

RESPIRATOR FILTERS IN PROTECTION AGAINST LOW-BOILING COMPOUNDS

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INTRODUCTION

Today the use of filters for respirator protection against harmful gases and vapors is widespread both **in** industry and at all other places where dangerous or unpleasant contaminants are present or can be expected to be present in the air.

The more common filter types are the so-called **A**, **B**, **E** and **K-filters** as classified in accordance with the new **CEN-proposals** for a European **Standard**.¹

The **mode** of action of these filters is one or more of the following as outlined in Table 1.

TABLE 1

Mode of Action	Active Substance	Examples
Adsorption	Sorbent	Activated Charcoal
Chemical Interaction	Impregnant or Chemical Filling	Metal Salts or Soda Lime
Catalytic Interaction	Impregnant or Chemical Filling	Metal Salts

The reason for having **different** types of filters based on different working principles is that substances, organic as well as inorganic, are generally poorly retained in a sorbent filter if these substances have low boiling **points**, i.e., boiling points below approximately 65°C. The filter types **B**, **E** and **K** have been known for many years and are designed to deal with a number of inorganic gases, e.g., Hydrogen Cyanide, Chlorine, Sulphur dioxide and Ammonia, but only recently attention has been paid to the problems of protection against low-boiling organic compounds. The type-A filter, which contains activated charcoal as the active substance, has generally been used for protection against gases and vapours of organic compounds regardless of the boiling points of these compounds. It is well known that the capacity of a sorbent filter decreases with decreasing boiling point of the sorbate, i.e., the contaminant, and this gives rise to two important questions when the **A-filters** are used against the lower-boiling organic compounds:

1. Is the capacity of the filter sufficiently high to give reasonable protection for a reasonably long time?
2. Will desorption take place if a filter has been partly used and then is re-used at a later time?

LOW-BOILING ORGANIC COMPOUNDS

Low-boiling organic compounds are **defined** as organic compounds with a boiling point lower than 65° C. This limit has not been arbitrarily set. It was set to include the critical substance methanol into the group of low-boiling organic compounds. **Special** problems arise with methanol as the capacity of a charcoal **filter** for this substance is much smaller than would be expected for a substance with a boiling point of 64° C. A number of other organic compounds with lower boiling **points**, e.g. acetone (**b.p.** 56° C) and **diethylether** (b.p. 35° C), are better retained in a charcoal **filter** than methanol. A comparison of the results obtained in breakthrough tests with methanol and e.g. **tetrachloromethane** (b.p. 77° C) on the same filters under the same test conditions shows that the breakthrough time with methanol is about five times shorter. The results are shown in Table 2. Information on filter capacities for most of the low-boiling organic compounds is **insufficient**. Some results have been published e.g. on Vinyl **Chloride**², Methyl Bromide ³ and a few other **substances**^{4,5}, but for the majority of compounds no information exists. Some examples are given in Table 3.

In our laboratory a study was undertaken to determine the **efficiency** for removal of methanol of four different European respirator filters of the A-type. The study included a normal sorption test i.e. determination of the breakthrough time at specified conditions and in addition to the breakthrough test a desorption test was carried out on partly used filters.

EXPERIMENTS WITH METHANOL

Respirator Filters Tested

Type-A filters from four European manufacturers were tested. In the following they are denoted types **I-IV**. They were all medium capacity **filters** with carbon content ranging from 112 to 176 grams (dry **weight**). The filters were tested in the "as **received**" state i.e. with their original water content of a few percent.

Apparatus

The apparatus is shown in Figure 1. A primary air stream is purified in a column containing activated **carbon**, silica gel and Ascarite. Then it is passed to a **vapourization** spiral in the top of which the liquid test substance is injected from a peristaltic pump (LKE 12,000 **Varioperpex**). A secondary air stream is also purified in a column containing activated **carbon**, silica gel and Ascarite. Then it is passed to a bubbling tower for **humidification**. The primary and the secondary air streams are combined in a mixing bottle of 25 liters and either led to the filter under test or to a bypass which enables the filters to be changed without interrupting the flow of test gas. Part of the effluent air (30 ml/min) is led to a flame ionization detector (**Perkin-Elmer F11**) and the signal of the detector is continuously recorded during the test. The main stream of test gas is passed through a **flowmeter** (**Rotameter**) and a wet and dry bulb **psycrometer** to an outlet.

TABLE 2

TEST SUBSTANCE	TEST CONCENTRATION PPM	BREAKTHROUGH MIN.	TIME CAPACITY G/FILTER	BOILING POINT OF TEST SUB- STANCE °C
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CCl ₄ ^x	10000	35	67	77
CH ₃ OH ^{xx}	10000	7.8	3.1	64

FILTER TYPE I, 30 ± 0.5 1/min. 75 + 5% R.H..

^x BREAKTHROUGH CONCENTRATION: 10 PPM

^{xx} BREAKTHROUGH CONCENTRATION: 200 PPM

TABLE 3

SUBSTANCE	TLV PPM	BOILING POINT °C
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ACROLEIN	0.1	52
ETHANETHIOL	0.5	37
ETHYLENEIMINE	0.5 Cane.	56
CHLOROPRENE	10	59
DIAZOMETHANE	0.2 Canc.	-24
KETONE	0.5	-56
METHYLISOCYANATE	0.02	37
PROPYLENEIMINE	2 Canc.	63
VINYL BROMIDE	?	16

TABLE 4

TYPE OF FILTER	AMOUNT OF CHARCOAL G	BREAKTHROUGH TIME ^x MIN	DOSING TIME ^x MIN	DOSING TIME IN PERCENT OF BREAK-- THROUGH TIME	MAX. EFFLUENT CONCENTRATION PPM	TIME SPAN, MIN, C_E IS GREATER THAN C_{MAC}
I	112	11.4 - 14.6	7	48-61	431-515	78-87
II	152	23.6 - 23.9	12	50-51	603-621	121-126
III	176	7.9 - 14.1	5	35-63	302	61
IV	173	9.5	5	53	538-556	50-53

^x TEST CONDITIONS: $C_I = 5500$ PM V = 30 ± 0.5 L/Min. and $75 \pm 5\%$ R.H.

Sorption Tests

Filter types **I-IV** were subjected to sorption tests to determine breakthrough times and **filter** capacities with a test concentration of 5500 ppm, a flow rate of 30 l/min and a test humidity of 75%.

The threshold limit value of **methanol** (200 ppm) was taken as the breakthrough **concentration**. The results are given in the first columns of Table 4.

Filter type I was subjected to further breakthrough tests at lower concentrations. These results are given in the first columns of Table 5 and it follows that the breakthrough capacity increases with increasing test concentration. Additional tests carried out have shown that the relationship between breakthrough capacity and influent concentration can be mathematically described by a **Langmuir** expression i.e.

$$M = \frac{c_i \cdot \sigma}{1 + \nu c_i}$$

where M is the breakthrough **capacity**, c_i is the influent concentration and σ and ν are **constants**. The resulting curve is given in Figure 2.

Desorption Tests

Filter types **I-IV** were dosed at the previous test conditions to about **fifty** per cent of their breakthrough capacity. After dosing, the filters were stored for about an hour before clean air (30 ± 0.5 l/min, $75 \pm 5\%$ R.H. and $22 \pm 1^\circ$ C) was passed through them. The effluent concentrations found and the time span during which the threshold limit value of 200 ppm was exceeded during the desorption tests are given in Table 4.

In some additional experiments filter type I was dosed with the same amount of methanol (0.6 g) at four different concentrations. The dosage corresponded to **20-80** per cent of the breakthrough capacity of the filters.

After dosing, the filters were stored for about an hour before desorption was started. The desorption was carried out with clean air (30 ± 0.5 l/min, $75 \pm 5\%$ R.H., 20 ± 2 and $25 \pm 2^\circ$ C) and the **effluent** concentration was continuously monitored. The results are shown in Figure 4-5 in Table 5.

RESULTS AND DISCUSSION

Breakthrough Times

The breakthrough times of the four filter types differed widely. The best results were obtained with filter type II. The difference between the breakthrough times found for filter types I and II is mainly due to the different amounts of charcoal in the filters as the capacities on a weight to weight basis are in the range of 0.03 grams of **methanol** per gram of charcoal for both filters. The poor results obtained in the tests on filter types III and IV are caused by the considerably lower activity of the charcoals in these filters as the amount of charcoal is about the same for both filter types and much higher than found in filter types I and II.

Desorption Curves

The highest concentration in the effluent air found during the desorption experiments amounted to 600 **ppm**. This was found for filter II which also had received the biggest dose as all filters were dosed to about 50 percent of their breakthrough capacity. This result caused us to conduct further experiments on a single filter type (I) to investigate the effect of the size of the dose and dosing concentration. Also the effect of desorption temperature was investigated in these tests.

The effect of concentration was found to be small. The effluent concentration increased only little with increasing dosing concentration when filters were dosed with the same amount of methanol (9.6 g) as seen from Fig. 4-5 and Table 5. The maximum effluent concentrations found were in the range of the threshold limit value of 200 ppm.

The effect of temperature was established. Desorption at 25° C gave a somewhat higher effluent concentration than desorption at 20° C as can also be seen from Fig. 4 and 5.

CONCLUSIONS

Safe Initial Dose

The results obtained in the desorption tests on filter type I show that a safe initial dose exists when this filter is used for protection against methanol.

If the filter is used under working conditions where it is loaded with 600 mg of methanol and then re-used at a later time in a clean **atmosphere**, then the maximum concentration of desorbed methanol in the effluent air will only be in the range of the threshold limit value.

Assuming that concentration of methanol vapours in the working environment is 1000 ppm (1333 mg/m³), and a breathing rate of 30 l/min. the following calculation of time can be performed:

$$t = \frac{M}{v c_i} = \frac{600}{0.030 \cdot 1300} = 15 \text{ min}$$

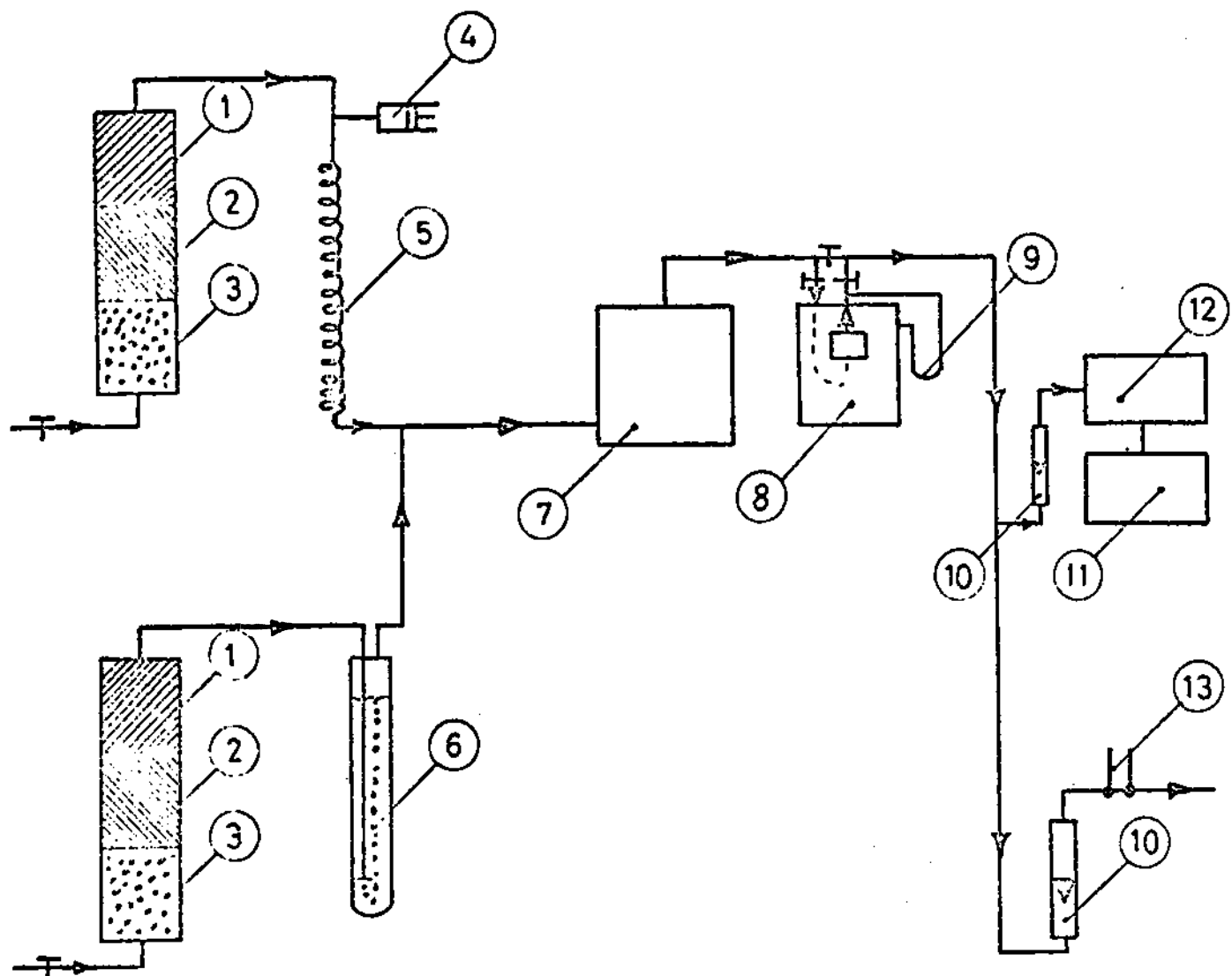
where M is the safe initial dose (mg), v is the breathing rate (m³/min) and c_i is the ambient concentration of methanol (mg/m³). Under these circumstances the filter can be used for 15 minutes in the contaminated area and if used in clean air later on the desorption can be neglected.

Impact on Standardization

The results presented together with the other results referred to have formed the basis for part of the new draft for a European Standard (CEN) for combined filters.¹ It is said in the draft: "Filters for use against substances boiling below 65° C shall be capable of passing a desorption test in addition to the normal sorption test, as specified." The specified test conditions for the desorption tests are almost identical to those presented here.

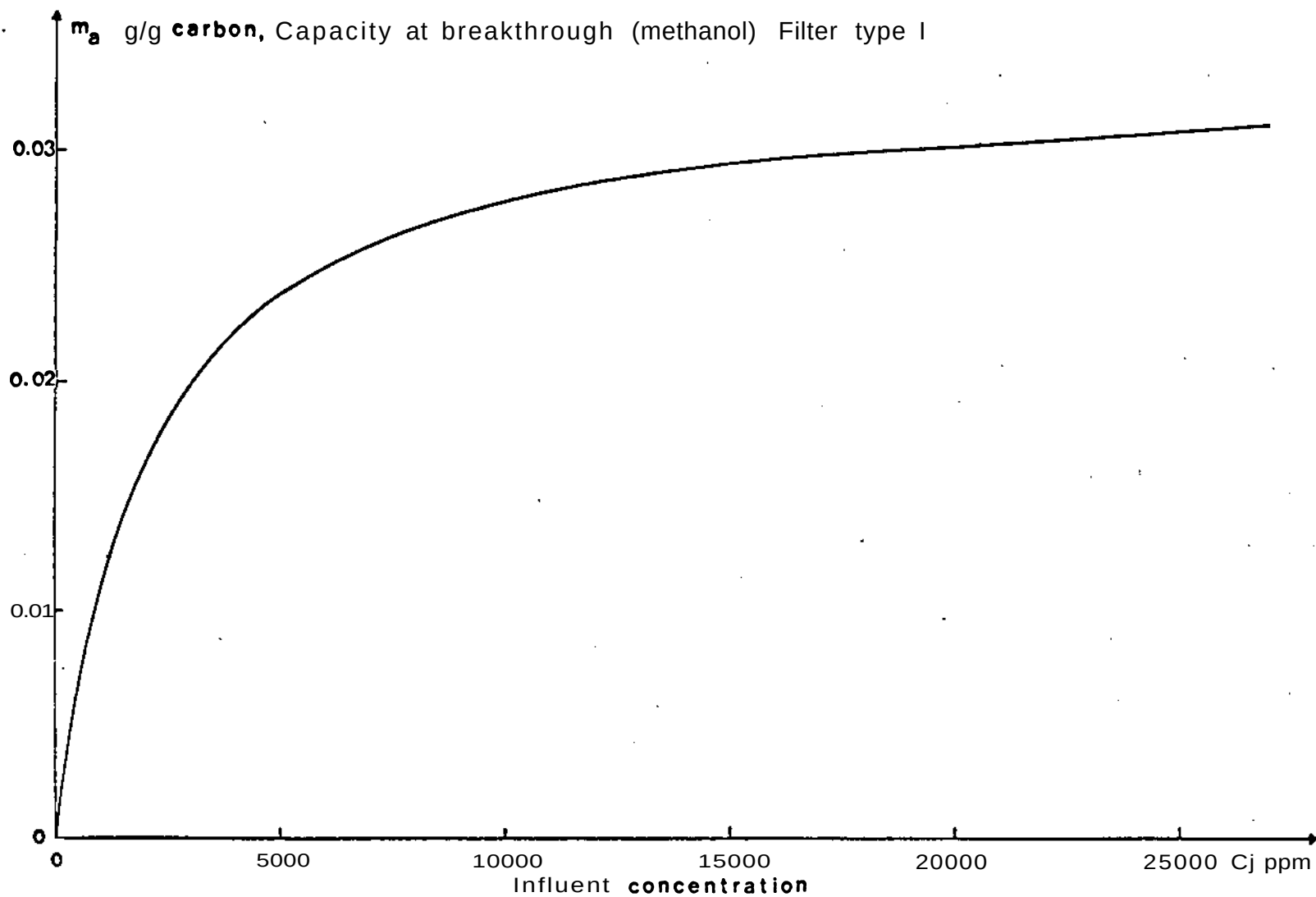
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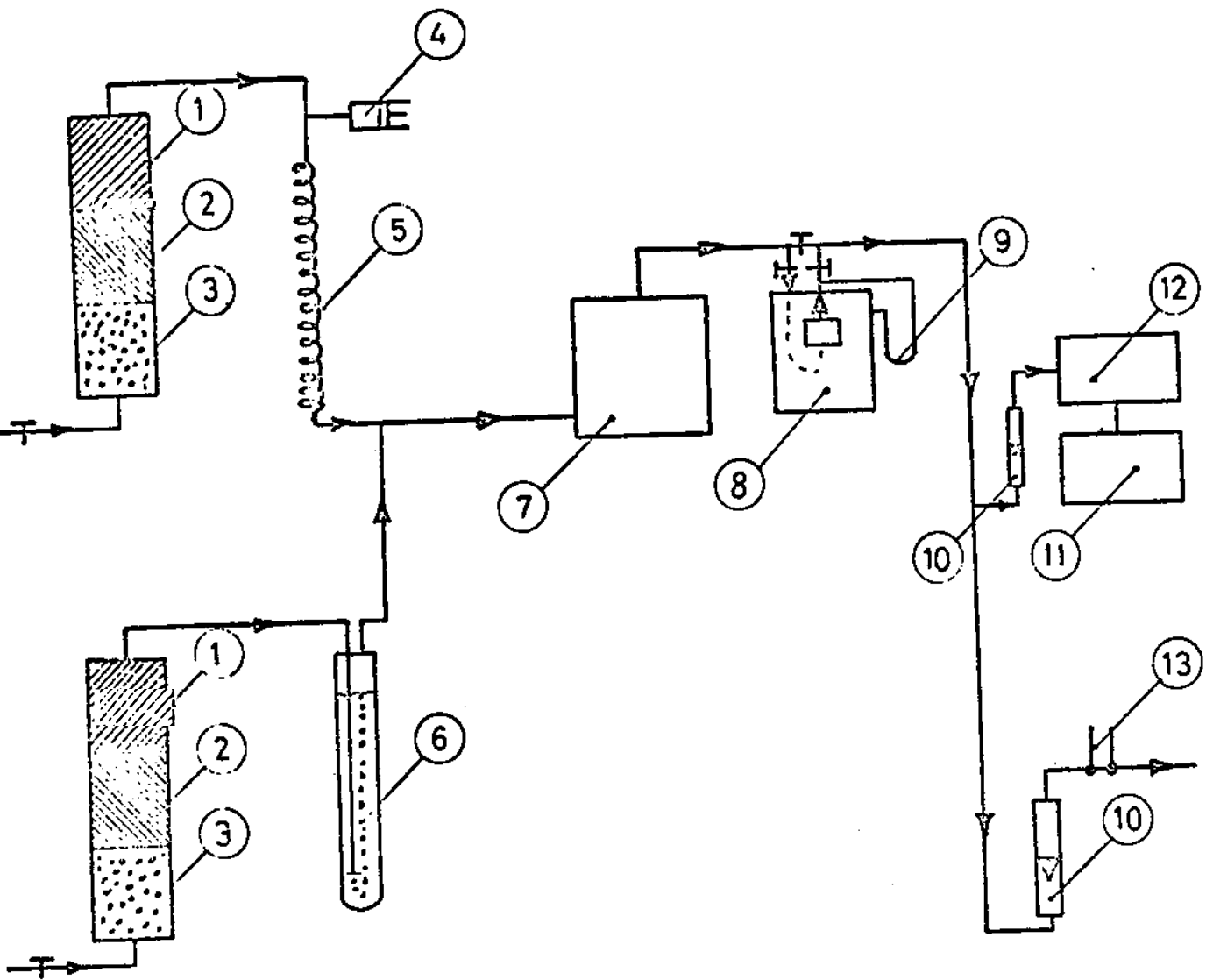
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3. Maggs, F. A. P. Ann. Occup. Hyg. 18 (1975) 111.
4. Nelson, G. Ann. Industrial Hygiene Association J. 35 (1974) 391.
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1. Ascarite.
2. Activated carbon.
3. Silica gel.
4. Peristaltic pump.
5. Vapourization spiral.
6. Humidifier.
7. Mixing bottle.
8. Filter under test.
9. Manometer.
10. Flowmeter.
11. Recorder.
12. Flame ionization detector.
13. Pycrometer.

Fig. 1.





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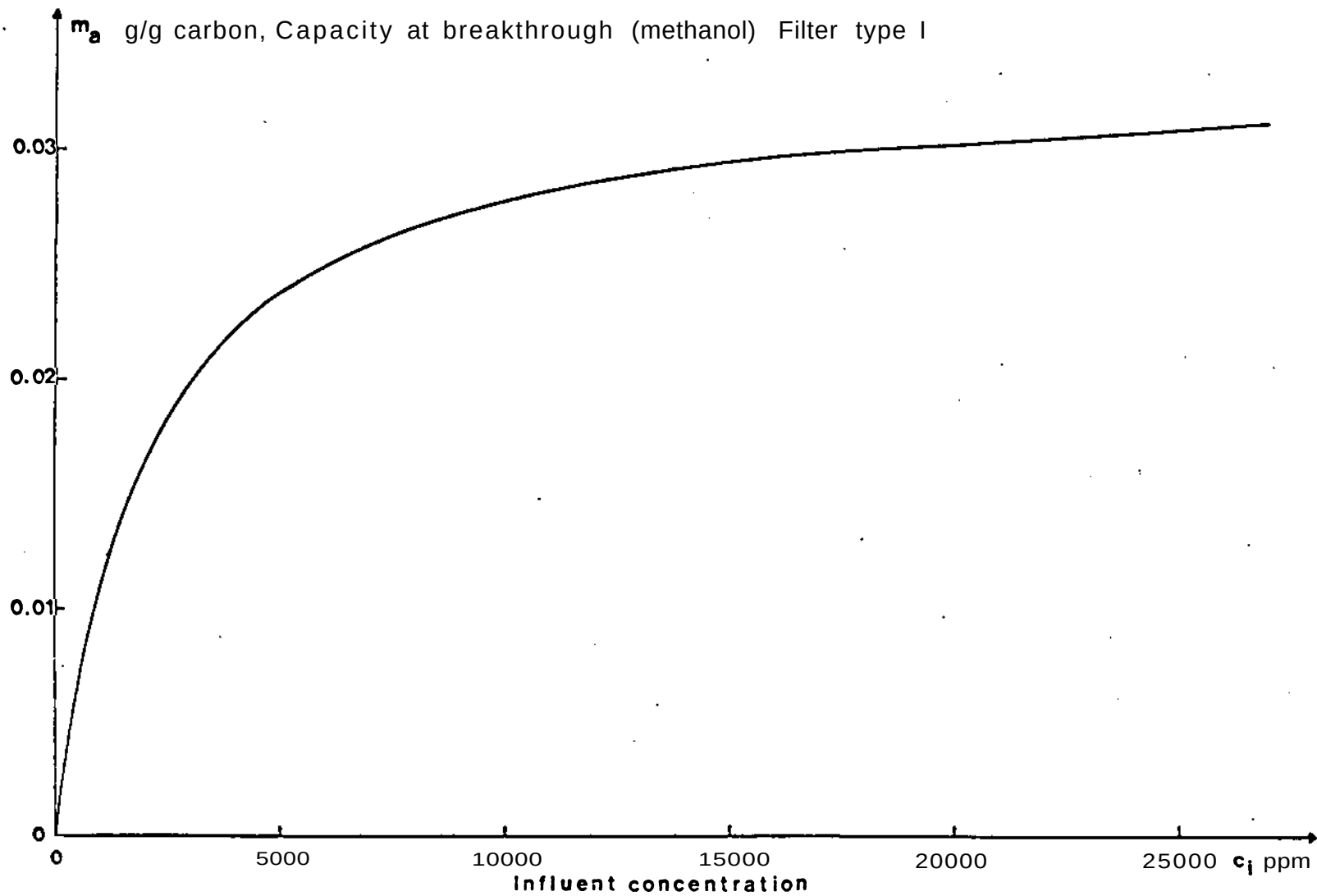
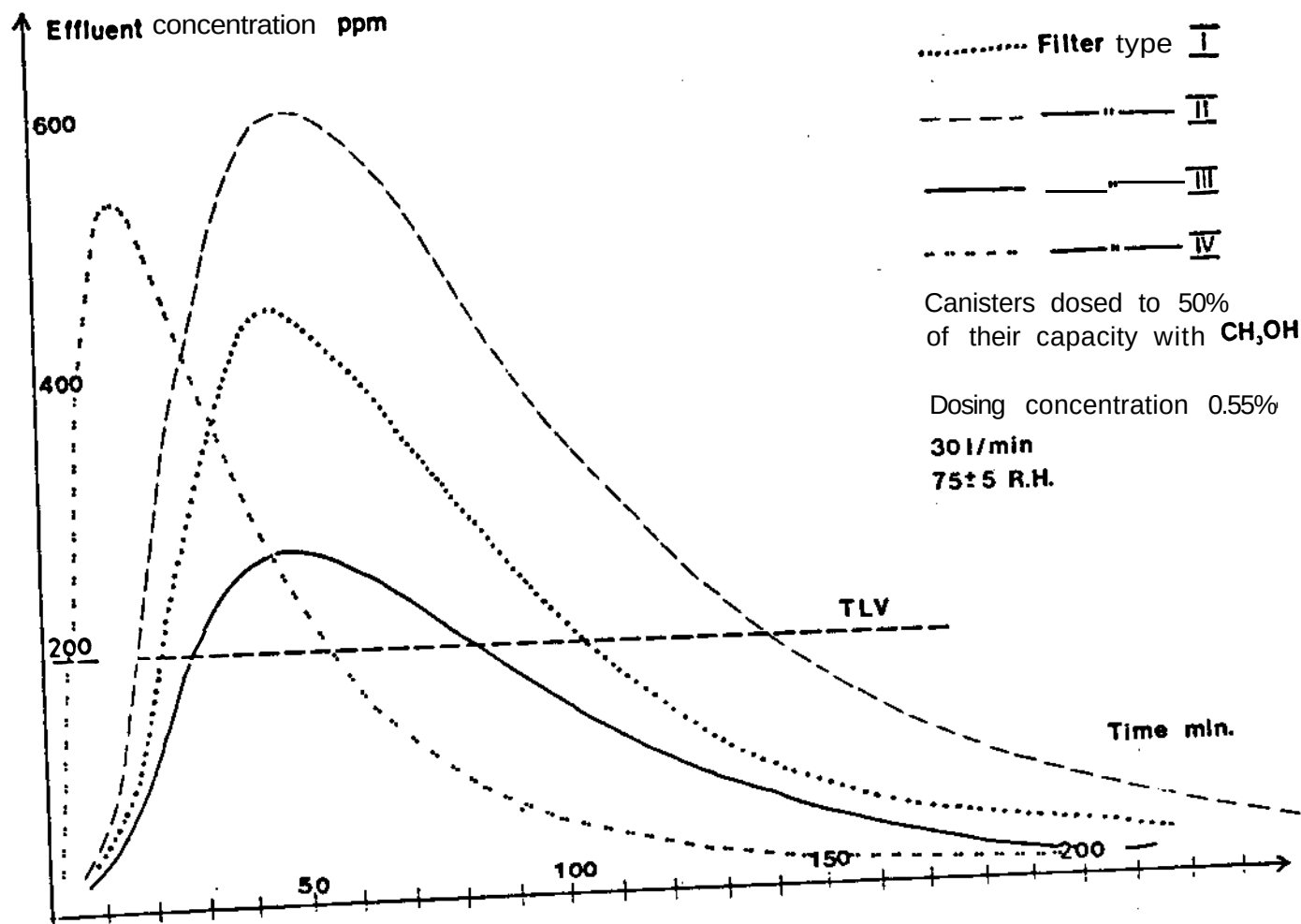


Fig. 2.



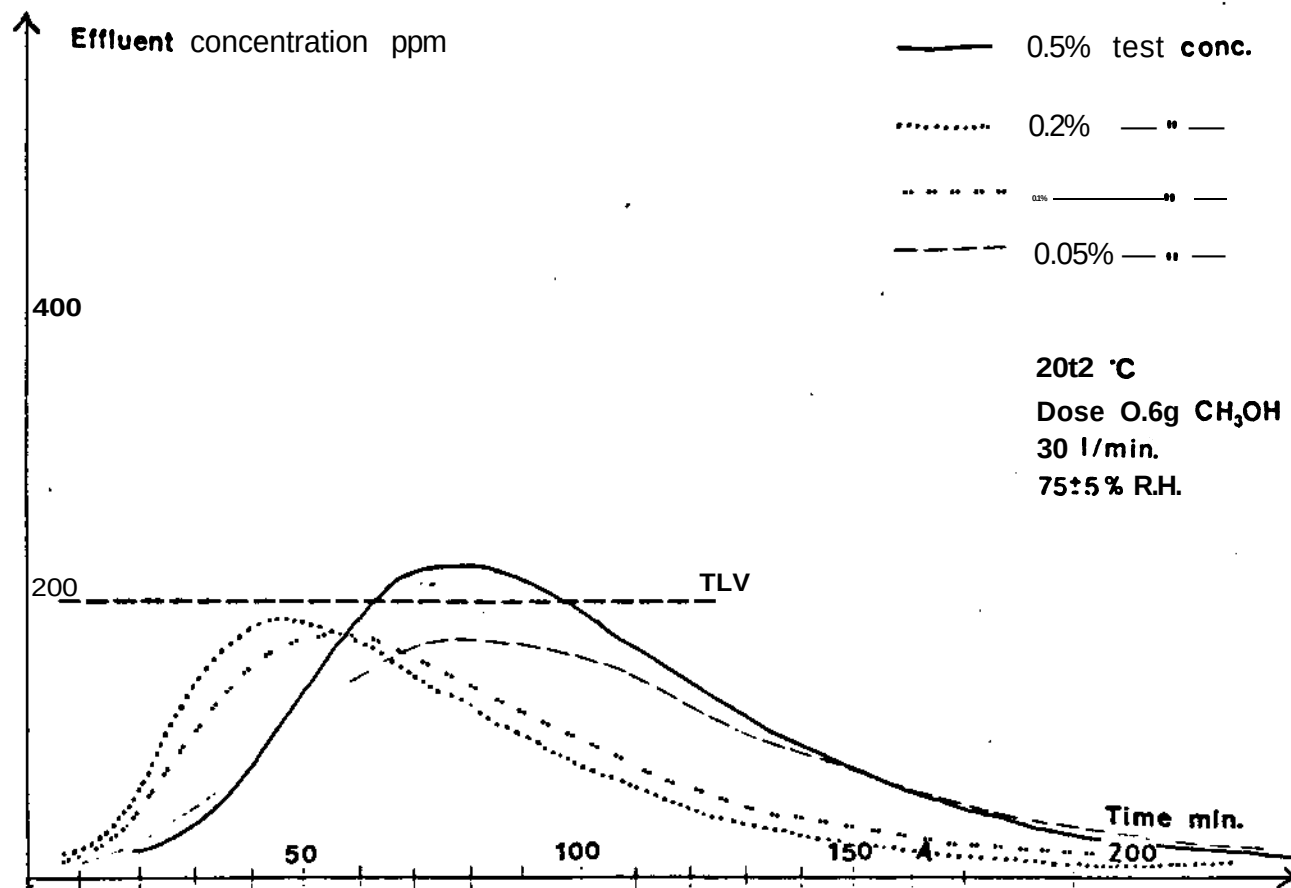


Fig. 4.

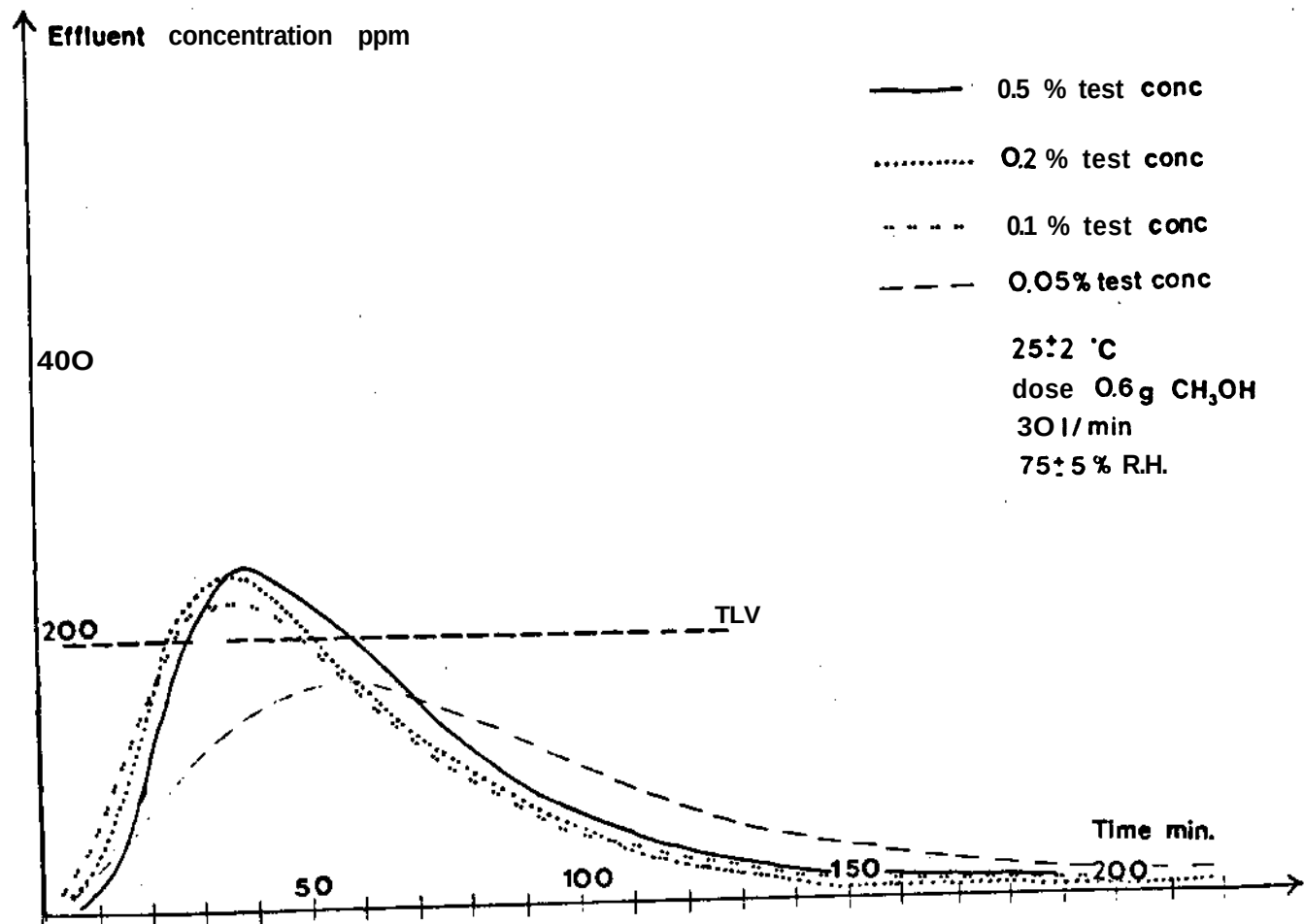


Fig. 5.