

DEVELOPMENT OF CONTINUOUS ORGANIC LEAD-IN-AIR MONITORS

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The large-scale manufacture of highly toxic lead alkyl Antiknock Compounds requires very close control of ambient air quality at all times. The paper outlines the evolution of continuous multi-point organic lead-in-air monitors used in the alkyl lead industry to ensure safe and efficient working conditions.

INTRODUCTION

The addition to a gasoline of a small proportion of a lead alkyl is the most economic method of increasing the octane value of the fuel. The Associated Octel Company Limited is the major supplier of lead alkyl Antiknock Compound to the oil industry outside the USA and manufactures tetra methyl lead (TML) and tetra ethyl lead (TEL) at several establishments in the UK and Europe.

Lead alkyls are highly toxic materials and may enter the body by inhalation of the vapour, by ingestion of the liquid or by penetration of the liquid through the skin. The threshold limit values (TLV's) are 0.150 mg/M^3 and 0.100 mg/M^3 for TML and TEL respectively.

The highly toxic properties of lead alkyls necessitate careful selection of personnel and very strict observance of safety precautions during manufacture and handling. All process personnel are monitored regularly for lead-in-urine levels. Retrospective monitoring of plant atmospheres is carried out using conventional 24-hour scrubbers, containing iodine monochloride, located at strategic points throughout each Works. The contents of these scrubbers are analysed for lead concentration after 24 hours' sampling and results obtained from these units may take up to another 6 hours before they are available to process management. The information obtained in this way gives a historical indication of the general state of hygiene on each Works. Retrospective monitoring is useful to the medical officers, the industrial

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hygienists and process management since it can highlight operational areas where hygiene standards need to be improved. An 'instantaneous' knowledge of the concentrations of lead alkyl in air to which operators are exposed, and the immediate location of high organic lead-in-air levels as they occur is clearly desirable in the interests of operational safety and efficiency since it enables process management to take immediate remedial action.

The First Continuous Monitor

Our first continuous monitor was installed in 1967 at Ellesmere Port and used a modified Technicon Auto-analyser. Fig. 1 gives a schematic diagram of the instrument.

This system used a colorimetric measurement based on the well-known reaction of dithizone with alkyl leads to form a coloured complex. The response of this system was slow, requiring about 10 minutes to develop a measurable colour reaction and was limited to the monitoring of 5 points plus a standard each hour. Despite subsequent improvements in the chemistry including the use of an improved colorimetric reagent, the system required continuous attention from highly skilled chemists and was eventually abandoned.

Concurrently with this development, our associate company, Octel Kuhlmann (Thilliez, G., 1967) were investigating the possible use of atomic absorption spectrophotometry and eventually designed, constructed and operated an instrument. Their system which is shown in Fig. 2 had many limitations and we decided to adopt a more conventional approach using, where possible, proprietary instrumentation.

Specification for Second Octel Continuous Lead-in-Air Monitor

Our outline specifications for the instrument required:

- (i) A sampling rate of not less than 20 points per hour.
- (ii) Automatic zero correction.
- (iii) Automatic range correction.
- (iv) A sensitivity of 10 microgram Pb/M³.
- (v) A range of 0-200 microgram Pb/M³ with the option of logarithmic display to 1500 microgram Pb/M³.
- (vi) Flame failure protection.
- (vii) Unattended operation for up to 8 hours.
- (viii) Analogue presentation of data.

Basically a conventional atomic absorption spectrophotometer consists of a stable light source, usually a hollow cathode discharge lamp which emits sharp resonance lines of the element undergoing analysis, and an optically aligned monochromator tuned to a

selected resonance line. Interposed between these units is a flame (usually air/acetylene) into which an aqueous sample is nebulised. Atoms of the metal under investigation absorb radiation from the hollow cathode lamp and the reduction in intensity of the transmitted radiation is measured and is a function of the population of metal atoms present in the flame. The intensity of the radiation transmitted is detected by a photomultiplier, amplified and displayed.

Normally absorption is directly proportional to sample concentration and path length. The technique has a number of advantages, being both specific and highly sensitive.

The basic system used is shown in the schematic drawing Fig.3.

The spectrophotometer selected was the Evans Electro Selenium Model 240. Some six litres of air (sample) per minute are required for combustion by the acetylene burner of this instrument. With the required sensitivity level of 10 microgram Pb/M³ this air rate is equivalent to the measurement of 10⁻⁹g Pb per second. Using the "integration" mode of the instrument and an integration time of 15 seconds the instrument can detect 15 nanograms Pb.

Used in the "integration" mode, only the following minor additions and modifications to the basic Model 240 unit were required for the prototype monitor:-

1. Conversion from the conventional liquid aspiration and nebulisation system to that of using plant air exclusively for combustion.
2. The addition of a platinum probe into the flame for control of the acetylene feed block valve, i.e. a flame-failure device.
3. Base-line stability achieved by servo controlling the zero of the instrument while using pure air as the sample.
4. Sensitivity control, using a similar servo arrangement as for the "zero" but analysing a known concentration of TML in air. Such a stream at the TLV level can be reliably generated using a diffusion dilution technique (McKelvey, J.M., and Hoelscher, H.E., 1957) by connecting together two chambers through an interchangeable orifice, the lower chamber containing a 1% V/v mixture of TML in toluene at constant temperature, sweeping the vapour from the upper chamber with clean air at a fixed flowrate and maintaining the chambers at constant pressure. Since TML and toluene have virtually the same vapour pressure at any given temperature over the range used, the rate of evolution of lead remains reasonably constant over long periods and the mixture in the lower chamber need only be changed every six months.

A schematic diagram of the dilution chamber is shown as Fig.4.

Operational Experience. After bench testing for some 20,000 analyses without fault, running at a frequency of one per minute, the completed prototype was installed and commissioned in

September 1971.

Unfortunately, the contractors had installed sampling pipework that allowed only half of the necessary air to be drawn and it was found that transmission of TEL was far worse than anticipated. The dual 24 port rotary valve developed for this duty allowed 90 seconds for purging before analysis commenced on any given point. This was sufficient for three air changes on the longest pipe run but TEL took 5 minutes to emerge from what were, in effect, sample pipes acting as gas-solid chromatographic columns.

There were no problems with the more volatile TML.

It was therefore concluded that continuous purging on standby is essential, switching streams sequentially with 3-way valves for analysis.

Selection of Materials for Sample Pipework. Another important point confirmed in subsequent laboratory tests was that mild steel used in the earliest sampling pipework must be avoided. A TEL-in-air stream of about 20 x TLV was passed through 2 metre length tubes of various materials for three minutes and then purged with clean air. The response to these streams was monitored continuously at one-minute intervals. Mild steel showed tailing for some 30 minutes and rose to only 30% of the expected maximum in the 3-minute exposure. This behaviour was unaffected by treatment with solvents, strong acids or heat. A second sample of steel tube gave similar results.

The transmission characteristics of untreated stainless steel, glass, copper and aluminium were all acceptable with little to choose between them, although aluminium had to be rejected due to its reported reaction with chlorinated hydrocarbons and lead alkyls.

Nylon was only slightly inferior but also was rejected after fracturing experienced elsewhere. PVC and rubber were poor, as expected, but were still quite superior to mild steel.

PTFE was not tested, costing some 20 times more than multi-bore copper.

Development of the Third Octel Continuous Organic Lead-in-Air Monitor

Some three years' accumulated operating experience with the second continuous organic lead-in-air monitor involving 1½ million analyses have revealed some shortcomings in the design. It soon became clear that extraction of data from an analogue chart was a very tedious undertaking. Also the 24 port rotary sample valve limited the total number of sample points and did not allow any flexibility in sample point programming.

Our latest instruments present lead-in-air concentrations in typewritten tabulated digital form and sample streams are selected using 3-way solenoid valves preprogrammed by a sequencer unit. A schematic of the system is shown as Fig. 6.

The analyser is again based mainly on available commercially made units. The EEL Model 240 spectrophotometer is again used. Its output is linearised and converted into a BCD output by the EEL Model 236 readout unit, which also provides an automatic electronic zero correction. Incorporation of a "level detector" allows lead-in-air concentration levels near zero to be ignored so that those of interest are not lost in a mass of printed zeros whilst excessively high concentrations may be printed out in red, making fault conditions on the plant instantly recognisable.

The tabulated presentation of the data on a single sheet (a typical readout is shown as Fig. 7) readily allows calculations of average 24-hour organic lead-in-air concentrations and allows process management to pinpoint any potentially hazardous condition and take the appropriate remedial action.

DISCUSSION AND CONCLUSION

Atomic absorptiometry is the most rapid, sensitive and specific method of measuring, continuously, the concentration of organic lead vapours in air. An atomic absorptiometer coupled to a suitable sampling pipe network by selector valves can be used to monitor the ambient air quality at any selected point in a factory. However, if absorption/desorption in the sampling pipework is severe, the analyser will give a false and misleading read-out of actual plant conditions and very careful selection of materials of construction for sample lines is necessary to avoid degeneration of sample concentration profiles and "memory" effects.

It has been suggested that the read-out from each point could be electronically integrated and the average 24 hour lead-in-air concentration level at each sample point computed. This suggestion has been rejected since, for instance, with a 20 point system the actual time any point is monitored is only about 1% of the total cycle time. Integrated values are, therefore, not regarded as reliable and the 24 hour chemical scrubber units have been retained at our factories.

The two atomic absorption units described are used for early warning and diagnostic purposes. One of the instruments, which has now completed one and a half million analyses, has been used to monitor continuously, at a central location, lead-in-air levels throughout the factory. Process management have been enabled to locate quickly, any potentially hazardous situation and to take action to maintain hygiene standards.

REFERENCES

Thilliez, G., 1967, Analytical Chemistry, 39, No. 4, pp.427-432.

McKelvey, J.M., and Hoelscher, H.E., 1957, Analytical Chemistry, 29, p.123.

Time	(1)	(2)	(3)	(4)	Zero	Cal	(5)	(6)	(7)	(8)
10.07	06.5
10.17	06.5
10.27	.	00.8	.	.	.	06.5
10.37	.	01.4	.	.	.	06.6
10.47	.	02.8	.	.	.	06.5
10.57	.	03.5	.	.	.	06.6
11.07	.	03.8	.	.	.	06.5
11.17	.	03.4	.	.	.	06.5
11.27	.	02.2	.	.	.	06.5	.	-00.1	.	-00.1
11.37	.	01.6	.	-00.1	.	06.5
11.47	.	00.7	.	.	.	06.6
11.57	06.6
12.07	06.5
12.17	.	.	-00.1	.	.	06.5
12.27	06.5	.	00.9	.	.
12.37	06.5	.	02.1	.	.
12.47	06.6	.	03.1	.	.
12.57	.	.	-00.1	.	.	06.5	.	03.4	.	.
13.07	06.5	.	03.5	.	.
13.17	06.5	.	02.8	.	.
13.27	06.5	.	01.8	.	.
13.37	06.6	.	00.8	.	.
13.47	06.5
13.57	06.6
14.07

Fig. 7 Readout from Third Octel Lead-in-Air Monitor

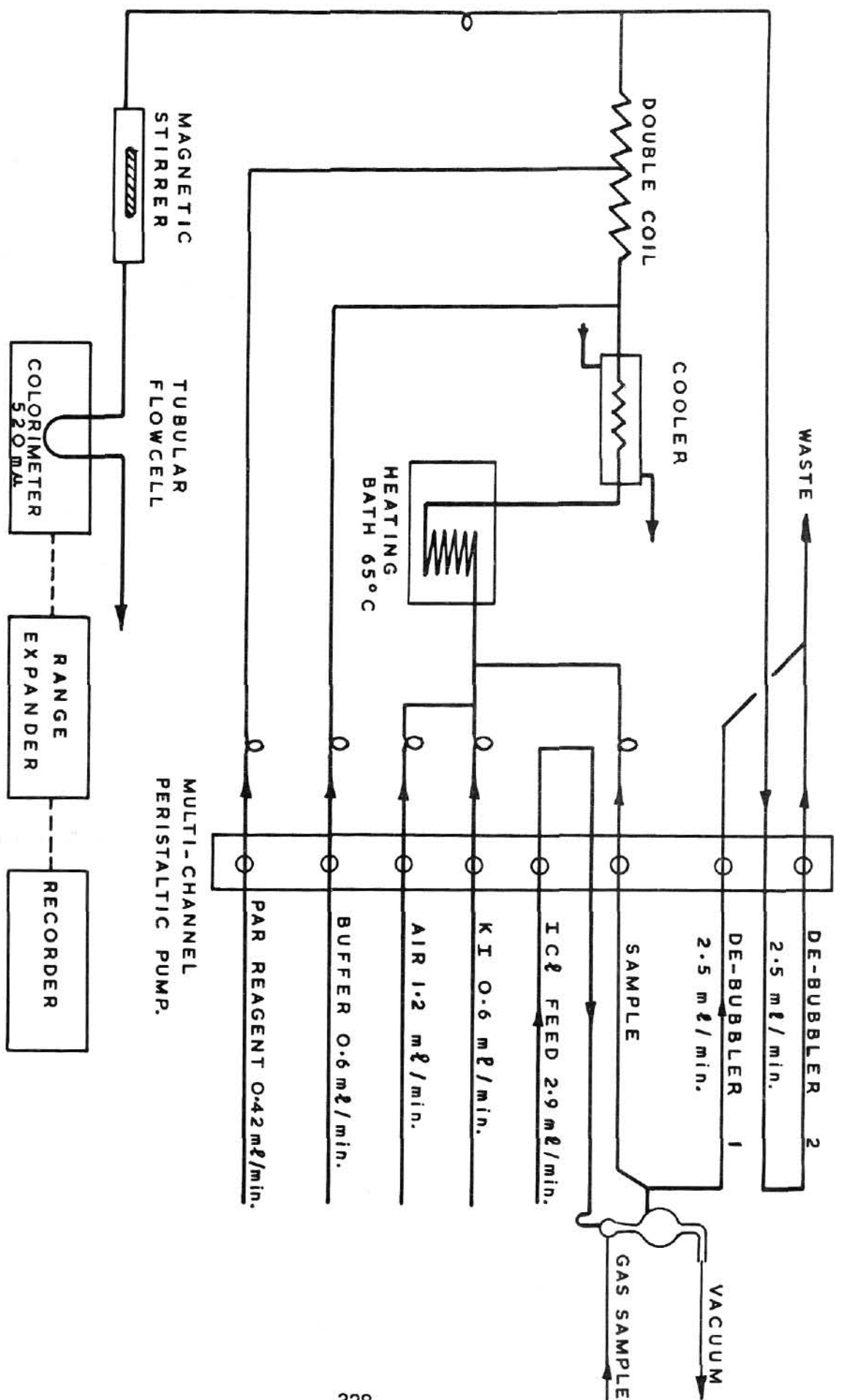


FIG. 1. MANIFOLD ASSEMBLY & SCHEMATIC OF TECHNICON LEAD-IN-AIR MONITOR.

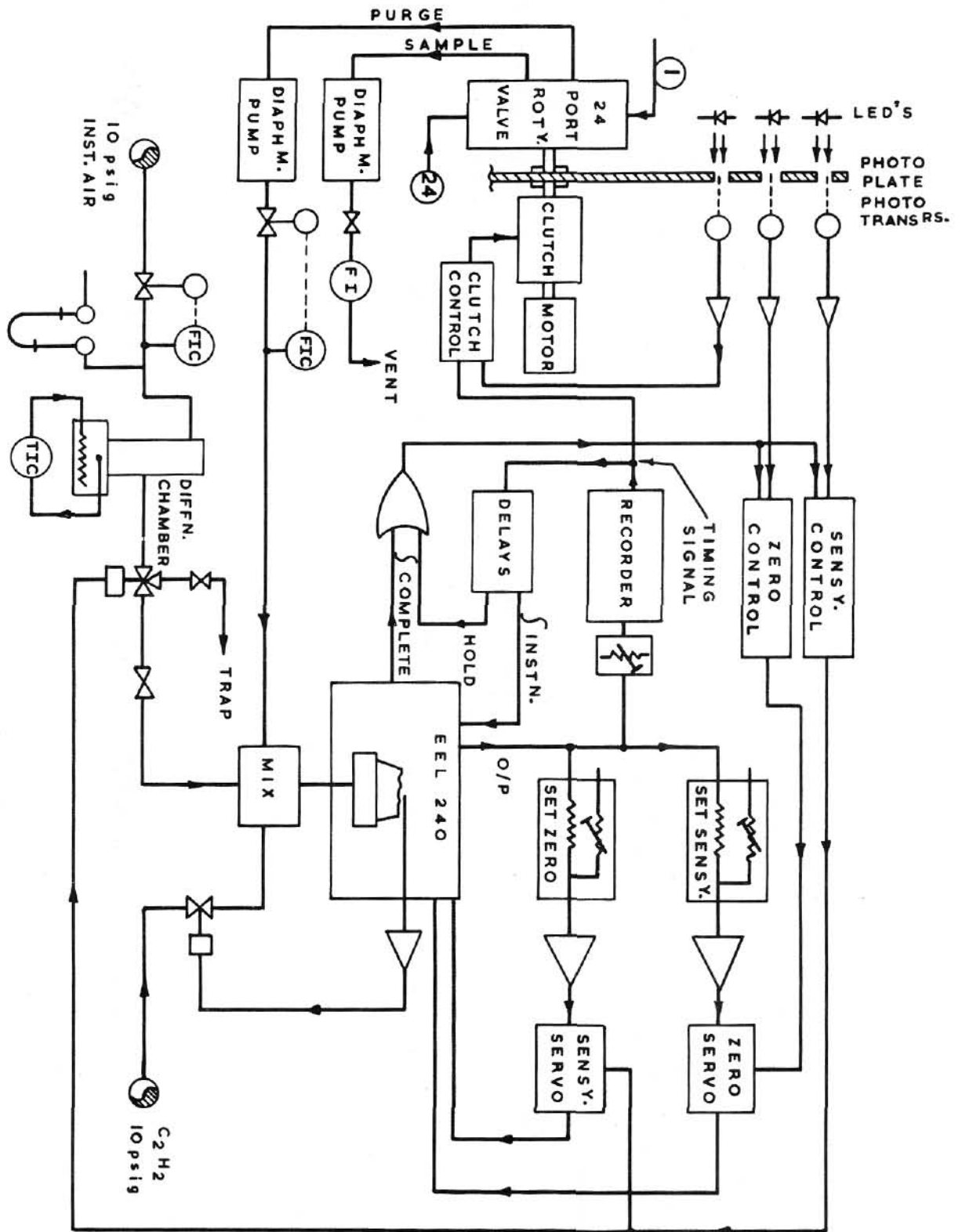
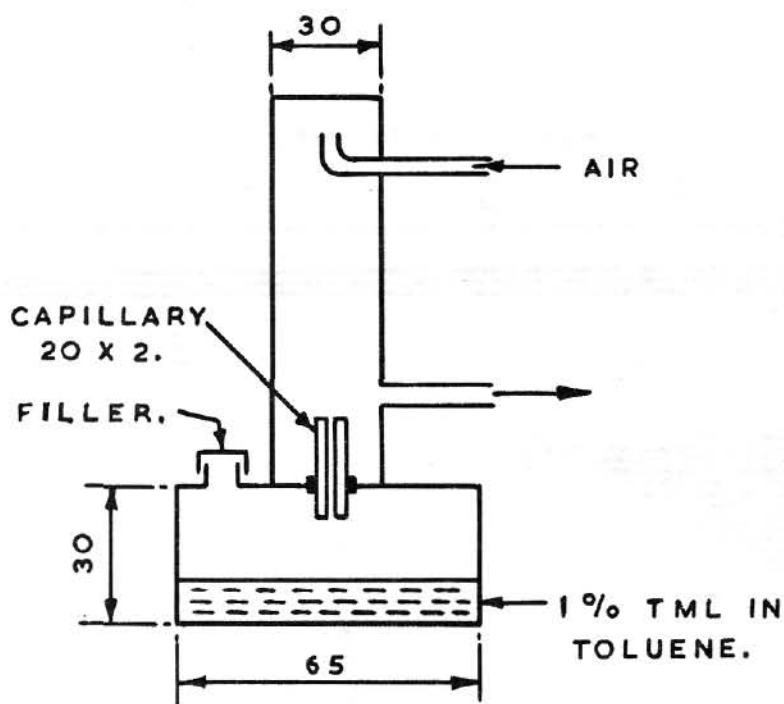


FIG. 3. SECOND OTEL CONTINUOUS LEAD-IN-AIR MONITOR.



SCHEMATIC AND NOT TO SCALE.

DIMENSIONS IN mm.

$$r = \frac{D P M A}{R T L} \ln \pi$$

WHERE:

r = DIFFUSION RATE G/SEC.

M = MOLECULAR WT.

P = TOTAL PRESSURE.

A = CROSS SECTION OF TUBE.

L = LENGTH OF TUBE.

T = ABSOLUTE TEMPERATURE.

R = GAS CONSTANT.

D = DIFFUSION COEFFICIENT.

p = VAPOUR PRESSURE.

$$\pi = \left(\frac{P}{P-p} \right)$$

FIG. 4. DIFFUSION DILUTION CHAMBER.

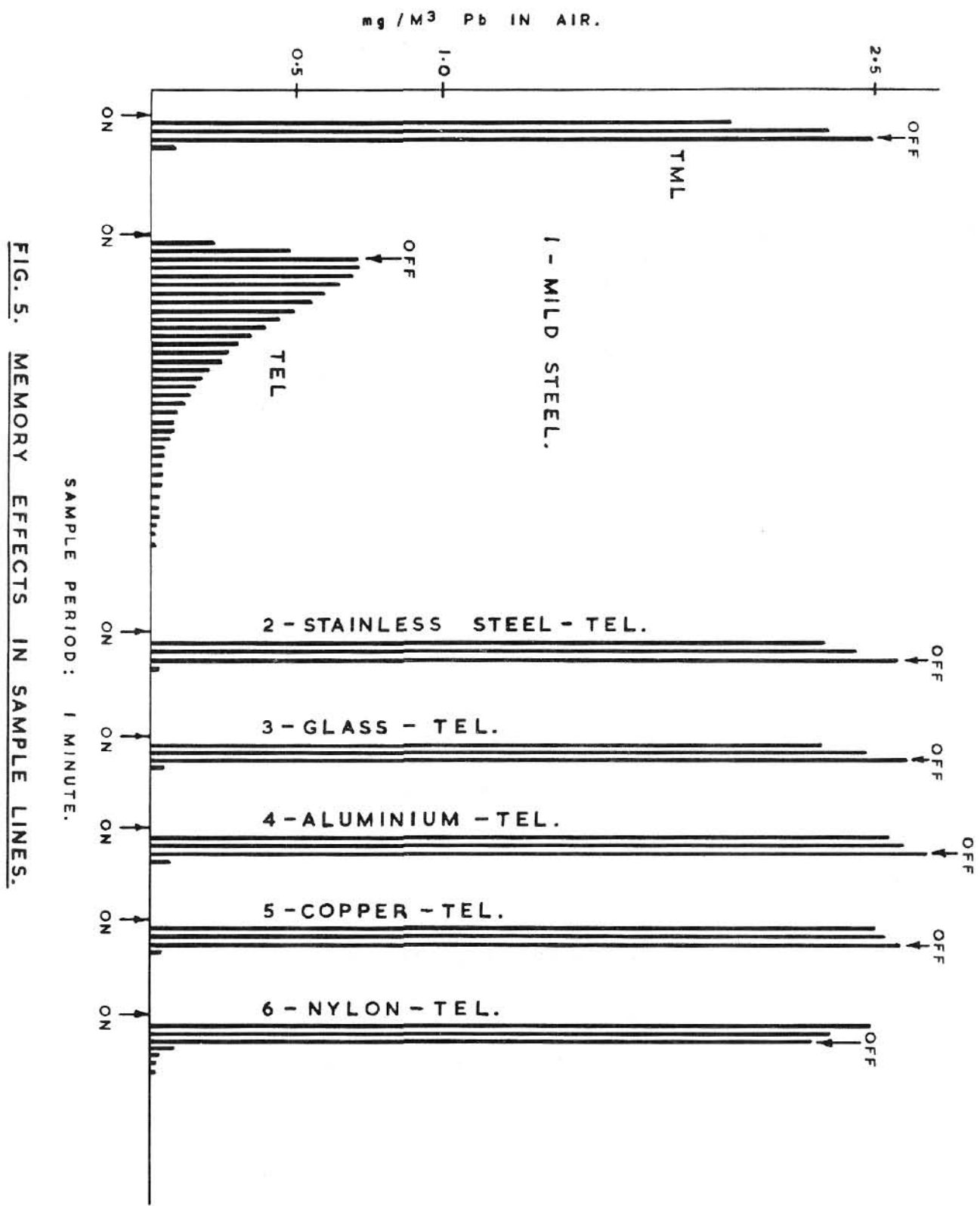


FIG. 5. MEMORY EFFECTS IN SAMPLE LINES.

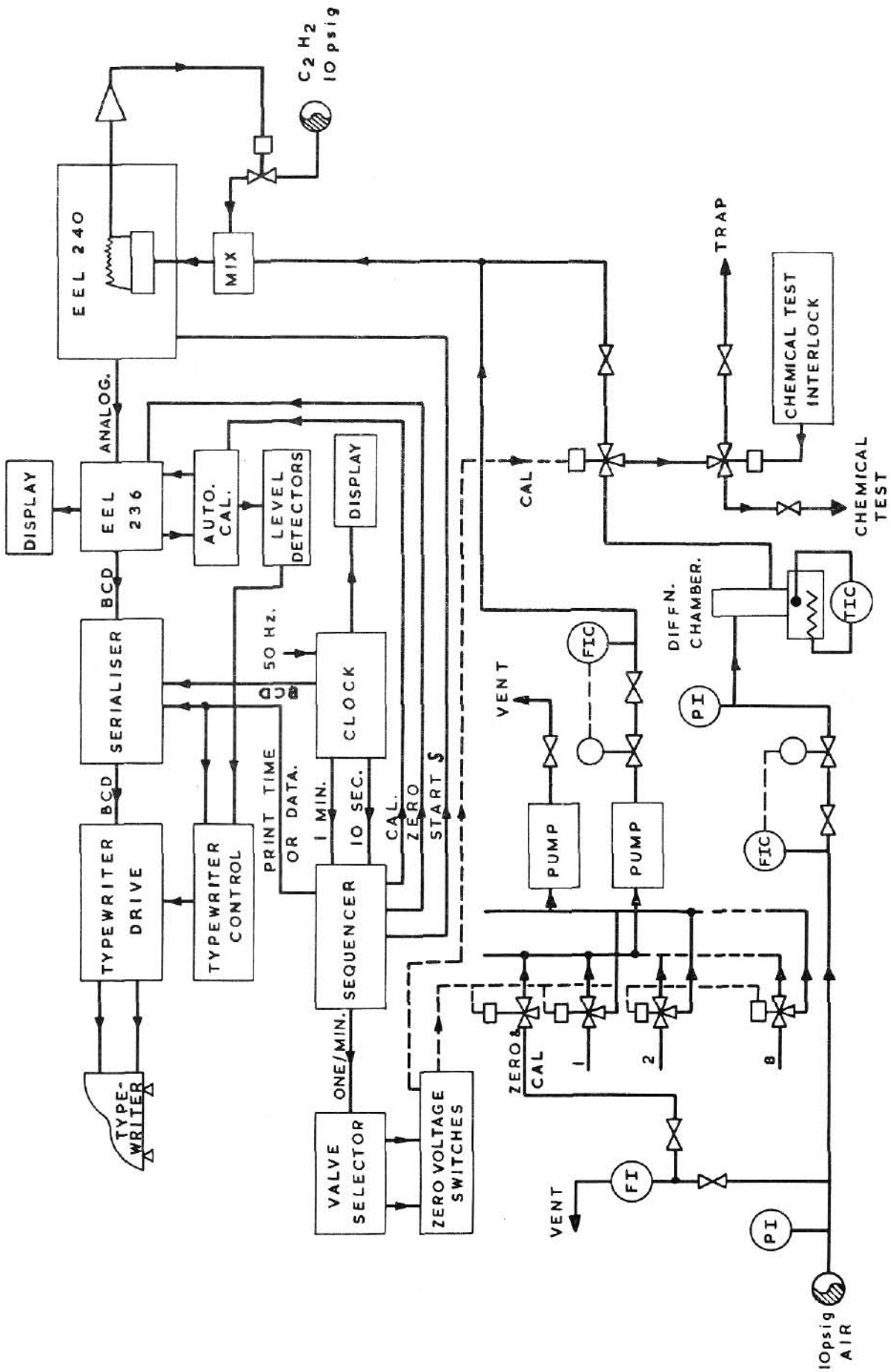


FIG. 6. THIRD OCTEL CONTINUOUS ORGANIC LEAD-IN-AIR MONITOR.

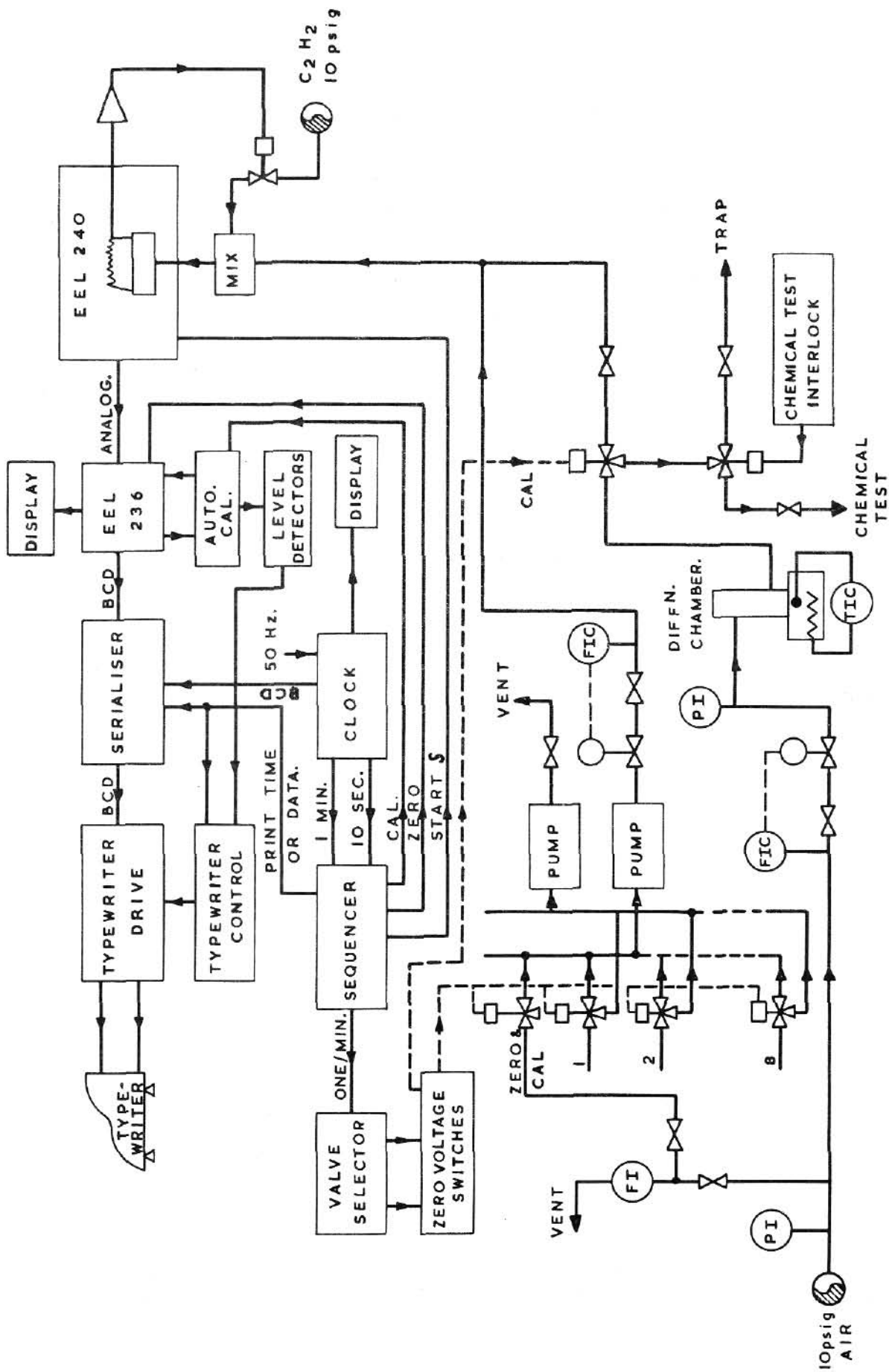


FIG. 6. THIRD OCTEL CONTINUOUS ORGANIC LEAD-IN-AIR MONITOR.