION     DEG OF F      SUM OF SQ     VAR EST      F VALUE
LIN EFFECT        1         .282462E+03   .282462E+03
QUAD EFFECT       1         .102478E+00   .102478E+00  .469245E-01
OVERALL EFF       2         .282565E+03
DEVIATION         6         .131034E+02   .218390E+01
TOTAL             8         .295668E+03


    Y=   .845525E+01  -.251729E+00 X   .150871E-01 XX  -.105022E-03 XXX
REGRESSION COEFFICIENT =  .986708
VARIATION     DEG OF F      SUM OF SQ     VAR EST      F VALUE
LIN EFFECT        1         .282462E+03   .282462E+03
QUAD EFFECT       1         .102478E+00   .102478E+00
CUB EFFECT        1         .529556E+01   .529556E+01  .339118E+01
OVERALL EFF       3         .287860E+03
DEVIATION         5         .780785E+01   .156157E+01
TOTAL             8         .295668E+03


    Y=   .518796E+01   .586459E+00 X  -.410315E-01 XX   .116920E-02 XXX  -.774256E-05 XXXX
REGRESSION COEFFICIENT =  .989176
VARIATION     DEG OF F      SUM OF SQ     VAR EST      F VALUE
LIN EFFECT        1         .282462E+03   .282462E+03
QUAD EFFECT       1         .102478E+00   .102478E+00
CUB EFFECT        1         .529556E+01   .529556E+01
QUART EFF         1         .144188E+01   .144188E+01  .905991E+00
OVERALL EFF       4         .289302E+03
DEVIATION         4         .636597E+01   .159149E+01
TOTAL             8         .295668E+03
```

Olympia Car Park, October 22nd, 1975.

X : CH_4

Y : Total hydrocarbons

Linear regression : F-value : 38.83, $P > 0.10$
insignificant correlation.

Square regression : F-value : 9.32, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 5.16, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.47, $P > 0.10$
insignificant correlation.

```
       X                Y
    2.23000          4.43000
    2.24000          4.02000
    2.19000          4.23000
    2.26000          4.30000
    2.22000          4.06000
    2.34000          5.00000
    2.26000          4.63000
    2.61000          6.07000
    2.60000          4.84000
    2.64000          5.24000
    2.92000          8.55000
    2.78000          6.24000


      Y=   -.598651E+01    .455610E+01 X
REGRESSION COEFFICIENT =   .891756
VARIATION        DEG OF F        SUM OF SQ       VAR EST         F VALUE
LIN EFFECT           1            .147443E+02    .147443E+02    .388350E+02
OVERALL EFF          1            .147443E+02
DEVIATION           10            .379664E+01    .379664E+00
TOTAL               11            .185409E+02



      Y=    .522381E+02  -.421794E+02 X    .928207E+01 XX
REGRESSION COEFFICIENT =   .943364
VARIATION        DEG OF F        SUM OF SQ       VAR EST         F VALUE
LIN EFFECT           1            .147443E+02    .147443E+02
QUAD EFFECT          1            .193133E+01    .193133E+01    .931859E+01
OVERALL EFF          2            .166756E+02
DEVIATION            9            .186530E+01    .207256E+00
TOTAL               11            .185409E+02

      Y=   -.513219E+03    .624867E+03 X   -.251560E+03 XX    .338195E+02 XXX
REGRESSION COEFFICIENT =   .968952
VARIATION        DEG OF F        SUM OF SQ       VAR EST         F VALUE
LIN EFFECT           1            .147443E+02    .147443E+02
QUAD EFFECT          1            .193133E+01    .193133E+01
CUB EFFECT           1            .731867E+00    .731867E+00    .516564E+01
OVERALL EFF          3            .174075E+02
DEVIATION            8            .113344E+01    .141680E+00
TOTAL               11            .185409E+02

      Y=    .163411E+04  -.279605E+04 X    .178494E+04 XX   -.503068E+03 XXX    .528853E+02 XXXX
REGRESSION COEFFICIENT =   .970947
VARIATION        DEG OF F        SUM OF SQ       VAR EST         F VALUE
LIN EFFECT           1            .147443E+02    .147443E+02
QUAD EFFECT          1            .193133E+01    .193133E+01
CUB EFFECT           1            .731867E+00    .731867E+00
QUART EFF            1            .717399E-01    .717399E-01    .472997E+00
OVERALL EFF          4            .174792E+02
DEVIATION            7            .106170E+01    .151671E+00
TOTAL               11            .185409E+02
```

Olympia Car Park, October 22nd, 1975.

X : Number of petrol vehicles in area

Y : Total hydrocarbons

Linear regression : F-value : 7.14, $P > 0.10$
insignificant correlation.

Square regression : F-value : 3.44, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.74, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.87, $P > 0.10$
insignificant correlation.

```
                X                  Y
         245.00000            4.43000
         197.00000            4.23000
         222.00000            4.30000
         162.00000            4.63000
         213.00000            5.07000
         207.00000            4.84000
         213.00000            5.24000
         286.00000            8.55000
         240.00000            6.24000


       Y=   -.930952E+00    .286693E-01  X
REGRESSION COEFFICIENT =   .710688
VARIATION          DEG OF F          SUM OF SQ        VAR EST          F VALUE
LIN EFFECT             1              .784303E+01     .784303E+01     .714364E+01
OVERALL EFF            1              .784303E+01
DEVIATION              7              .768533E+01     .109790E+01
TOTAL                  8              .155284E+02


       Y=    .175817E+02  -.139465E+00  X    .373611E-03 XX
REGRESSION COEFFICIENT =   .827959
VARIATION          DEG OF F          SUM OF SQ        VAR EST          F VALUE
LIN EFFECT             1              .784303E+01     .784303E+01
QUAD EFFECT            1              .280190E+01     .280190E+01     .344254E+01
OVERALL EFF            2              .106449E+02
DEVIATION              6              .488343E+01     .813904E+00
TOTAL                  8              .155284E+02


       Y=   -.455615E+02    .747886E+00  X  -.369182E-02 XX    .607571E-05 XXX
REGRESSION COEFFICIENT =   .852046
VARIATION          DEG OF F          SUM OF SQ        VAR EST          F VALUE
LIN EFFECT             1              .784303E+01     .784303E+01
QUAD EFFECT            1              .280190E+01     .280190E+01
CUB EFFECT             1              .628426E+00     .628426E+00     .738456E+00
OVERALL EFF            3              .112734E+02
DEVIATION              5              .425500E+01     .851000E+00
TOTAL                  8              .155284E+02


       Y=    .969595E+03  -.181998E+02  X    .126984E+00 XX  -.388876E-03 XXX    .441600E-06 XXXX
REGRESSION COEFFICIENT =   .880287
VARIATION          DEG OF F          SUM OF SQ        VAR EST          F VALUE
LIN EFFECT             1              .784303E+01     .784303E+01
QUAD EFFECT            1              .280190E+01     .280190E+01
CUB EFFECT             1              .628426E+00     .628426E+00
QUART EFF              1              .759648E+00     .759648E+00     .869323E+00
OVERALL EFF            4              .120330E+02
DEVIATION              4              .349535E+01     .873838E+00
TOTAL                  8              .155284E+02
```

Olympia Car Park, October 22nd, 1975.

X : Number of petrol vehicles from car park exit

Y : Total hydrocarbons

Linear regression : F-value : 71.03, $0.10 > P > 0.05$

slight correlation,

$Y : 0.046X + 3.91$

$r : 0.95$

Square regression : F-value : 0.89, $P > 0.10$

insignificant correlation.

Cubic regression : F-value : 6.48, $0.10 > P > 0.05$

slight correlation,

$Y : -0.00004X^3 + 0.005X^2 - 0.10X + 4.71$

$r : 0.98$

Y cannot ever become negative

Quartic regression : F-value : 3.67, $P > 0.10$

insignificant correlation.

```
        X                  Y
    20.00000           4.43000
     5.00000           4.23000
    13.00000           4.30000
    28.00000           4.63000
    35.00000           6.07000
    20.00000           4.84000
    30.00000           5.24000
   105.00000           8.55000
    35.00000           6.24000

     Y=     .391194E+01    .457813E-01  X
REGRESSION COEFFICIENT =   .954092
VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
LIN EFFECT             1             .141353E+02     .141353E+02      .710301E+02
OVERALL EFF            1             .141353E+02
DEVIATION              7             .139303E+01     .199005E+00
TOTAL                  8             .155284E+02

     Y=     .354228E+01    .675522E-01  X   -.186231E-03  XX
REGRESSION COEFFICIENT =   .960130
VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
LIN EFFECT             1             .141353E+02     .141353E+02
QUAD EFFECT            1             .179477E+00     .179477E+00      .887361E+00
OVERALL EFF            2             .143148E+02
DEVIATION              6             .121356E+01     .202259E+00
TOTAL                  8             .155284E+02

     Y=     .471196E+01   -.102531E+00  X    .529138E-02  XX   -.377774E-04  XXX
REGRESSION COEFFICIENT =   .982840
VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
LIN EFFECT             1             .141353E+02     .141353E+02
QUAD EFFECT            1             .179477E+00     .179477E+00
CUB EFFECT             1             .685198E+00     .685198E+00      .648424E+01
OVERALL EFF            3             .150000E+02
DEVIATION              5             .528357E+00     .105671E+00
TOTAL                  8             .155284E+02

     Y=     .334372E+01    .248476E+00  X   -.182094E-01  XX    .495829E-03  XXX   -.324235E-05  XXXY
REGRESSION COEFFICIENT =   .991089
VARIATION          DEG OF F          SUM OF SQ        VAR EST           F VALUE
LIN EFFECT             1             .141353E+02     .141353E+02
QUAD EFFECT            1             .179477E+00     .179477E+00
CUB EFFECT             1             .685198E+00     .685198E+00
QUART EFF              1             .252859E+00     .252859E+00      .367130E+01
OVERALL EFF            4             .152529E+02
DEVIATION              4             .275498E+00     .688745E-01
TOTAL                  8             .155284E+02
```

Olympia Car Park, October 22nd, 1975.

X : Number of petrol vehicles in area

Y : CH_4

Linear regression : F-value : 3.78, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.13, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.41, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.91, $P > 0.10$
insignificant correlation.

```
       X                   Y
  245.00000           2.23000
  197.00000           2.19000
  222.00000           2.26000


  162.00000           2.26000
  213.00000           2.61000
  207.00000           2.60000
  213.00000           2.64000
  286.00000           2.92000
  240.00000           2.78000

      Y=    .147968E+01    .462110E-02 X
REGRESSION COEFFICIENT =    .592377
VARIATION       DEG OF F          SUM OF SQ         VAR EST           F VALUE
LIN EFFECT          1              .203770E+00      .203770E+00      .378434E+01
OVERALL EFF         1              .203770E+00
DEVIATION           7              .376919E+00      .538456E-01
TOTAL               8              .580689E+00

      Y=    .246250E+01  -.430501E-02 X    .198347E-04 XX
REGRESSION COEFFICIENT =    .603747
VARIATION       DEG OF F          SUM OF SQ         VAR EST           F VALUE
LIN EFFECT          1              .203770E+00      .203770E+00
QUAD EFFECT         1              .789701E-02      .789701E-02      .128399E+00
OVERALL EFF         2              .211667E+00
DEVIATION           6              .369022E+00      .615037E-01
TOTAL               8              .580689E+00

      Y=   -.108624E+02    .102950E+00 X   -.838079E-03 XX    .128214E-05 XXX
REGRESSION COEFFICIENT =    .642420
VARIATION       DEG OF F          SUM OF SQ         VAR EST           F VALUE
LIN EFFECT          1              .203770E+00      .203770E+00
QUAD EFFECT         1              .789701E-02      .789701E-02
CUB EFFECT          1              .279852E-01      .279852E-01      .410296E+00
OVERALL EFF         3              .239652E+00
DEVIATION           5              .341037E+00      .682073E-01
TOTAL               8              .580689E+00

      Y=    .281918E+03  -.528172E+01 X    .368499E-01 XX   -.112626E-03 XXX    .127361E-06 XXXX
REGRESSION COEFFICIENT =    .722162
VARIATION       DEG OF F          SUM OF SQ         VAR EST           F VALUE
LIN EFFECT          1              .203770E+00      .203770E+00
QUAD EFFECT         1              .789701E-02      .789701E-02
CUB EFFECT          1              .279852E-01      .279852E-01
QUART EFF           1              .631873E-01      .631873E-01      .909662E+00
OVERALL EFF         4              .302839E+00
DEVIATION           4              .277849E+00      .694624E-01
TOTAL               8              .580689E+00
```

Olympia Car Park, October 22nd, 1975.

X : Number of petrol vehicles from car park exit

Y : CH_4

Linear regression : F-value : 9.50, $P > 0.10$
insignificant correlation

Square regression : F-value : 2.39, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.46, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 0.30, $P > 0.10$
insignificant correlation.

```
        X                    Y
    20.00000             2.23000
     5.00000             2.19000
    13.00000             2.26000
    28.00000             2.26000
    35.00000             2.61000
    20.00000             2.60000
    30.00000             2.64000
   105.00000             2.92000
    35.00000             2.78000


      Y=     .227124E+01    .704083E-02 X
REGRESSION COEFFICIENT =   .758771
VARIATION         DEG OF F         SUM OF SQ        VAR EST          F VALUE
LIN EFFECT            1             .334322E+00     .334322E+00      .949905E+01
OVERALL EFF           1             .334322E+00
DEVIATION             7             .246367E+00     .351953E-01
TOTAL                 8             .580689E+00


      Y=     .203993E+01    .206631E-01 X   -.116530E-03 XX
REGRESSION COEFFICIENT =   .834715
VARIATION         DEG OF F         SUM OF SQ        VAR EST          F VALUE
LIN EFFECT            1             .334322E+00     .334322E+00
QUAD EFFECT           1             .702724E-01     .702724E-01      .239436E+01
OVERALL EFF           2             .404594E+00
DEVIATION             6             .176095E+00     .293491E-01
TOTAL                 8             .580689E+00


      Y=     .221142E+01  -.427387E-02 X     .686580E-03 XX    -.553880E-05 XXX
REGRESSION COEFFICIENT =   .849773
VARIATION         DEG OF F         SUM OF SQ        VAR EST          F VALUE
LIN EFFECT            1             .334322E+00     .334322E+00
QUAD EFFECT           1             .702724E-01     .702724E-01
CUB EFFECT            1             .147294E-01     .147294E-01      .456399E+00


OVERALL EFF           3             .419324E+00
DEVIATION             5             .161365E+00     .322730E-01
TOTAL                 8             .580689E+00


      Y=     .192401E+01    .694573E-01 X   -.424990E-02 XX     .106548E-03 XXX   -.681075E-06 XXXX
REGRESSION COEFFICIENT =   .861004
VARIATION         DEG OF F         SUM OF SQ        VAR EST          F VALUE
LIN EFFECT            1             .334322E+00     .334322E+00
QUAD EFFECT           1             .702724E-01     .702724E-01
CUB EFFECT            1             .147294E-01     .147294E-01
QUART EFF             1             .111570E-01     .111570E-01      .297109E+00
OVERALL EFF           4             .430481E+00
DEVIATION             4             .150208E+00     .375520E-01
TOTAL                 8             .580689E+00
```

Olympia Car Park, October 22nd, 1975.

X : Number of petrol vehicles from car park exit

Y : Number of petrol vehicles in the area

Linear regression : F-value : 6.38, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.39, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 0.05, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 2.44, $P > 0.10$
insignificant correlation.

```
       X                  Y
   20.00000          245.00000
    5.00000          197.00000
   13.00000          222.00000
   28.00000          162.00000
   35.00000          213.00000
   20.00000          207.00000
   30.00000          213.00000
  105.00000          286.00000
   35.00000          240.00000


    Y=     .193993E+03    .821520E+00  X
REGRESSION COEFFICIENT =   .690641
VARIATION       DEG OF F          SUM OF SQ      VAR EST         F VALUE
LIN EFFECT          1            .455150E+04    .455150E+04    .638394E+01
OVERALL EFF         1            .455150E+04
DEVIATION           7            .499073E+04    .712961E+03
TOTAL               8            .954222E+04


    Y=     .209233E+03  -.759853E-01  X    .767760E-02  XX
REGRESSION COEFFICIENT =   .713409
VARIATION       DEG OF F          SUM OF SQ      VAR EST         F VALUE
LIN EFFECT          1            .455150E+04    .455150E+04
QUAD EFFECT         1            .305040E+03    .305040E+03    .390603E+00
OVERALL EFF         2            .485654E+04
DEVIATION           6            .468569E+04    .780948E+03
TOTAL               8            .954222E+04


    Y=     .200086E+03    .125404E+01  X  -.351566E-01  XX   .295414E-03  XXX
REGRESSION COEFFICIENT =   .716480
VARIATION       DEG OF F          SUM OF SQ      VAR EST         F VALUE


LIN EFFECT          1            .455150E+04    .455150E+04
QUAD EFFECT         1            .305040E+03    .305040E+03
CUB EFFECT          1            .419001E+02    .419001E+02    .451141E-01
OVERALL EFF         3            .489844E+04
DEVIATION           5            .464379E+04    .928757E+03
TOTAL               8            .954222E+04


    Y=     .859968E+02    .305224E+02  X  -.199474E+01  XX   .447896E-01  XXX   -.270359E-03  XXXX
REGRESSION COEFFICIENT =   .835217
VARIATION       DEG OF F          SUM OF SQ      VAR EST         F VALUE
LIN EFFECT          1            .455150E+04    .455150E+04
QUAD EFFECT         1            .305040E+03    .305040E+03
CUB EFFECT          1            .419001E+02    .419001E+02
QUART EFF           1            .175810E+04    .175810E+04    .243698E+01
OVERALL EFF         4            .665653E+04
DEVIATION           4            .288569E+04    .721422E+03
TOTAL               8            .954222E+04
```

Olympia Car Park, October 22nd, 1975.

X : Total vehicles (petrol & diesel) in the area

Y : CO

Linear regression	: F-value : 4.02, $P > 0.10$ insignificant correlation.
Square regression	: F-value : 2.07, $P > 0.10$ insignificant correlation.
Cubic regression	: F-value : 2.04, $P > 0.10$ insignificant correlation.
Quartic regression	: F-value : 6.43, $P \simeq 0.05$ significant correlation - doubtful use - inadequate number of data points.

```
      X               Y
  287.00000        7.65000
  219.00000        7.12000
  244.00000        8.77000


  195.00000       10.46000
  233.00000       12.28000
  240.00000        8.79000
  231.00000       11.69000
  308.00000       26.78000
  255.00000       15.36000

      Y=   -.142753E+02    .107314E+00  X
REGRESSION COEFFICIENT =    .604104
VARIATION        DEG OF F         SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1           .107902E+03    .107902E+03      .402261E+01
OVERALL EFF          1           .107902E+03
DEVIATION            7           .187766E+03    .268238E+02
TOTAL                8           .295668E+03

      Y=    .109091E+03   -.880655E+00  X     .194400E-02  XX
REGRESSION COEFFICIENT =    .726722
VARIATION        DEG OF F         SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1           .107902E+03    .107902E+03
QUAD EFFECT          1           .482480E+02    .482480E+02      .207491E+01
OVERALL EFF          2           .156150E+03
DEVIATION            6           .139518E+03    .232531E+02
TOTAL                8           .295668E+03

      Y=   -.865969E+03    .111978E+02  X   -.472665E-01  XX    .659125E-04  XXX
REGRESSION COEFFICIENT =    .815371
VARIATION        DEG OF F         SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1           .107902E+03    .107902E+03
QUAD EFFECT          1           .482480E+02    .482480E+02
CUB EFFECT           1           .404193E+02    .404193E+02      .203934E+01
OVERALL EFF          3           .196569E+03
DEVIATION            5           .990991E+02    .198198E+02
TOTAL                8           .295668E+03

      Y=    .103131E+05   -.171335E+03  Y     .105947E+01  XX   -.268949E-02  XXX    .293356E-05  XXXX
REGRESSION COEFFICIENT =    .933541
VARIATION        DEG OF F         SUM OF SQ       VAR EST          F VALUE
LIN EFFECT           1           .107902E+03    .107902E+03
QUAD EFFECT          1           .482480E+02    .482480E+02
CUB EFFECT           1           .404193E+02    .404193E+02
QUART EFF            1           .611056E+02    .611056E+02      .643327E+01
OVERALL EFF          4           .257675E+03
DEVIATION            4           .379935E+02    .949837E+01
TOTAL                8           .295668E+03
```

Olympia Car Park, October 22nd, 1975.

X : Total vehicles (p&d) in the area

Y : Total hydrocarbons

Linear regression : F-value : 4.18, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.90, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 2.11, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 3.13, $P > 0.10$
insignificant correlation.

```
      X                Y
 287.00000         4.43000
 219.00000         4.23000
 244.00000         4.30000
 195.00000         4.63000
 233.00000         6.07000
 240.00000         4.84000
 231.00000         5.24000
 308.00000         8.55000
 255.00000         6.24000


     Y=   -.724563E+00    .248875E-01 X
REGRESSION COEFFICIENT =   .611332
VARIATION        DEG OF F          SUM OF SQ         VAR EST           F VALUE
LIN EFFECT           1            .580337E+01       .580337E+01      .417724E+01
OVERALL EFF          1            .580337E+01
DEVIATION            7            .972409E+01       .138928E+01
TOTAL                8            .155284E+02


     Y=    .193308E+02  -.135724E+00 X     .316031E-03 XX
REGRESSION COEFFICIENT =   .675161
VARIATION        DEG OF F          SUM OF SQ         VAR EST           F VALUE
LIN EFFECT           1            .580337E+01       .580337E+01
QUAD EFFECT          1            .127511E+01       .127511E+01      .905415E+00
OVERALL EFF          2            .707848E+01
DEVIATION            6            .844988E+01       .140831E+01
TOTAL                8            .155284E+02


     Y=   -.223395E+03    .287102E+01 X   -.119341E-01 XX      .164079E-04 XXX
REGRESSION COEFFICIENT =   .785583
VARIATION        DEG OF F          SUM OF SQ         VAR EST           F VALUE
LIN EFFECT           1            .580337E+01       .580337E+01
QUAD EFFECT          1            .127511E+01       .127511E+01
CUB EFFECT           1            .250471E+01       .250471E+01      .219651E+01


OVERALL EFF          3            .958318E+01
DEVIATION            5            .594517E+01       .118903E+01
TOTAL                8            .155284E+02


     Y=    .268740E+04  -.348429E+02 X     .216733E+00 XX   -.594220E-03 XXX     .606115E-06 XXXX
REGRESSION COEFFICIENT =   .886074
VARIATION        DEG OF F          SUM OF SQ         VAR EST           F VALUE
LIN EFFECT           1            .580337E+01       .580337E+01
QUAD EFFECT          1            .127511E+01       .127511E+01
CUB EFFECT           1            .250471E+01       .250471E+01
QUART EFF            1            .260855E+01       .260855E+01      .312719E+01
OVERALL EFF          4            .121917E+02
DEVIATION            4            .333662E+01       .834154E+00
TOTAL                8            .155284E+02
```

Olympia Car Park, October 22nd, 1975.

X : Total vehicles (p&d) in the area

Y : CH_4

Linear regression : F-value : 1.95, $P > 0.10$
insignificant correlation.

Square regression : F-value : 0.03, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 1.19, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 3.26, $P > 0.10$
insignificant correlation.

```
       X                     Y
  287.00000             2.23000
  219.00000             2.19000
  244.00000             2.26000
  195.00000             2.26000
  233.00000             2.61000
  240.00000             2.60000
  231.00000             2.64000
  300.00000             2.92000
  255.00000             2.78000


      Y=    .159527E+01    .367656E-02  X
REGRESSION COEFFICIENT =    .467014
VARIATION          DEG  OF  F          SUM  OF  SQ        VAR  EST          F  VALUE
LIN  EFFECT             1               .126649E+00      .126649E+00      .195256E+01
OVERALL  EFF            1               .126649E+00
DEVIATION               7               .454039E+00      .648628E-01
TOTAL                   8               .580689E+00


      Y=    .788136E+00    .101404E-01  X    -.127188E-04  XX
REGRESSION COEFFICIENT =    .470806
VARIATION          DEG  OF  F          SUM  OF  SQ        VAR  EST          F  VALUE
LIN  EFFECT             1               .126649E+00      .126649E+00
QUAD  EFFECT            1               .206527E-02      .206527E-02      .274167E-01
OVERALL  EFF            2               .128715E+00
DEVIATION               6               .451974E+00      .753290E-01
TOTAL                   8               .580689E+00


      Y=   -.444908E+02    .571029E+00  X    -.229791E-02  XX      .306079E-05  XXX
REGRESSION COEFFICIENT =    .609719
VARIATION          DEG  OF  F          SUM  OF  SQ        VAR  EST          F  VALUE
LIN  EFFECT             1               .126649E+00      .126649E+00
QUAD  EFFECT            1               .206527E-02      .206527E-02
CUB  EFFECT             1               .871603E-01      .871603E-01      .119459E+01
OVERALL  EFF            3               .215875E+00
DEVIATION               5               .364814E+00      .729628E-01
TOTAL                   8               .580689E+00


      Y=    .534829E+03   -.888390E+01  X     .550293E-01  XX    -.150025E-03  XXX     .151954E-06  XXXX
REGRESSION COEFFICIENT =    .808761
VARIATION          DEG  OF  F          SUM  OF  SQ        VAR  EST          F  VALUE
LIN  EFFECT             1               .126649E+00      .126649E+00
QUAD  EFFECT            1               .206527E-02      .206527E-02
CUB  EFFECT             1               .871603E-01      .871603E-01
QUART  EFF              1               .163951E+00      .163951E+00      .326494E+01
OVERALL  EFF            4               .379826E+00
DEVIATION               4               .200863E+00      .502157E-01
TOTAL                   8               .580689E+00
```

Pooling of all results, June-October, 1975.

X : CO

Y : Pb

Linear regression : F-value : 3.23, P $>$ 0.10
insignificant correlation.

Square regression : F-value : 0.25, P $>$ 0.10
insignificant correlation.

Cubic regression : F-value : 1.86, P $>$ 0.10
insignificant correlation.

Quartic regression : F-value : 1.78, P $>$ 0.10
insignificant correlation.

```
    X           Y
 .43000      4.10000
 .34000      1.40000
 .14000      2.60000

 .98000      2.70000
1.44000      5.10000
2.21000      4.20000
1.77000      4.70000
1.32000      5.30000
1.44000      6.30000
2.50000      6.70000
 .96000      5.10000
3.54000      9.60000
3.76000      9.71000
5.90000      5.45000
5.05000      3.44000
1.76000      3.38000
1.50000      3.19000
2.13000      4.74000
1.70000      5.00000
2.01000      2.78000
3.92000      3.69000
7.44000      3.12000
3.36000      4.16000
2.99000      2.81000
3.72000      3.48000
3.10000      3.53000
4.67000      4.11000
2.75000      2.73000
4.58000      2.93000
3.80000      2.82000
3.65000      4.49000
3.02000      3.22000
3.05000      3.99000
5.72000      3.06000
1.50000      3.33000
7.25000      3.37000
2.52000      2.97000
2.39000      2.46000
2.13000      4.44000
3.58000      4.06000
3.68000      4.62000
3.50000      3.00000
4.12000      2.63000
2.36000      2.94000
 .55000       .57000
 .44000      1.04000
 .43000       .36000
 .34000       .43000
 .38000       .92000
 .37000       .74000
1.01000       .47000
 .35000       .47000
 .39000       .45000
 .34000       .25000
 .39000      1.99000
 .31000       .73000
 .33000       .57000
 .43000       .97000
 .29000      1.05000
 .42000       .76000
 .59000       .73000
 .40000       .64000
 .22000       .19000
 .30000       .51000
 .25000       .37000
 .43000       .64000
 .86000      2.57000
7.65000      5.13000
7.55000      4.59000
7.12000      5.33000
 .77000      4.97000
 .35000      5.24000
9.67000      4.92000
0.46000      6.53000
2.29000      8.41000
 .79000      4.49000
1.63000      4.45000
6.75000     11.27000
5.36000      5.62000
```

```
     Y=     .315661E+01    .324785E+00 X
REGRESSION COEFFICIENT =    .203620
VARIATION         DEG OF F          SUM OF SQ        VAR EST        F VALUE
LIN EFFECT            1              .143598E+03     .143598E+03     .322909E+01
OVERALL EFF           1              .143598E+03
DEVIATION            77              .342420E+04     .444702E+02
TOTAL                78              .356780E+04


     Y=     .281246E+01    .503694E+00 X   -.956411E-02 XX
REGRESSION COEFFICIENT =    .208370
VARIATION         DEG OF F          SUM OF SQ        VAR EST        F VALUE
LIN EFFECT            1              .143598E+03     .143598E+03
QUAD EFFECT           1              .112499E+02     .112499E+02     .250514E+00
OVERALL EFF           2              .154848E+03
DEVIATION            76              .341295E+04     .449073E+02
TOTAL                78              .356780E+04

     Y=     .159371E+01    .162897E+01 X   -.166388E+00 XX    .447309E-02 XXX
REGRESSION COEFFICIENT =    .258073
VARIATION         DEG OF F          SUM OF SQ        VAR EST        F VALUE
LIN EFFECT            1              .143598E+03     .143598E+03
QUAD EFFECT           1              .112499E+02     .112499E+02
CUB EFFECT            1              .827736E+02     .827736E+02     .186417E+01
OVERALL EFF           3              .237622E+03
DEVIATION            75              .333018E+04     .444024E+02
TOTAL                78              .356780E+04

     Y=     .279238E+00    .357384E+01 X   -.694469E+00 XX    .472351E-01 XXX   -.960343E-03 XXXX
REGRESSION COEFFICIENT =    .297540
VARIATION         DEG OF F          SUM OF SQ        VAR EST        F VALUE
LIN EFFECT            1              .143598E+03     .143598E+03
QUAD EFFECT           1              .112499E+02     .112499E+02
CUB EFFECT            1              .827736E+02     .827736E+02
QUART EFF             1              .782365E+02     .782365E+02     .178032E+01
OVERALL EFF           4              .315858E+03
DEVIATION            74              .325194E+04     .439452E+02
TOTAL                78              .356780E+04
```

Pooling of all results, June-October, 1975.

X : CO

Y : Total hydrocarbons

Linear regression : F-value : 40.37, $P > 0.10$
insignificant correlation.

Square regression : F-value : 11.32, $P > 0.10$
insignificant correlation.

Cubic regression : F-value : 3.26, $P > 0.10$
insignificant correlation.

Quartic regression : F-value : 21.76, $P < 0.01$
highly significant correlation,
$Y : 0.06X^4 + 0.91X^3 + 4.50X^2 - 7.03X + 7.87$
$r : 0.76$

```
      X           Y
   1.43000     1.73000
   1.04000     1.37000
   1.14000     1.64000


    .98000     1.49000
   1.44000     2.58000
   2.21000     1.87000
   1.77000     1.52000
   1.32000     1.64000
   1.44000     1.37000
   2.50000     1.59000
    .96000     1.32000
   3.54000     2.35000
   3.76000     2.50000
   5.90000     1.91000
   6.05000     2.25000
   1.76000     2.10000
   1.50000     1.44000
   2.10000     1.90000
   1.70000     2.01000
   2.01000     1.73000
   3.92000     1.95000
   7.44000     1.70000
   3.36000     2.56000
   2.99000     1.86000
   3.72000     2.37000
   3.10000     2.07000
   4.67000     2.21000
   2.76000     1.88000
   4.56000     2.24000
   3.80000     2.06000
   3.65000     2.30000
   3.02000     2.20000
   3.05000     1.43000
   5.72000     2.02000
   1.50000     2.01000
   7.25000     1.95000
   2.52000     1.90000
   2.89000     1.93000
   2.13000     1.63000
   3.58000     1.94000
   3.68000     2.12000
   3.50000     2.88000
   4.12000     2.07000
   2.36000     2.01000
    .55000     1.40000
    .44000     1.36000
    .43000     1.46000
    .34000     1.40000
    .38000     1.54000
    .37000     1.42000
   1.01000     2.05000
    .85000     2.48000
    .39000     1.58000
    .34000     1.55000
    .39000     1.48000
    .31000     1.39000
    .33000     1.37000
    .43000     1.48000
    .29000     1.38000
    .42000     1.55000
    .59000     1.49000
    .40000     1.50000
    .22000     1.39000
    .30000     1.45000
    .25000     1.33000
    .43000     1.49000
    .78000     1.52000
   4.43000     7.65000
   4.02000     7.55000
   4.23000     7.12000
   4.30000     8.77000
   4.06000     6.35000
   5.00000     9.67000
   4.63000    10.46000
   6.07000    12.28000
   4.84000     8.79000
   5.24000    11.69000
   8.55000    26.78000
```

```
     Y=     .259514E+00    .109183E+01 X
REGRESSION COEFFICIENT  =    .589003
VARIATION         DEG OF F        SUM OF SQ        VAR EST          F VALUE
LIN EFFECT            1          .371074E+03      .371074E+03      .403735E+02
OVERALL EFF           1          .371074E+03
DEVIATION            76          .698517E+03      .919102E+01
TOTAL                77          .106959E+04



     Y=     .172204E+01   -.436663E+00 X     .232230E+00 XX
REGRESSION COEFFICIENT  =    .657684
VARIATION         DEG OF F        SUM OF SQ        VAR EST          F VALUE
LIN EFFECT            1          .371074E+03      .371074E+03
QUAD EFFECT           1          .915766E+02      .915766E+02      .113162E+02
OVERALL EFF           2          .462650E+03
DEVIATION            75          .606941E+03      .809254E+01
TOTAL                77          .106959E+04

     Y=     .669012E+00    .154794E+01 X    -.439241E+00 XX     .573265E-01 XXX
REGRESSION COEFFICIENT  =    .675621
VARIATION         DEG OF F        SUM OF SQ        VAR EST          F VALUE
LIN EFFECT            1          .371074E+03      .371074E+03
QUAD EFFECT           1          .915766E+02      .915766E+02
CUB EFFECT            1          .255789E+02      .255789E+02      .325568E+01
OVERALL EFF           3          .488229E+03
DEVIATION            74          .581362E+03      .785624E+01
TOTAL                77          .106959E+04

     Y=     .367091E+01   -.703179E+01 X     .449975E+01 XX    -.911847E+00 XXX     .598447E-01 XXXX
REGRESSION COEFFICIENT  =    .762420
VARIATION         DEG OF F        SUM OF SQ        VAR EST          F VALUE
LIN EFFECT            1          .371074E+03      .371074E+03
QUAD EFFECT           1          .915766E+02      .915766E+02
CUB EFFECT            1          .255789E+02      .255789E+02
QUART EFF             1          .133506E+03      .133506E+03      .217614E+02
OVERALL EFF           4          .621736E+03
DEVIATION            73          .447856E+03      .613501E+01
TOTAL                77          .106959E+04
```

4.2 Summary of significant correlations.

Key to grading :
o – no correlation
x – slight correlation
xx – significant correlation
xxx – highly significant correlation

Sites	Parameters	Correlation	Order of polynomial	r	Comments
Exhib 1	(CO,Pb)	x	2.	0.85	
–	(THC,Pb)	xx	3.	0.83	see p. 195
Exhib 2	(CO,THC)	x	2.	0.51	see p. 213
–	$(\text{THC},\Delta\text{CH}_4)$	x	4.	0.53	see p. 213
Tee 1	(CO,THC)	xxx	4.	0.98	see p. 229
–	(–)	xx	3.	0.93	–
–	(CH_4,CO)	x	3.	0.68	see p. 231
–	$(\Delta\text{THC},\text{CO})$	x	2.	0.96	see p. 233
–	(–)	xx	3.	0.98	–
–	(THC,CH_4)	xx	3.	0.87	see p. 235
Tee 2	(CO,Pb)	xx	2.	0.96	see p. 239
–	(CH_4,Pb)	xx	4.	0.85	see p. 243
Oly 1	(THC,CO)	x	1.	0.98	see p. 264
–	(CH_4,CO)	x	2.	0.95	
–	(–)	xx	3.	0.98	see p. 266
–	(N_{pvg},CO)	x	1.	0.98	see p. 270
–	(N_{pvg},THC)	x	1.	0.95	
–	(–)	x	3.	0.98	see p. 276
–	(N_{tpdv},CO)	x	4.	0.93	
Pooled	(CO,THC)	xxx	4.	0.76	see p. 292

4.3 Correlation Matrices.

Exhibition Road 1:

	CO				THC				CH_4				Pb			
	1.	2.	3.	4.	1.	2.	3.	4.	1.	2.	3.	4.	1.	2.	3.	4.
CO	————				o	o	o	o	o	o	o	o	o	x	o	o
THC					————				o	o	o	o	o	o	xx	o
CH_4									————				o	o	o	o
Pb													————			

Exhibition Road 2:

CO	————				o	x	o	o	o	o	o	o	o	o	o	o
THC					————				o	o	o	x	o	o	o	o
CH_4									————				o	o	o	o
Pb													————			

Teeside 2:

CO	————				o	o	o	o	o	o	o	o	o	xx	o	o
THC					————				o	o	o	o	o	o	o	o
CH_4									————				o	o	o	xx
Pb													————			

Teeside 1:

	CO				THC				CH_4				THC-CH_4				Pb			
	1.	2.	3.	4.	1.	2.	3.	4.	1.	2.	3.	4.	1.	2.	3.	4.	1.	2.	3.	4.
CO	————				o	o	xx	xxx	o	o	x	o	o	x	xx	o	o	o	o	o
THC					————				o	o	xx	o	o	o	o	o	o	o	o	o
CH_4									————				o	o	o	o	o	o	o	o
THC-CH_4													————				o	o	o	o
Pb																	————			

Olympia Car Park :

	CO	THC	CH_4	N_{tpv}	N_{pvg}	Pb
	1.2.3.4.	1.2.3.4.	1.2.3.4.	1.2.3.4.	1.2.3.4.	1.2.3.4.
CO	———	x o o o	o x xx o	o o o o	x o o o	o o o o
THC		———	o o o o	o o o o	x o x o	o o o o
CH_4			———	o o o o	o o o o	o o o o
N_{tpv}				———	o o o o	o o o o
N_{pvg}					———	o o o o
Pb						———

5. Discussion.

As the summaries and matrices have shown, the search for significant correlations has been much in vain. Out of 50 correlations, with 4 polinomials being tested out in each case, only 20 out of those 200 showed, from "slight" to "highly significant" correlation. It is interesting to notice how the order of significance increases as the order of the polinomials goes up.

Order	No. of correlations	Significance x	xx	xxx
1.	3	3	0	0
2.	5	4	1	0
3.	7	2	5	0
4.	5	2	1	2

As the order of the polinomial approaches the number of data points, this in inevitable.

If notice is taken of the constraint that the correlation must under all conditions be positive, i.e. a positive value of "X" must under all circumstances give a positive value of "Y". So, if the "comments" on page 294 are taken into consideration the table above is reduced to the following:

Order	No. of correlations	Significance x	xx	xxx
1.	1	1	0	0
2.	2	2	0	0
3.	0	0	0	0
4.	2	1	0	1

We are reduced down to 5 correlations, out of which only one is "highly significant", and the other four only "slightly significant".

The one highly significant correlation is the relationship between CO and Total Hydrocarbons in the case when all the data points are pooled together. The fact that the correlated Polynomial is of the fourth order makes further interpretation difficult, apart from stressing that the interaction of pollutants is a complex matter.

These correlations fail completely to show a significant relationship between CO and lead.

Sampling times were kept relatively short, i.e. 10 minutes to 1 hour. None of the linear correlations were significant, not even to the 90 % significance level. If the equations given by the computational analysis are compared, one cannot but notice the difference in both their slopes and intercepts:

Ex 1 : $Pb = 11.08\ CO - 7.51$

Ex 2 : $Pb = 0.056\ CO + 3.58$

Tee 1 : $Pb = -0.39 CO + 0.88$

Tee 2 : $Pb = 3.16\ CO - 0.46$

Oly : $Pb = 0.32\ CO + 2.49$

It is reasonable to expect the three environments, Ex, Tee, and Oly, to be different, but Ex 1 and Ex 2 as well as Tee 1 and Tee 2 to be of a similar nature. As can be seen, the slope of Ex 1 is nearly 200 times greater than that of Ex 2, and the intercepts hold different signs. For Tee 1 and 2, the same goes for the intercepts. Tee 1 has got a negative slope, so the equation is meaningless. Normalising the rest of the slopes by Ex 2, the variation in the slopes stands out more clearly:

Ex 1 :	198
Ex 2 :	1
Tee 2 :	56
Oly :	5.7

If the overall equation of all the data pooled together,

a) $Pb = 0.32\ CO + 3.16$

is compared with the equation suggested by Brief et al., 1960,

b) $Pb = 0.268\ CO + 0.516$

the slopes seem somewhat similar. But when correlations by other authors are looked at, they vary considerably,

1) $Pb = 1.47\ CO - 0.93$ (Colucci et al. Detroit, 1968)
2) $Pb = 0.63\ CO + 1.26$ - New York -
3) $Pb = 1.13\ CO - 0.80$ - Los Angeles
4) $Pb = 1.12\ CO - 9.84$ (U.S., PHS Publ. No.999-AP-12, 1965)
5) $Pb = 0.82\ CO - 5.97$ - - West Los Angeles -
6) $Pb = 0.82\ CO - 6.99$ - - Pasadena -
7) $Pb = 0.63\ CO + 1.30$ (Georgii , Frankfurt, 1971)

If these are normalised by b), the slopes vary as follows:

1) 5.5
2) 2.4
3) 4.2
4) 4.2
5) 3.0
6) 3.0
7) 2.4

So, compared with b), the slopes vary from 2.4x to 5.5x.

Some of the intercepts are negative, e.g. 1),3),4),5),6). Low values of CO could therefore give a negative value of Pb, according to the regression, which must cast a doubt on the value of the work. All seven cases quoted are said to be significant to the 99% level, but one wonders.

One thing is clear, at any rate, by this stage:

There doesn't exist any universal relationship between carbon monoxide and lead.

The best that can be hoped for is similar looking regressions for similar environments. This seems to hold out in some cases in the literature but isn't substantiated by my work at all.

In general, one cannot predict accurately the levels of one pollutant by simply measuring another, as Bayley and Dockerty suggested in a Royal Society of Health paper in 1972. Atmospheric pollutants behave in a much more complex manner.

We then come to the all-important question: Do these correlations support the manifestation that most of the atmospheric pollutants captured in an urban environment come from automotive sources?

If an overall material balance is made of the emissions we are concerned with, the majority will prove petroleum originated. What is more in question is how well one can pinpoint the source from the receptor site.

If the nature of the pollutants we are dealing with is considered, all the gaseous pollutants are of similar character, whereas the lead, in a particulate state, is not. Different transpost mechanisms in the atmosphere can therefore be expected.

Hirchler et al.(1957, 1964) showed that the size and the amount of lead containing particles from exhaust are sensitive functions of driving mode. At cruising speeds, the exhaust fraction varied between 14 and 54%. During full throttle acceleration, however, large amounts of lead were re-entrained from the exhaust system giving exhaust fractions up to 200% of the input. Other studies (Mueller et al., 1964), (Ter Haar et al., 1972), (Habibi, 1970, 1973), have confirmed Hirchler's general results. Ter Haar found that the lead exhaust fraction increased with age, indicating that a break-in period of several thousand miles was necessary before the exhaust system deposits stabilized. With the highly irregular fashion of urban driving modes, this break-in period can be of even much longer duration.

Size distributions of lead particles also vary with age. For an automobile operated solely on a chassis dynamometer programmed to the 1968 U.S. Federal Accumulation Schedule (Habibi, 1970), the mass median diameter of the particulate lead increased from about 1 μm at 5000 accumulated miles to greater than 15 μm at 28000 miles. At this latter mileage, 57% of the mass of the lead was associated with particles larger than 9 μm in diameter and 77% larger than 1 μm. A car that had been driven on the road under typical consumer conditions for 15000 miles followed by about 18000 miles on the chassis dynamometer also gave a lead aerosol with 57% by weight in particles larger than 9 μm in diameter and a mass median diameter greater than 15 μm. Similar results have been obtained by Ter Haar.

Many site studies in urban environments confirm that around 70% of airborne lead is below 1 μm in diameter, with a mass median equivalent diameter of 0.3 μm (Cholak et al., 1968). In Ter Haar's study, at the receptor site, distributions of only 2-7% of the mass is in the greater than 9 μm fraction as compared to 57% for the auto exhaust distribution. The difference between the source and receptor size distributions is due to the rapid deposition of very large particles near the roadway. Habibi found that approximately one half to two thirds of the greater than 9 μm fraction is deposited within 7 meters of the automobile exhaust pipe in wind tunnel experiments.

Submicron particles may remain airborne for long periods.

Some eventually deposit in the urban area by convective diffusion and other mechanisms(Chamberlain, 1967), (Sehmel, 1972). It is not at all certain that eddy diffusion, which is largely responsible for the dispersion of the relatively unreactive CO, affects the submicron lead particles in a similar way. As can be seen from the summary of my results (p.294), the correlation between Total Hydrocarbons and CO shows up much more significant than that between Pb and CO. This follows, since the THC and CO must be transported by the same mechanism, whereas the Pb might not.

There could be an interesting analysis undertaken to see whether a better correlation of Pb with CO would be obtained using a time-lagging procedure, i.e. shifting the levels of one pollutant measured along the axis of the other to see if one was lagging the other in time.

The conclusion of my short-term sampling at the various sites must therefore be that the receptor site identification of emissions in relation to source was unsuccessful. Both CO and submicron Pb-particles are relatively well conserved, so a great deal of the amount measured might stem from different sources than those we are observing and monitoring, thus not correlating with one another. Long term sampling (2-24 hrs), as mentioned above, indicates that some of these pollutants are positively correlated to very high significance levels. It would be interesting to assess what minimum sampling time were needed for such high levels.

One possible flaw in my sampling method, when compared with the methods of other correlators, is that whilst sampling for Pb continuously, only 5 minute spot samples were being taken of CO and averaged to get a "continuous" value in our sampling routine. A statistical analysis of the standard deviations expressed on a percentile basis shows the following:

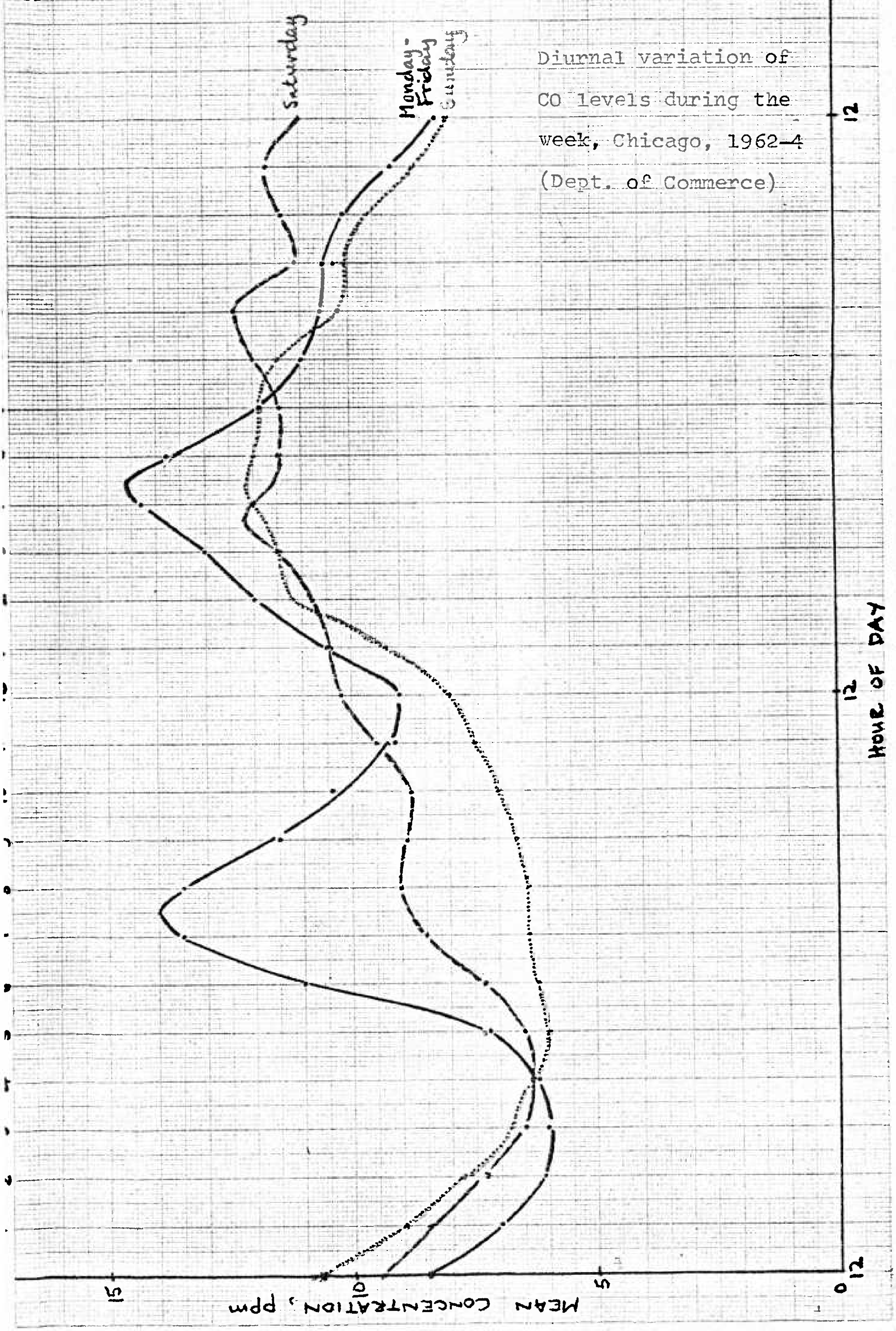
	THC			CH_4			CO		
	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min
Ex 1	31.8	66.0	10.2	3.7	10.9	0.0	71.5	150.8	18.4
Ex 2	13.6	40.5	0.5	8.9	21.9	0.6	45.1	129.3	0.8
Tee 1	8.2	37.1	1.4	3.0	6.2	1.4	23.4	60.0	5.1
Tee 2	6.1	17.5	1.3	2.8	4.2	1.0	42.0	92.7	8.2
Oly	22.2	32.0	9.8	10.1	22.0	4.0	44.1	85.7	21.2
Average	16.4			5.7			45.2		

Thus, the variation in CO looks by far the greatest. But if looked at more closely, the variations in CO are more uniform than those of THC and CH_4. If we therefore assess the inherent variation, i.e. the standard deviation of the standard deviation a following table is constructed:

	THC	CH_4	CO
Ex 1	60	97	49
Ex 2	72	70	77
Tee 1	135	53	75
Tee 2	85	43	66
Oly	33	52	44
Average	77	63	54

Comparing these variations, e.g. in CO to continuous readings and their standard deviations; work undertaken by the U.S. Dept. of Commerce (1967),(see graph 5) reported 26% variation in their standard deviation, and Chovin (1967) reports over 100% variation in some cases in Paris. My deviations fall well within these. Graph 3, p.160 also demonstrates visually that the CO - time curve is relatively smooth and resembles corresponding time period in graph 5 quite well. Our averaging is therefore well comparable with a continuous CO reading. Ideally, the air which has been sampled for lead should be drawn into a plastic bag, wherefrom a highly reliable average of CO could be obtained

5.



Diurnal variation of CO levels during the week, Chicago, 1962-4 (Dept. of Commerce) afterwards.

A point worth mentioning, when comparing correlations in the literature is the variable pore-size of filters used for the lead sampling. Some of those sizes are well above the mean diameter of the particles and a reliable lead reading cannot be expected. The varying types of filters used by different researchers will also assist to give different regressions, when the results are analysed.

6. Conclusion.

Out of 50 correlations undertaken, only one proves to be highly significant, that between Total Hydrocarbons and Carbon Monoxide.

Correlations fail completely to show a significant relationship between CO and lead.

Highly significant correlations quoted in the literature show a variable Pb/CO ratio for different environments.

The conclusion of this work is therefore, that there doesn't exist any universal relationship between CO and lead and the practice of predicting the levels of one pollutant by the monitored levels of the other must be used with great care.

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8. Appendix I - Computer Program for Statistical Analysis.

```
5/07/25   IMPERIAL  COLLEGE  FORTRAN  COMPILER         KRONOS  2.1.X  PSR2+
              MNF(B=BIN,R=0,E=3,C=0)
000000B             1.           PROGRAM REG(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
004040B             2.           DIMENSION X(1000),Y(1000)
004040B             3.           DIMENSION C(5,5),B(5),D(4,5),YA(4)
004040B             4.           DIMENSION A(25)
004040B             5.           REAL MU(9,2)
004040B             6.           REAL MU2
004040B             7.           READ (5,)NI,NII
010127B             8.    23     READ (5,) N
010133B             9.           IF(N.EQ.0) STOP
010136B            10.           READ (5,) (X(I),Y(I),I=1,N),X0,X1,DX
010155B            11.           READ (5,) MA
010161B            12.           IF(NI) 21,20,21
010162B            13.    21     WRITE (6,502) (X(I),Y(I),I=1,N)
010176B            14.    502    FORMAT (7X,1HX,11X,1HY/(1X,2F12.5))
010176B            15.    20     NSING=0
010176B            16.           MU(1,1) =1.0
010177B            17.           DO 2 M=1,MA
010202B            18.           IF(M-1) 3,3,4
010204B            19.    3      L1=1
010205B            20.           L2=2
010206B            21.           GO TO 5
010207B            22.    4      L1=M+1
010211B            23.           L2=M+1
010211B            24.    5      L3=2*M
010213B            25.           L4=L3+1
010214B            26.           DO 8 I=L1,L2
010217B            27.           MU(I,2)=0.0
010217B            28.           DO 6 J=1,N
010222B            29.    6      MU(I,2)=MU(I,2)+(X(J)**(I-1))*Y(J)
010237B            30.    8      MU(I,2)=MU(I,2)/FLOAT(N)
010244B            31.           DO 9 I=L3,L4
```

```
010246B         MU(I,1)=0.0
010246B         DO 7 J=1,N
010251B    7    MU(I,1)=MU(I,1)+X(J)**(I-1)
010265B    9    MU(I,1)=MU(I,1)/FLOAT(N)
010272B         UM2=0.0
010272B         DO 30 J=1,N
010274B   30    UM2=UM2+Y(J)*Y(J)
010301B         UM2=UM2/FLOAT(N)
010301B         MP=M+1
010303B         DO 11 I=1,MP
010305B         DO 11 J=1,MP
010307B         K=I+J-1
010310B   11    C(I,J)=MU(K,1)
010315B   10    B(I)=MU(I,2)
010321B         K=0
010321B         DO 1 J=1,MP
010323B         DO 1 I=1,MP
010325B         K=K+1
010326B    1    A(K)=C(I,J)
010333B         CALL SIMQ(A,B,MP,NSING)
010337B         IF(NSING) 29,28,29
010340B   29    WRITE (6,510)
010344B  510    FORMAT (11H   SINGULAR)
010344B   28    SIG=0.0
010344B         DO 13 I=1,MP
010347B   13    SIG=SIG+B(I)*MU(I,2)
010354B         MU2= MU(1,2)*MU(1,2)
010354B         RO=(SIG-MU2)/(UM2-MU2)
010361B         RO=SQRT(RO)
010363B         WRITE (6,515)
010367B  515    FORMAT(/)
010367B         GO TO (14,15,16,17),M
010374B   14    WRITE(6,503) (B(I),I=1,MP)
010406B  503    FORMAT(7X,2HY=,2E14.6,2H X)
010406B         GO TO 18
010406B   15    WRITE (6,504) (B(I),I=1,MP)
010421B  504    FORMAT(7X,2HY=,2E14.6,2H X,E14.6,3H XX)
010421B         GO TO 18
010421B   16    WRITE (6,505) (B(I),I=1,MP)
010434B  505    FORMAT(7X,2HY=,2E14.6,2H X,E14.6,3H XX,E14.6,4H XXX)
010434B         GO TO 18
010434B   17    WRITE (6,506) (B(I),I=1,MP)
010447B  506    FORMAT(7X,2HY=,2E14.6,2H X,E14.6,3H XX,
               1E14.6,4H XXX,E14.6,5H XXXX)
010447B   18    WRITE (6,507) RO
010454B  507    FORMAT (28H   REGRESSION COEFFICIENT = ,F8.6)
010454B         WRITE (6,500)
010460B  500    FORMAT(31H   VARIATION       DEG OF F      ,
               135HSUM OF SQ      VAR EST          F VALUE)
010460B         IF(M.NE.1) GO TO 19
010461B         SUML=0.0
010462B         SUMLL=0.0
010462B         AL=B(1)
010463B         BL=B(2)
010465B         DO 12 I=1,N
010470B         YP=AL+BL*X(I)
010472B         SUMLL=SUMLL+YP
010474B   12    SUML=SUML+YP*YP
010477B         SUML=SUML-SUMLL*SUMLL/N
010501B         SUMT=0.0
010502B         SUMTT=0.0
010502B         DO 26 I=1,N
010504B         SUMTT=SUMTT+Y(I)
010505B   26    SUMT=SUMT+Y(I)**2
010510B         SUMT=SUMT-SUMTT*SUMTT/N
010512B         SUMU=SUMT-SUML
010513B         NDFT=N-1
010515B         NDFL=1
010516B         NDFU=N-2
010517B         VARU=SUMU/NDFU
010521B         FVAL=SUML/VARU
010522B         WRITE (6,501) NDFL,SUML,SUML,FVAL
010533B         WRITE (6,512) NDFL,SUML,NDFU,SUMU,VARU,NDFT,SUMT
010546B         GO TO 31
010546B   19    IF(M.NE.2) GO TO 32
010550B         NDFO=2
010551B         AL=B(1)
010552B         BL=B(2)
010554B         CL=B(3)
010555B         SUMO=0.0
010556B         SUMOO=0.0
010557B         DO 33 I=1,N
010562B         YP=AL+BL*X(I)+CL*Y(I)*X(I)
010565B         SUMOO=SUMOO+YP
010567B   33    SUMO=SUMO+YP*YP
```

```
0105733          SUMC=SUMC-SUMCO*SUMCO/N
0105755          SUMQD=SUMO-SUML
0105777          SUMU=SUMT-SUMO
0106013          NDFU=N-3
0106023          VARU=SUMU/NDFU
0106033          FVAL=SUMQD/VARU
0106051          WRITE (6,501) NDFL,SUML,SUML
0106151   501    FORMAT (13H    LIN EFFECT,I9,E21.6,2E14.6)
0106152          WRITE (6,511) NDFL,SUMQD,SUMQD,FVAL
0106253   511    FORMAT(14H    QUAD EFFECT,I8,E21.6,2E14.6)
0106255          WRITE (6,512) NDFO,SUMO,NOFU,SUMU,VARU,NDFT,SUMT
0106403   512    FORMAT(14H    OVERALL EFF,I8,E21.6/12H    DEVIATION,T12,
                1E21.6,E14.5/8H     TOTAL,I14,E21.6)
0106405          GO TO 31
0106405   32     IF(M.NE.3) GO TO 34
0106425          AL=B(1)
0106433          BL=B(2)
0106453          CL=B(3)
0106466          DL=B(4)
0106500          SUMC=SUMO
0106510          SUMO=SUMOO=0.0
0106533          DO 75 I=1,N
0106566          YP=AL+BL*X(I)+CL*X(I)*X(I)+DL*(X(I)**3)
0106645          SUMOO=SUMOO+YP
0106665   35     SUMO=SUMO+YP*YP
0106713          SUMO=SUMO-SUMOO*SUMOO/N
0106733          SUMC=SUMO-SUMC
0106755          SUMU=SUMT-SUMO
0106777          NDFO=3
0107003          NDFU=N-4
0107013          VARU=SUMU/NDFU
0107033          FVAL=SUMC/VARU
0107055          WRITE (6,501) NDFL,SUML,SUML
0107155          WRITE (6,511) NDFL,SUMQD,SUMQD
0107244          WRITE (6,513) NDFL,SUMC,SUMC,FVAL
0107334   513    FORMAT(13H    CUB EFFECT,I9,E21.6,2E14.6)
0107343          WRITE (5,512) NDFO,SUMO,NOFU,SUMU,VARU,NDFT,SUMT
0107473          GO TO 31
0107477   34     AL=B(1)
0107503          BL=B(2)
0107523          CL=B(3)
0107533          DL=B(4)
0107551          EL=B(5)
0107563          SUMQT=SUMO
0107606          SUMO=SUMOO=0.0
0107613          DO 76 I=1,N
0107643          YP=AL+BL*X(I)+CL*X(I)*X(I)+DL*(X(I)**3)+EL*(X(I)**4)
0107753          SUMOO=SUMOO+YP
0107773   36     SUMO=SUMO+YP*YP
0110023          SUMO=SUMO-SUMOO*SUMOO/N
0110043          SUMQT=SUMO-SUMQT
0110055          SUMU=SUMT-SUMO
0110073          NDFO=4
0110103          NDFU=N-5
0110123          VARU=SUMU/NDFU
0110143          FVAL=SUMQT/VARU
0110153          WRITE (6,501) NDFL,SUML,SUML
0110253          WRITE (5,511) NDFL,SUMQD,SUMQD
0110343          WRITE (6,513) NDFL,SUMC,SUMC
0110433          WRITE (6,514) NDFL,SUMQT,SUMQT,FVAL
0110533   514    FORMAT(12H    QUART EFF,I10,E21.6,2E14.6)
0110533          WRITE (6,512) NDFO,SUMO,NOFU,SUMU,VARU,NDFT,SUMT
0110654   31     DO 2 I=1,MP
0110703    2     D(4,I)=B(I)
0111003          IF (KII) 22,23,22
0111013   22     XA=X1
0111011          WRITE (6,509)
0111026   509    FORMAT(19H         FITTED VALUES/6X,1HY,10X,7HLIN,8X,4HQU
                19X,7HCUB,8X,5HQUART)
0111066   27     DO 24 M=1,MA
0111103          YA(M)=0.0
0111103          K=M+1
0111112          DO 24 I=1,K
0111155   24     YA(M)=YA(M)+D(M,I)*(XA**(I-1))
0111365          WRITE (6,505) XA,(YA(M),M=1,MA)
0111515   508    FORMAT(1X,5F12.5)
0111513          IF (XA-X1+0.000001) 25,25,23
0111543   25     XA=XA+DX
0111563          GO TO 27
0111573          END
```

PART III

Stability Tests of Organic Lead in Iodine monochloride Solutions.

1. Introduction.

There are several reported methods for the collection and analysis of organic lead in air (Cantuti, V. and Carton, G.P., 1968), (Hirchler, D.A. and L.F. Gilbert, 1964), (Harrison, R.M. et al., 1974),(Linch, A.L. et al., 1970), (Moss, R. and E.V. Browett 1966), (Purdue, L.J. et al., 1973) and (Snyder, L.J., 1967).

Most of those are particularly suited for sampling in an industrial environment with high levels of organic lead compounds or long term sampling is needed under street air conditions to obtain sufficient quantity for analysis.

Lekkas, T. D. in a 1974 dissertation from this section of the department, tried out the method described by Associated Octel for organic lead levels in urban air. He was able to detect 0.04 $\mu g/m^3$ during a 30 minute sampling period at the sampling rate of 3 liters per minute.

A point needing further investigation was the stability of the organic lead in the iodine monochloride solution into which the air was bubbled. This section reports stability tests carried out on tetramethyl-and tetraethyllead solutions prepared in the laboratory, kept for differing time periods under differing light conditions and then analysed.

2. Experimental Procedure.

2.1 Solutions -

a) Iodine Monochloride Solution 1.0 M.

80 ml of de-ionized water and 492 ml of concentrated hydrochloric acid (s.g. 1.18) are added to 317 ml of 35% w/v potassium iodide. The solution is cooled to room temperature and 75 g of potassium iodate added slowly whilst stirring, until all the free iodine formed has redissolved to yield a clear orange-red solution. The solution is then made up to 1 litre (1.0 M).

From the stoichiometry of the reactions taking place,

i) $4\,KI + 6\,HCl + KIO_3 \longrightarrow ClI + 2I_2 + 3H_2O + 5KCl$

ii) $2\,I_2 + KIO_3 + 6\,HCl \longrightarrow 5\,ClI + KCl + 3\,H_2O$

it can be calculated, that the potassium iodate was added in excess to ensure that all the iodine formed was redissolved.

b) Iodine Monochloride Solution 0.1 M.

Solution a) was diluted down ten times.

c) Organic Lead Solutions.

The calculated amounts of dimethyllead chloride, $(CH_3)_2PbCl_2$, and diethyllead chloride, $(C_2H_5)_2PbCl_2$, are dissolved in methanol and diluted to 50 ml in de-ionized water. These were then diluted further down, respectively, to give the concentrations 8ng/ml and 200 ng/ml. The solutions were prepared daily, as the experiments were carried out.

d) Dithizone Solution 20 mg/litre.

2 mg of dithizone were dissolved in 100 ml of carbon tetrachloride. This solution was kept in a blacked out bottle.

e) Buffer Solution.

160 ml of 12.5% sodium sulphite solution was mixed with 20 ml of 40% w/v ammonium citrate solution and 160 ml ammonia (s.g. 0.88) solution. The mixture was diluted to 1 litre.

f) Acid Solution.

1 ml (B.D.H. High Purity ARISTAR, 70 w/v) nitric acid and 1 ml (B.D.H. ARISTAR, 100 volumes) hydrogen peroxide were mixed and diluted to 100 ml of water.

2.2 Analytical Method -

i) Chemistry.

The tetraalkyllead compounds are rapidly and quantitatively converted to the corresponding dialkyllead compounds by iodine monochloride. Dithizone added to a solution containing dialkyllead ions and inorganic lead ions would form complexes with both. All these dithizone-lead complexes are colored and give different spectra in a spectrophotometer. The amounts of of lead of interest are, however, well below the detection limits of colorimitric methods.

The determination of lead concentration was carried out by Atomic Absorption Spectrometry (described in Section 2), by previous decomposition of the dialkyllead dithizonates in order to inject lead in the inorganic form into the graphite tube (cf. Section 2).

It was found that the inorganic lead present in some of the prepaired solutions was of such a large order that it would interfere with the determination of the organic lead. Inorganic lead must therefore be removed from the solution prior to addition of the dithizone. This is accomplished by the addition of E.D.T.A. disodium, which combines with the inorganic lead so only the dialkylated lead is available for the formation of the dialkyllead dithizonate, which is extracted in the tetrachloride phase, while the inorganic lead-E.D.T.A. complex remains in the aqueous phase.

Tadashi, F. and T. Nobuynki, 1966, reported on the "Dissociation Reactions of Ethylenediamine-tetraacetato complexes of Cd, Zn and Pb, Studied with the Aid of the Polarographic Kinetic Current".

$$MY^{2-} + H^{+} \underset{}{\overset{k_1}{\rightleftarrows}} M^{2+} + HY^{3-}$$

It seems that the k_1 value for the lead followed the relationship:

$$k_1 = 3 \times 10^3 \left[H^+\right]$$

Although the Japanese chemical system is slightly different it is clear, that the higher the pH of our system, the greater the amount of inorganic lead is removed from it.

ii) Procedure.

15 ml of 0.1 M iodine monochloride solution are placed in a blacked out teflon tube. 1 ml of the diluted organic lead standard is added to the solution. This is repeted for several tubes which are in turn kept for varying time periods and analysed subsequently, to observe the time effect on the stability of the organic lead in the suspension.

When the desired time is up, the solution is diluted with 50 ml of de-ionized, twice distilled water. 10 ml of the buffer solution are added and the tube shaken immediatly to reduce the free iodine initially formed.

1 ml of 0.1 M E.D.T.A. disodium solution is then added and the mixture shaken up again.

5 ml of the dithizone solution are added and the mixture shaken for standard 30 seconds. The two layers formed are then allowed to separate in an all-teflon separating funnel, and then the carbon tetrachloride layer was run off into a teflon tube.

2 ml of the acid solution are added to the carbon tetrachloride solution in the teflon tube and the lead was back extracted in the aqueous phase by shaking the tube for another standard 30 seconds. The two layers were centrifuged for 1 minute and had then separated perfectly.

iii) Analysis.

The analysis was carried out on the same instrument as described in section 2. Analogous temperature program was used as in section 2 along with "gas stop".

All results are expressed in relation to "zero time concentration", i.e. the chart recorder reading of a sample that was not stored for any time period. The blank has been subtracted in all cases.

iv) Special Precautions.

All the apparatus used for the solutions was washed thoroughly, first with 10% w/v nitric acid, followed by deionized water. Pipettes, etc., which were in use every day, went through the same cleaning procedure.

Where there had been glassware used in the procedure once the organic lead was added, it was replaced by teflon. This was done in case the glass adsorbed some of the lead in the solution. All the chemical procedure was carried out in a temperature controlled dark room with safety light.

3. Results.

a) Dimethyllead dichloride, 200 pg in a 25 µl final solution

Results are given in percentages of organic lead remaining from initial solution after a specified time interval.

Minutes	% Remaining
0	100
15	39
40	29
65	0

b) Another run, same as a):

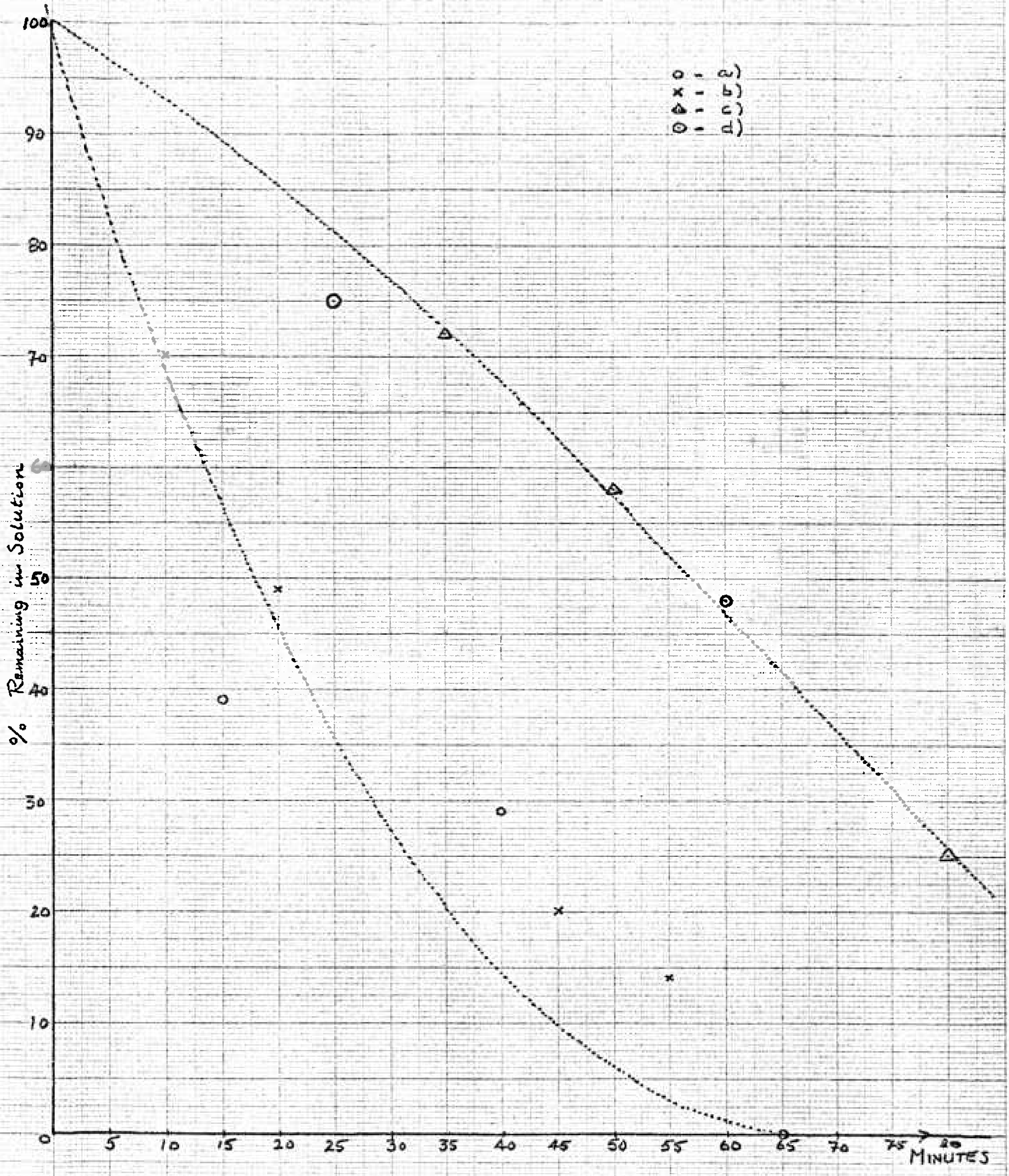
0	100
10	70
20	49
45	20
55	14

c) 5 ng DMDC per 25 µl final solution

0	100
35	72
50	58
80	25

d) Diethyllead dichloride, 5 ng per 25 ul final solution

0	100
25	75
60	48



Graph 6. Decomposition of TML and TEL in a Iodine Monochloride Solution.

4. Discussion.

From the work undertaken, it appears that organic lead is highly unstable in an iodine monochloride solution and consequently not valid for the work Lekkas did in 1974.

The weaker solutions seem to decay faster, which could be due to adsorption of the organic lead onto the container walls.

Similar work carried out at Lancaster University (Harrison, R.M., verbal communication, May,1976) does not reflect a breakdown of this sort, and it has been suggested that decay has taken place in the dimethyl-and diethyllead dichloride solutions that were being used. Further work, using fresh reagents, is needed before anything can be positively concluded about these stability tests.

5. References.

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