Original

ēir	Technische Mitteilung	TM-HL-235

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Betrifft: Synthesis and Gas Chromatography of Selected Metal Chlorides.	Datum: 20.8.74
	45 Seiten
	Zeichnungen

Contents

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1. Synthesis of Molybdenum Chlorides

1.1. Aim of Work

In the project of a Molten Salt Fast Breeder Reactor[1] the chloride of plutonium-239 (15%) diluted by sodium chloride is the molten fuel. Molten fertile material is UCl_3-238 (65%) plus sodium chloride besides newly bred $PuCl_3$ and fission products which acts also as blanket material and as coolant. Molybdenum is one of the fission products and forms low volatile chlorides with chlorides present. It is also one of the most important construction materials and will probably be used in this type of reactor.

Therefore, our aim was to synthesize molybdenum (V,III,II) chloride-samples which could be used in the experiments for the project.

1.2. Introduction

Experiments were done to synthesize molybdenum penta- and tri-chlorides.

1.2.1. Synthesis of Molybdenum Pentachloride:

The method used was the reaction of molybdenum(VI)oxide with boiling hexachloropropene.

$$MoO_3 + 3 C_3Cl_6 \rightarrow MoCl_5 + 3 C_3Cl_4O + 1/2 Cl_2$$
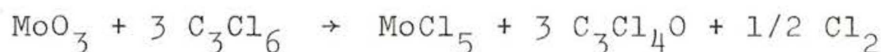
Porterfield and Tyree, Jr[2] showed that the method used by Herman and Suttle for the preparation of uranium(IV)chloride[3] from uranium(IV)oxide and hexachloropropene can be conveniently extended to other polyvalent metal chlorides.

$$M_2O_n + nC_3Cl_6 \rightarrow 2\ MCl_n + nC_3Cl_4O$$

They added: "These chlorides are well characterized and have long been prepared by satisfactory means. However, the method described has the advantages of greater convenience and rapidity, indifference to small amounts of water on the oxides (the water is converted to hydrogenchloride and trichloro-acrylic acid)

$$C_3Cl_6 + 2\ H_2O \rightarrow C_3Cl_3O_2H + 3\ HCl$$

relatively complete conversion of the oxide to the chloride, and products which are easy to separate and purify."

1.2.2. Synthesis of Molybdenum Trichloride

Two methods were used for the synthesis of molybdenum trichloride.

1.2.2.1. Reduction of Molybdenum pentachloride with hydrogen:

This reduction is carried out by passing a current of pure and dry hydrogen over molybdenum pentachloride.

$$MoCl_5 + H_2 \rightarrow MoCl_3 + 2HCl$$

The purification of hydrogen is very important, because the formation of oxychloride must be avoided. It is also necessary to Keep the reaction temperature under $194^\circ C$ in order to avoid the formation of a cake in the molybdenum pentachloride mass (see table 1).

Substance	mp, $^{\circ}C$	color
$MoCl_5$	194	black
$MoCl_4$	317	brown
$MoCl_3$	1027	dark red
$MoCl_2$	decomp.	yellow
$MoOCl_3$		green
$MoOCl_4$		green

Table 1 Physical properties of molybdenum chlorides
and oxychlorides[4]

1.2.2.2. Reaction of Molybdenum(VI)oxide with Hexachloropropene

The analysis of molybdenum chloride which had been synthesized
by the method (1.2.1.) showed that the stoichiometric ratio of
chlorine to molybdenum was close to 3 (see 1.4.1.) that shows
another possibility to synthesize molybdenum trichloride by the
same method but for a longer time as to complete the reduction.
Besides this Larson and Moore[5] reported that in preparation of
molybdenum tetrachloride by the reaction of molybdenum penta-
chloride with refluxed chlorobenzene, substantial formation of
molybdenum trichloride occured after extended reflux periods
(greater than 10 hours). It is possible that hexachloropropene
can be used instead of chlorobenzene in excess, due to its resem-
blance also being unsaturated, and able to reduce molybdenum
pentachloride to -trichloride.

1.3. Experimental

1.3.1. Synthesis of Molybdenum Pentachloride

200 ml of hexachloropropene (1.41 mole) and 20 g of molybdenum(VI) oxide (0.14 mole) were put in a 250 ml round-bottomed flask with a reflux condenser. The upper end of the condenser terminated in a drying tube. The flask was filled with argon. The reaction mixture was brought to the boiling temperature by means of a heating mantle and refluxed for 15 minutes, until reaction was complete shown by a color change from yellow to dark red. Argon was continuously flushed through the system. The more slowly the cooling process is performed, the larger is the size of the individual crystals obtained. Therefore, the flask was well insulated and allowed to cool to room temperature for 3 hours. The crystals were very dark-colored under a dark red solution. The flask was removed from the reflux condenser and closed immediately with a sintered glass filter tube. The upper end of the tube terminated in a round-bottomed flask in which the filtrate can be collected.

Then the whole system was inverted and the metal chloride was separated from the solution by filtration. During this time, argon was still in charge into the reaction flask. The filtering operation was completed slowly in about 3 hours. Before the filtration was completed, the crystals were washed three times with previously dried CCl_4 which was added by opening the system when the crystals were still covered by solution.

After the filtration process, the round-bottomed flasks at both ends of the filter tube were replaced by dry argon filled flasks. The molybdenum pentachloride crystals were then sucked and dried under vacuum. Finally, the system was transported into the glove-box and opened.

1.3.2. Synthesis of Molybdenum Trichloride

### 1.3.2.1. Reduction of molybdenum pentachloride with hydrogen

The reaction vessel was made of quartz glass. It was equipped with a porous glass try on which the molybdenum pentachloride crystals were put.

After molybdenum pentachloride had been put inside the vessel, in the glove-box, the vessel was placed in a vertical electrical oven (Fig. 1). The vessel had a spiral tube in its lower part so that the entering gas (hydrogen/argon 1:1) was preheated before coming into contact with molybdenum pentachloride. At its upper end the vessel terminated in a drying tube. The leaving gas was passed through water in order to absorb hydrochloric acid to be determined afterwards. The vessel was insulated with glass wool and the reaction was carried out at $167-175^\circ$C for 11 hours. The hydrogen and argon mixture was passed through the molybdenum pentachloride mass in order to prevent back sucking in a possible stop of the hydrogen current. During the reaction the vessel was vibrated continuously to prevent cake formation.

1.3.2.2. Reaction of Molybdenum(VI)oxide with Hexachloropropene

90 ml of hexachloropropene (0.63 mole) and 6 g of molybdenum(VI)-oxide (0.042 mole) were put in a 250 ml round-bottomed flask and the same procedure as for the synthesis of molybdenum pentachloride was followed with the only exception that the mixture was refluxed for 20 hours.

Fig. 1   Reduction of $MoCl_5$ to $MoCl_3$
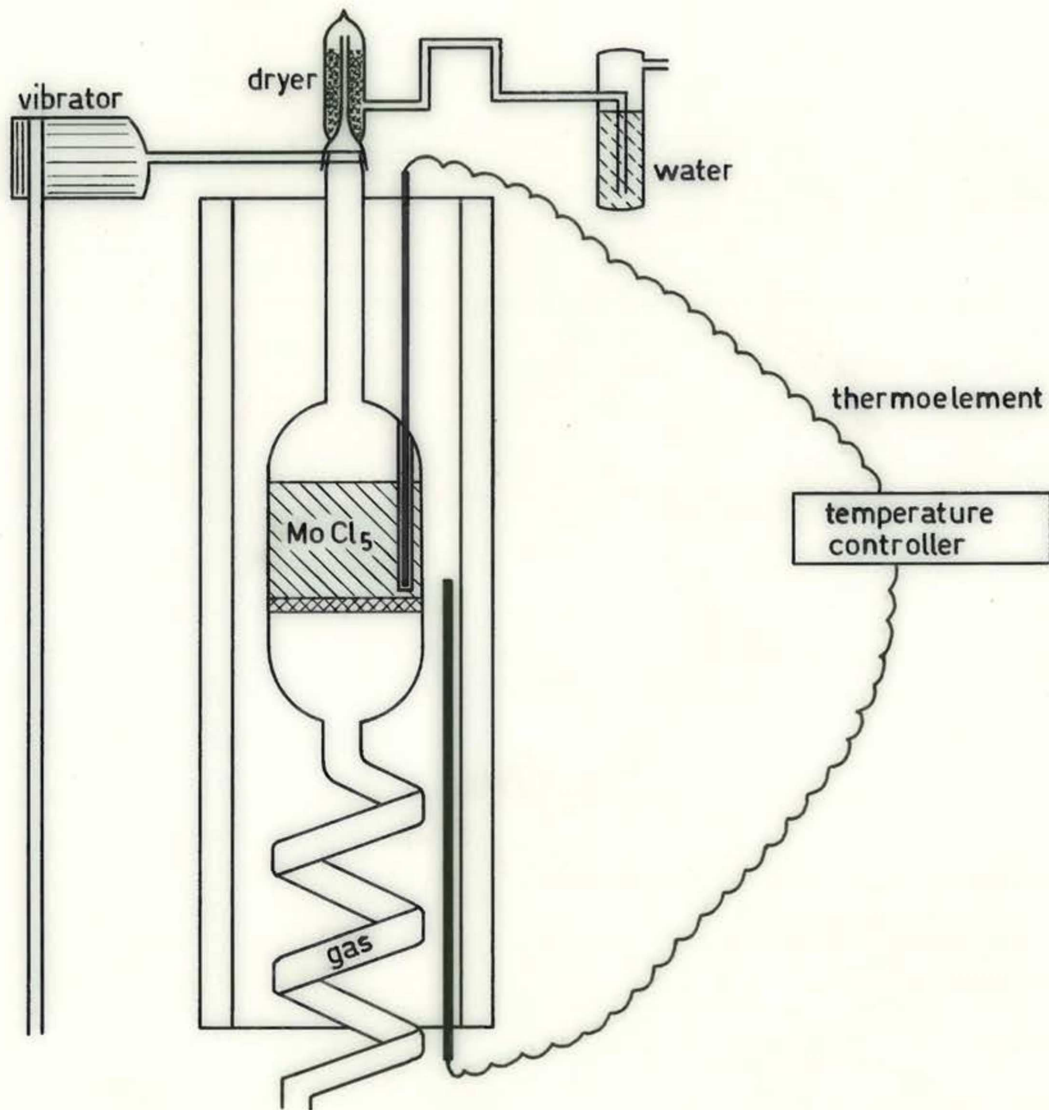
1.4. Results and Discussion

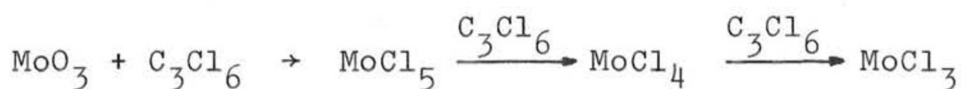### 1.4.1. Synthesis of Molybdenum Pentachloride

Molybdenum pentachloride produced by the method 1.3.1. was analyzed colorimetrically for molybdenum and by a potentiometric method for chlorine *). It was found that the ratio in moles of chlorine to molybdenum was 3.64 and the mass balance of molybdenum and chlorine gave 100.8 percent.

An analysis was also carried out for the chlorine content of molybdenum pentachloride samples by the gravimetric method[6]. The results are shown in table 2 (assuming the absence of impurities)

no	sample weight	chlorine		molybdenum		Cl/Mo
		wt. g	moles	wt. g	moles	in moles
1	0.0766 g	0.0405	0.00114	0.0361	0.00038	3.02
2	0.1277 g	0.0691	0.00195	0.0586	0.00060	3.25

Table 2   Analysis of molybdenum pentachloride samples

From the results of these analyses, the sequence of the following reactions seems reasonable and possible.

$$MoO_3 + C_3Cl_6 \rightarrow MoCl_5 \xrightarrow{C_3Cl_6} MoCl_4 \xrightarrow{C_3Cl_6} MoCl_3$$

On the other hand, because the water content in our glove-box was very high (39 ppm) the hydrolization and oxidation of molybdenum pentachloride could cause deviations in the results.

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*) Performed by R. Keil, EIR-CH

1.4.2. Synthesis of Molybdenum Trichloride

1.4.2.1. Reduction of Molybdenum Pentachloride with Hydrogen

This experiment was done two times with (a) the so called molybdenum pentachloride synthesized in 1.3.1. and (b) the commercial molybdenum pentachloride.

The first one was abondoned afterwards because the results of analysis of molybdenum pentachloride showed the stated composition $MoCl_{3-4}$. Therefore, it was tried to reduce the commercial molybdenum pentachloride to -trichloride. But during the preparation of the reaction vessel, high water content in the glovebox (80 ppm) caused some amount of molybdenum pentachloride to hydrolize and as a result of this hydrolization, the green crystals of molybdenum oxychlorides were observed (see table 1).

The eluted HCl was titrated with sodium hydroxide after 11 hours of reaction time. Table 3 shows the results.

No	N NoOH	VHCl, ml	V NaOH, ml	N HCl	N HCl (expected)*	N HCl/N HCl (expected)
1	0.20	25	10.86	0.0869	0.4654	18.7 %
2	0.25	40	16.19	0.1012	0.4654	21.7 %

Table 3   Determination of the degree of reduction of $MoCl_5$ to $MoCl_3$.

* $MoCl_5$ input = 7 g (0.0256 mole)
  HCl expected = 2 x 0.0256 = 0.0512 mole
  water   = 110 ml
  HCl expected: 0.0512 (1000/110) = 0.4654 N

However, it seems possible to us to perform this reaction under anhydrous conditions.

1.4.2.2. Reaction of Molybdenum(VI)Oxide with Hexachloropropene

Molybdenum trichloride produced by this method was analyzed again by the colorimetric method for molybdenum and by the potentiometric method for chlorine[*] and it was found that the chlorine: molybdenum ratio, in moles, was 3.30 whereas the mass balance of molybdenum plus chlorine gives 100 %.

A gravimetric analysis was as before, carried out for chlorine content of our molybdenum trichloride. Table 4 shows the results (assuming the absence of impurities).

No	sample weight, g	chlorine		molybdenum		Cl/Mo in moles
		wt, g	moles	wt, g	moles	
1	0.2359	0.1284	0.00362	0.1075	0.00112	3.23
2	0.1887	0.1026	0.00289	0.0861	0.00090	3.21

Table 4   Analysis of molybdenum trichloride samples

From the mass balance of molybdenum and chlorine, which is 100 %, it is clear that our product contains no impurity, ie oxides, oxychlorides. In this case the molar ratio of chlorine to molybdenum makes us to think about the incomplete reduction of molybdenum pentachloride to -trichloride. In this case molybdenum trichloride can be separated from the other by means of an appreciable organic solvent in which only it is soluble (ie, alcohol, ether).

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* Performed by R. Keil, EIR-CH

2. Gas Chromatography of Volatile Metal Chlorides at High Temperature

2.1. Aim of Work

Our work is a part of the project of a Molten Salt Fast Breeder Reactor. How are the volatile metal chlorides formed? As already mentioned, the molten fuel, the molten fertile material, the coolant and the blanket material contain chlorides. From the fission products, germanium, arsenic, tin and antimony form volatile chlorides while zinc, gallium, rubidium, zirconium, niobium, molybdenum, cadmium, indium and cesium form low volatile chlorides[7]. Therefore it is possible to collect information about the formation of these volatile metal chlorides by gas chromatography.

2.2. Introduction

Gas chromatography is a technique for separating volatile substances by percolating a gas stream over a stationary phase. It is in analytical application widely. Its greatest advantages are its speed, resolution, qualitative and quantitative analysis and its very great sensitivity.

In general, gas chromatography has largely been concerned with the separation of volatile organic compounds and not too much has been done with metal chlorides. Three trends are apparent in the results reported so far. They involve the use of fused salts, slightly volatile liquids and solid materials as the stationary phase. Fused salts, while useful at very high temperatures, are difficult to prepare on the support, especially in anhydrous form and are subject to reaction with the solutes. The slightly volatile liquids are lost from the column, redistribute on the support, may be thermally unstable, and are capable of reactions with the solutes[8].

The main problem in the qualitative and quantitative application
of gas chromatography in determination of inorganic volatile
chlorides is the choice of an appropriate liquid phase which
does not react with these compounds. In general, reactivity may
be a question of [9]

a)   interaction between solute and the liquid phase (sometimes due
     to the metallic tubing of the columns) resulting in the crea-
     tion of interaction products

b)   sorption of the solute on the solid support, or

c)   the way by which the solutes are dissolved in the liquid phase.

The reactivity of inorganic volatile chlorides with respect to
packing materials and occasionally the difficulty in determining
the magnitude of this effect has often led to different opinions
on the stability of various substances that might be used as
packing materials for the separation of inorganic chlorides.

Conclusions regarding the reactivity may be drawn from (a) obser-
vation of the chromatograms obtained, (b) the possible changes
occuring in the packing material after the experiments, (c) the
ratio of logarithms of specific retention volume to vapor pressure
of liquid phase.

The stability of the baseline and its deviation from zero, the
presence or absence of artefact peaks or the non-appearance of
expected peaks, the symmetry of the peaks looking for tailing and
skewing are the points to be examined so as to draw conclusions
regarding the reactivity. Possible retention of some of the solutes
in the column can be ascertained by checking whether there is any
difference in the weight or color of the column packing material

before and after any series of experiments. Finally one can
obtain indications as to whether or not the solutes are ideally
dissolved in the liquid phase, without any change of their mole-
cular structure, by examining the plot of logarithm of specific
retention volume vs logarithm of vapor pressure which should be a
straight line with a slope equal to unity.

Since in analytical gas chromatography, mg or sub mg amounts of
sample are brought into contact with at least a thousand-fold
amount of column material, it is evident that when reactive sub-
stances are involved, the inertness of column materials has to
meet severe demands. When quantitative results are aimed at, the
use of metals and organic liquids except completely halogenated
products, and diatomaceous supports is not allowed.

The lack of inertness of metals such as copper and stainless
steel is perhaps best illustrated by the ready attack of these
by chlorinating agents. Further proof of the unsuitability of,
for example, copper is the violent reaction observed between it
and antimony (V) chloride, both in liquid and in gas phase.
Diatomaceous supports are unsuitable for the present purpose
because of their adsorptive properties. For example, large
amounts of HCl are   almost irreversibly adsorbed by Sil-O-Cel
C 22 (chromosorb R or P). These supports also have the great ad-
sorption affinity for metal halides. Even the white diatomaceous
supports, which are usually regarded as being less adsorptive than
the red ones, are unsuitable, because of the numerous metallic
impurities which may react. It was proved that even rigorous
acid treatment failed to remove these impurities completely[10].

Some of the chlorides, like $SbCl_5$, are active chlorinating agents,
or moreover, free chlorine may be present in the sample. The
stationary liquid should therefore be at least resistant to
chlorination. This condition is not met by most organic stationary

phases. Sie et al.[10] reported that a considerable amount of HCl was formed when chlorine was contacted with silicone grease, even at temperatures as low as room temperature.

Freiser[11] has reported the separation of tetrachlorides of tin and titanium at 102° by using n-hexadecane (31%) coated chromosorb. Both tin(IV) and titanium(IV) chlorides gave well defined, symmetrical bands. The ratio of vapor pressure of these two compounds was about the same as the inverse ratio of their retention times, showing the absence of reactions with the stationary phase.

This study was extended by Keller and Freiser[12] by including niobium(V) and tantalum(V) chlorides and use of somewhat less volatile stationary phases (n-octadecane and squalane) at temperatures of 150 to 200°. Keller[8] separately reported the use of apiezon T and silicon oil as stationary liquids on red chromosorb as a support in copper columns at temperatures of 100 to 200°. The separation of the four chlorides by these authors is more of a qualitative nature. Studying the chromatograms shown by Keller, it is concluded from the presence of shoulders, tails and artefact peaks that decomposition of solutes have occurred to a large extent within the column and both apiezon grease and silicon oil reacted with chlorides. Tin(IV)chloride on apiezon grease and titanium(IV)chloride on silicon oil at 100° did not appear. Keller concluded that the normal alkanes appear more satisfactory than branched chain compounds.

Wachi[13] was unable to elute tin(IV) and titanium(IV) chlorides at 125° using a stainless steel column packed with silicon grease or apiezon M on ground Sil-O-Cel C 22 insulating brick. Failure to obtain peaks was attributed to complete reaction of the chlorides

with the greases and the walls of the column. Wachi then turned to fused inorganic eutectics in glass columns and reported the separation of the pairs $SnCl_4$-$SbCl_5$ and $SnCl_4$-$TiCl_4$. Poor results with the latter pair were attributed to the insolubility of titanium(IV)chloride in eutectics. Wachi also reported the failure of nitrate eutectics to separate the transition metal chlorides due to the oxidizing properties of the nitrates. He attempted the gas-solid chromatography of tin and titanium tetrachlorides by using C-22 firebrick as stationary phase, but resolution was very poor.

Juvet and Wachi[14] used a eutectic mixture of $BiCl_3$ and $PbCl_2$ on Sil-O-Cel C-22 firebrick for a separation of titanium(IV) and antimony(V) chlorides at 240°. A pronounced baseline instability was observed. Their work was not of quantitative nature.

Tadmor[15] reported interaction between the silicon products and metal halides. He obtained well defined peaks attributable to reaction products when analyzing germanium(IV), tin(IV) and arsenic(III) chlorides with silicon grease as stationary phase.

In a later paper[16], Tadmor reported the separation of germanium(IV), tin(IV) and arsenic(III) chlorides and their interaction on a column packed with Sil-O-Cel C-22 insulating brick, by an isotopic exchange technique (hydrochloric acid labeled with Cl-36). The chromatograms obtained with the uncoated support showed irregular peaks and imperfect separations. The incomplete recovery of the chlorides (65% for $GeCl_4$, 78% for $AsCl_3$) at the column's outlet was attributed to losses due to hydrolysis occurring within the column. Better separation was obtained by coating the support with 1 percent nitrobenzene. The chromatograms shown exhibit peak shapes which are considerably distorted.

Tadmor[17] also studied the separation of arsenic(III)
chloride and germanium(IV) chloride on 17 different stationary
liquids on Sil-O-Cel brick and reported the changes in weight
of these immobile phases as a function of temperature, and the
maximum temperatures at which no change in weight had been
detected. The chromatogram of germanium(V) and arsenic(III)
chlorides on uncoated Sil-O-Cel brick exhibits during 110 minu-
tes only one peak for them. The ratio of the retention times
of these chlorides is approximately the inverse of their vapor
pressure ratio at 100°. This indicates the absence of reaction
with support.

Wilke et al.[18] reported the determination of the purity of
the tetrachlorides of silicon, tin and titanium by gas-liquid
chromatography. They used nitrobenzene, silicon oil and apiezon
N as stationary phases at about 100° on diatomaceous firebrick
supports (sterchamol, diaphorit). They found that well resolved
individual peaks for silicon (IV) and titanium(IV) chlorides
could only be obtained by preinjecting a sufficient quantity
of titatium(IV) chloride. Although a complete separation is
reported with a column thus treated, the peaks still exhibit
considerable tailing, as is evident from the chromatograms
shown. No proof is given of complete recovery of solutes from
the column.

Dennison and Freund[19] reported the separation of arsenic(III),
tin(IV), germanium(IV) and titanium(IV) chlorides on halocarbon
6-00 coated (24.5% W/W) chromosorb W at 107° and 126°. They used
new all-glass apparatus with a specially developed sampling
chamber. Elutions were in the order of their boiling points.
They also tried quantitative determination of arsenic(III) and
tin(IV) chlorides. Maximum error was 6 percent which was believed
to result primarily from the premature vaporization of the sam-
ples as they were being injected.

Brazhnikov and Sakodynski[20] reported certain regularities in
the retention of chlorine-containing inorganic and organometallic
compounds. They separated germanium(IV), silicon(IV), tin(IV) and
titanium(IV) chlorides on the solid support polychrom, a type of
teflon, which was coated with siloxane elastomer E-301, apiezon N,
n-octadecane, polyorganosiloxane liquid VKZh-94, liquid polytri-
fluoromonochloroethylene of the Kel F-10 type, Kel F-3 or AlBr$_3$.
From the chromatograms shown, the results are of only qualitative
nature.

Zado and Juvet[21] reported the elution characteristics of 11
transition metal chlorides including arsenic(III), tin(IV), anti-
mony(III), molybdenum(V), niobium(V), zirconium(IV) chlorides on
12 inorganic fused salt mixtures, by using acid-washed chromosorb
P, porous vycor, glass beads as solid support. They discussed that
most of the solutes studied are capable of forming chloro-complexes
with available chloride in the liquid phase melt, and the ratio of
the dissociation pressures of two chlorocomplexes is, in general
different from the relative volatility ratio of the uncomplexed
solutes and finally concluded that the separation of solutes based
on this difference in complex stability would be particularly
desirable for situations in which solutes have similar boiling
points.

Sie et al.[10] studied 19 substances including germanium(IV),
arsenic(III), tin(IV), antimony(III, V), gallium(III) chlorides
on Kel F-40 as stationary phase which was coated (15% W/W) on
haloport F as solid support. Except for the unstable tetra-
chloride of vanadium and pentachloride of antimony, all inorganic
chlorides examined have been found sufficiently stable to permit
a gas chromatographic separation. Besides small peaks attributable
to HCl, no artefact peaks were observed at all. With proper choice

of column materials and some adaption of apparatus and injection technique to the reactivity of these compounds, quantitative analyses are possible with an accuracy equal to that normally obtained in gas-liquid chromatography.

Stumpp[22] reported that graphite was a suitable stationary phase for separating metal chlorides by the technique of gas-solid chromatography. A special construction permitted the injection of the solid metal chlorides. The chromatograms obtained exhibit tailing to a large extent and are far from being of quantitative nature.

Parissakis et al.[9] investigated the interaction of some chlorides including tin(IV), germanium(IV), arsenic(III), antimony(V) chlorides upon the stationary phases Kel F-10, Kel F wax, silicon oil DC-550, silicon rubber, apiezon L, phasepack P and graphite. They reported that with the exception of antimony(V) and vanadium(IV) chlorides, the chlorides tested had shown no interaction with the above mentioned phases. Kel F wax on celite gave the most symmetrical peaks with negligible tailing. Titanium(IV) chloride caused darkening of apiezon L.

In another paper[23], Parissakis et al. also demonstrated the appropriate operation conditions for good qualitative and quantitative separation of mixtures of five inorganic volatile chlorides on the same stationary phases mentioned in the previous paragraph.

By gas chromatography, it is also possible to calculate some physico-chemical properties, ie heat of solution

For any given solute, the retention values are related to the column temperature by the following relationship[24].

$$Vg = \frac{J\,Fc(t_R - t_A)}{W_L}\frac{273}{Tc}$$

where Vg = specific retention volume

J = pressure drop correction factor

Fc = volumetric flow rate of the carrier gas measured at the outlet pressure and column temperature

t_R = retention time of substance

t_A = retention time of air

$t_{R'}$ = $t_R - t_A$

W_L = weight of liquid phase

Tc = column temperature, $^\circ K$

Through the experiments and temperatures, it can be assumed without any serious error that J and W_L remain constant. On the other hand, correction for the gas flow rate is

$$Fc = Fm\,\frac{Tc}{Td}$$

where Fm and Td are the flow rate observed and the detector temperature, respectively. Substituting into the main equation gives

$$Vg = \frac{JFm}{Wl}\,t_{R'}\,\frac{273}{Td} = K\cdot t_{R'}$$

where K is the new constant term defining (JFm 273/Wl Td). Taking logarithms

$$LnVg = LnK + Lnt_{R'}$$

As known[25]

$$LnVg = -\frac{\Delta Hs}{RT} + C$$

where ΔHs is the heat of solution of the substance in the liquid phase. Equating the last two equations

$$Ln\, t_R' = -\frac{\Delta Hs}{RT} + C'$$

where C' is equal to $(C-LnK)$

Rearranging

$$Log\, t_R' = -\frac{\Delta Hs}{2.303\, RT} + C''$$

The heat of solution may be determined directly from the slope of the straight line which will be obtained by plotting log t_R' vs reciprocal of the column temperature.

2.3. Experimental

The chromatograph used was a VARIAN 2100 equipped with a Ni-63 electron capture detector. Nitrogen was used as carrier gas at flow rates of 24-48 ml per minute. The flow rates were measured by the soap bubble method. The pressure regulator was used to assure a uniform pressure to the column inlet and thereby a constant rate of gas flow.

Columns used were U-shaped glass tubes (to avoid reactions of the highly corrosive chlorides) 2 mm ID, 1/4 inch OD, 170-180 cm long.

The recorder was A-25 VARIAN with different suitable chart speeds and mV ranges.

All columns were packed, under anhydrous conditions when necessary, by adding the packing material to the column by tapping the side of the tube gently with a spatula until the column packing material did not settle any further. In the case of gas-liquid chromatography with n-hexadecane as the stationary phase and carbopack A as the solid support, 16 g of carbopack A was suspended in a solution of 2 g of n-hexadecane in 10 ml of toluene. The solvent was removed on the water bath under vigorous stirring (26).

The columns were conditioned each time overnight (or 48 hours in the case of carbopack B) at the maximum recommended temperature. The effluent end of the column was not connected to the detector during the conditioning period.

Column oven temperatures varied depending on the packing material and the elution characteristics of the substances. In the injections, the temperature of the injection port was 30-50° higher than that of the column oven. The detector temperature was either 50° higher than that of the column oven or constant at 300°.

The elution characteristics of the volatile metal chlorides, arsenic(III), titanium(IV), tin(IV) and antimony(V) chlorides were studied. They were obtained from commercial sources. As it is known they are highly corrosive, volatile and very easily hydrolized to insoluble hydroxides and basic salts even in the presence of traces of moisture. To avoid this, the samples were prepared under nitrogen atmosphere in the glove-box and stored in glass-stoppered flasks.

Because of the very high sensitivity of the detector even for the smallest amounts of pure chlorides (for CCl_4, it is 10^{-12} - 10^{-10} g) our chlorides were introduced as their solutions in n-hexane. The metal chlorides used had satisfactory solubilities in n-hexane.

The samples were introduced by means of Hamilton 701 or S.E.G. lo A-FN-GP syringes.

Repetitive retention measurements were made for each solute at each temperature.

Packing materials:

1. SE-30 (methyl silicon), 3% W/W on varaport 30, 100/200 mesh
2. Carbopack A
3. Carbopack A, hydrogen treated
4. n-hexadecane, 12.5% W/W on carbopack A
5. Carbopack B, hydrogen treated (commercially)

Besides the metal chlorides, air, chlorine, hydrochloric acid and some hydrocarbon injections were carried out independently to compare them with the metal chloride chromatograms under the same conditions.

For each of the metal chlorides, three solutions with different concentrations were prepared.

$AsCl_3$:
1. 2.84×10^{-2} g/ml
2. 3.74×10^{-4} g/ml
3. 0.97×10^{-5} g/ml

$SnCl_4$:
1. 2.94×10^{-2} g/ml
2. 3.86×10^{-4} g/ml
3. 1.00×10^{-5} g/ml

$TiCl_4$:
1. 2.28×10^{-2} g/ml
2. 3.00×10^{-4} g/ml
3. 0.78×10^{-5} g/ml

$SbCl_5$
1. 3.10×10^{-2} g/ml
2. 4.08×10^{-4} g/ml
3. 1.06×10^{-5} g/ml

The packing material used first was SE-30 as the stationary phase
on varaport as the solid support. This column had already been in
use at the beginning of the present work.

The retention time of air in this column was determined as 0.40
min. n-Hexane exhibited many unexpected peaks (Fig. 2). As shown
having nearly the same area, two big peaks do not permit us to
think about any impurity in the sample as the reason. The peaks
show considerable tailing. The reaction of n-hexane with the
packing material is probably the reason for these findings. Since
no oxysorb was being used at that time, the impurities in the
carrier gas might cause the small peaks to appear.

Free chlorine and hydrochloric acid gases can play an important
role in the molten salts reactions which take place in the reactor.
This is the reason for examining them besides the metal chlorides
as solutions in n-hexane. When chlorine was injected, three shoul-
ders, one of which was Cl_2, were obtained on the first peak of
n-hexane (Fig. 3). The other shoulders may be attributed to
possible reaction products. With HCl, no special peak resulted.
It is quite possible that HCl is hidden in one of the n-hexane
peaks. When chlorine and HCl were injected as gases, they exhi-
bited many peaks, showing interaction inside the column (Fig. 4).

Arsenic(III) chloride solution was injected at temperature inter-
vals from 90° to 200°. Two peaks besides those for n-hexane were
obtained at 125, 130, 150, 175 and 200°. Figures 5-8 represents
small peaks, shoulders and tailing to a large extent. However,
the second peak disappeared at lower temperatures (90, 100, 110°)
(Fig. 9-11). This could be explained in two ways, (a) since these
temperatures are lower than the boiling point of arsenic(III)
chloride (130°) it might be retained inside the column, (b) as
a result of repetitive injections, the solution might oxidize
and hydrolize completely and arsenic trichloride might disappear.
as a result of both, the first peak is attributed to the reaction
product.

Tc, °K	1/Tc	t_R, min	$t_R-t_A=t_R'$, min	Log t_R'
398	0.00251	11.30	10.90	1.04
403	0.00248	9.33	8.93	0.95
423	0.00236	4.45	4.05	0.61
448	0.00223	2.20	1.80	0.26
473	0.00211	1.25	0.85	-0.09

The logarithm of adjusted retention time was plotted vs. the reciprocal of absolute column temperature for arsenic trichloride (Fig. 12). The slope of the straight line is 2815. Then

$$\Delta Hs = -(2815)(2.303)(1.987)$$

The heat of solution of arsenic(III) chloride in methyl silicon is -12.8 kcal per mol.

When the most diluted solution of titanium tetrachloride was injected (0.78 x 10^{-8} g) at 130, 150, 175 and 200°, one big and two small peaks were obtained (Fig. 13). The retention time of the biggest peak is identical to the unexpected peak of the arsenic(III) chloride chromatogram. When the more concentrated solution of titanium(IV) chloride was injected (3.00 x 10^{-7} g) at the same temperatures as above, too many peaks resulted, showing the interactions inside the column with increasing concentration of chlorine (Fig. 14).

When tin(IV) chloride was injected at 200 and 225°, a shoulder on the first peak of n-hexane was obtained with a retention time equal to those of the unexpected peaks of arsenic(III) and titanium(IV) chloride chromatograms. Two more peaks resulted, the second one probably being the tin tetrachloride peak (Fig. 15).

The case with antimony(V) chloride is similar to titanium(IV) chloride. When the least concentrated solution of antimony pentachloride was injected (1.06 x 10^{-8} g) at 130 and 150°, a big peak with a retention time again equal to those of the unexpected peaks were obtained (Fig. 16). When the more concentrated solution of antimony pentachloride was injected (4.08 x 10^{-7} g) including the temperatures 100 and 115° too many peaks were obtained (Fig. 17).

After the failure to determine and separate the metal chlorides with this column we turned to gas-solid chromatography and used carbopack A as the solid packing material.

When n-hexane was injected into this column a lot of unexpected peaks, also including a negative peak, were obtained (Fig. 18). HCl in gas form gave only one peak with considerable tailing. However, repetitive injections created new extra peaks. With chlorine injection in gas form four peaks resulted. Tin tetrachloride (1.0 x 10^{-8} g) gave a small peak (Fig. 19).

The column created two peaks itself when the baseline was drawn without any injection, by programmed temperature method (Fig. 20a). The number of the peaks was five when n-hexane was chromatographed by the same method (Fig. 20b). Then many organic solvents namely cyclohexane, heptane, iso-octane, toluol, benzol and decane were tested by both programmed temperature and constant temperature methods. But none of them exhibited chromatograms better than those of n-hexane. n-Hexanes from different commercial sources were also tried and with that from FLUKA three peaks

including the negative one were eliminated (Fig. 21). With injection of chlorine and HCl separately in n-hexane, many peaks were obtained. At 60°, HCl and chlorine have the same retention time.

Di Corcia and Bruner[27] reported that the use of gas-solid chromatography was extended to the elution of polar compounds by treating graphon, MT and FT with hydrogen at 1000°. "In comparing the adsorption isotherms before and after treatment, it appears that chemisorbed oxygen, always present in these adsorbents, is removed. Peak tailing is eliminated or strongly reduced."

Upon this, we treated carbopack A with hydrogen at 800^oC for seven hours (we couldn't manage to reach 1000°). After this treatment, we still couldn't eliminate the extra peaks for n-hexane, the number being 2 this time.

Then we again turned to gas-liquid chromatography and used n-nexadecane coated on carbopack A. We injected different organic solvents into this column and obtained only one peak at 40° for all of them, that of n-hexane being the most ideal one. The negative dip after this peak was attributed to detector contamination (Fig. 22).

When chlorine and HCl were injected separately in gas form, they gave only one peak with tailing to a large extent (Fig. 23, 24). Arsenic(III) chloride did not appear at 100° and the baseline exhibited pronounced instability. That was attributed to the column bleeding at this temperature which is quite higher than the maximum temperature allowed for n-hexadecane (50°).

Carbopack B treated with hydrogen at 1000° (commercial) was the last packing material we worked with. n-Hexane exhibited again two peaks with negative dips after them (Fig. 25). Arsenic(III) chloride did not appear at 140° in 80 minutes.

2.4. Conclusions

The major difficulty in the separation of metal halides is in finding a non-reactive packing material capable of use at the elevated temperatures required. At the end of our literature survey we have concluded that nobody had complete success about this subject quantitatively.

Qualitative separations would not be sufficient for our work and quantitative results were aimed at without any further help of the literature.

There is a close relationship between column packing material and the substances investigated by gas chromatography. Having a very sensitive detector for chlorides and the necessity to decrease the concentration of metal chlorides caused us to use an organic solvent and eventually created another class besides metal chlorides HCl and chlorine. That was really our major difficulty and we had extra peaks for n-hexane when chromatographed on the packing materials used except n-hexadecane. Since chlorine, HCl and some metal chloride peaks had retention times equal to those of extra peaks and quantitative results were aimed at, we insisted on eliminating these unexpected peaks by trying different packing materials and were able to do it with n-hexadecane only.

With all our packing materials, four metal chlorides which were tried either did not appear or gave extra peaks. From the presence of these peaks, unstable baselines and tailings we conclude that there are interactions between the packing materials and the samples. Those peaks of the metal chlorides with the same retention time on SE-30 make us to think that it is a common reaction product. The extra peaks were the results of not only these reactions but also of the reactions between packing materials and hydrolization and oxidation products of metal chlorides. With the introduction of chlorine and HCl, too many peaks were obtained.

When the concentration of chlorine was increased, the number of unexpected peaks also increased. The metal chlorides are highly corrosive, volatile and very easily hydrolized. To avoid this, we prepared the samples under nitrogen atmosphere. However, because the amounts of moisture and oxygen were quite high in the glove-box, hydrolization and oxidation of the metal chlorides could not be avoided. Opening the small bottles, to take metal chloride samples for injections naturally increased the degree of oxidation and hydrolization. This was observed easily from the precipitation of metal hydroxides in the bottles. In further working, the samples should be prepared under complete anhydrous conditions and bottles with penetrable septums should be used instead of those with stoppers used up to now to store metal chlorides.

In the results reported so far, Sie et al.[10] and Parissakis et al.[9] had success to a degree in separating metal chlorides quantitatively. The packing materials which were used by them, namely Kel F-40, Kel F-10, Kel F wax, silicon oil DC-550, silicon rubber, apiezon L, phasepack P should be tried. Although some of them had been ordered by us more than 2 months ago, to try, they still haven't arrived even after the completion of this report. One important point is that some reporters had completely failed with some of the above mentioned materials. Carbopack B (commercially hydrogen treated) should be continued trying.

In the case of failure with all these packing materials, capillary colums may be given trial.

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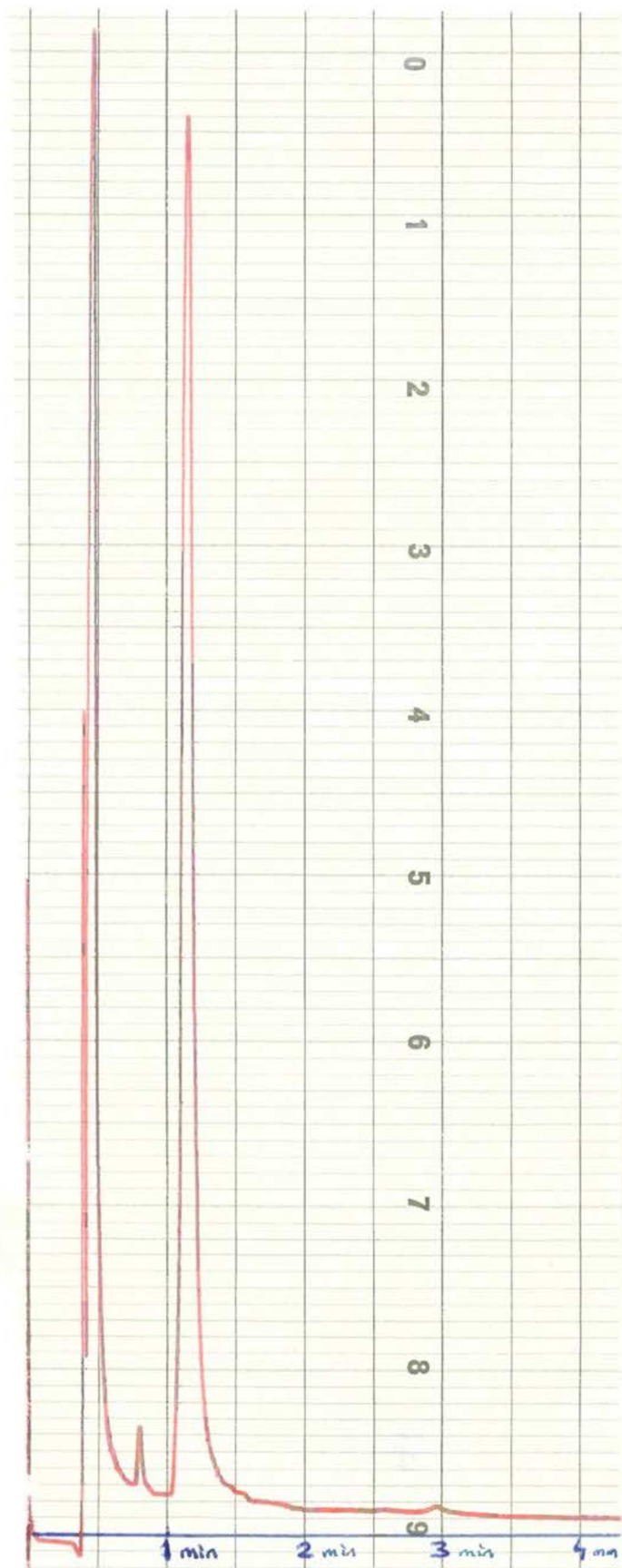
Fig. 2   n-Hexane
Packing mat.   SE-30
Tc = 150°C
Fc: 24 ml/min.
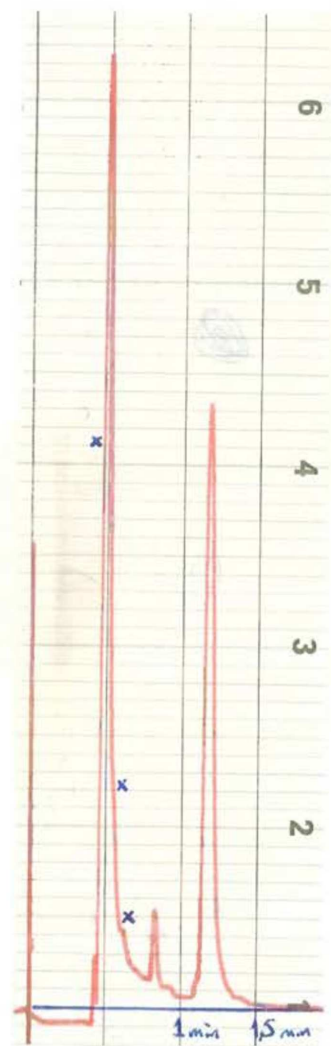
Fig. 3   Cl$_2$ in n-Hexane
Packing mat.   SE-30
Tc = 150°C
Fc: 24 ml/min
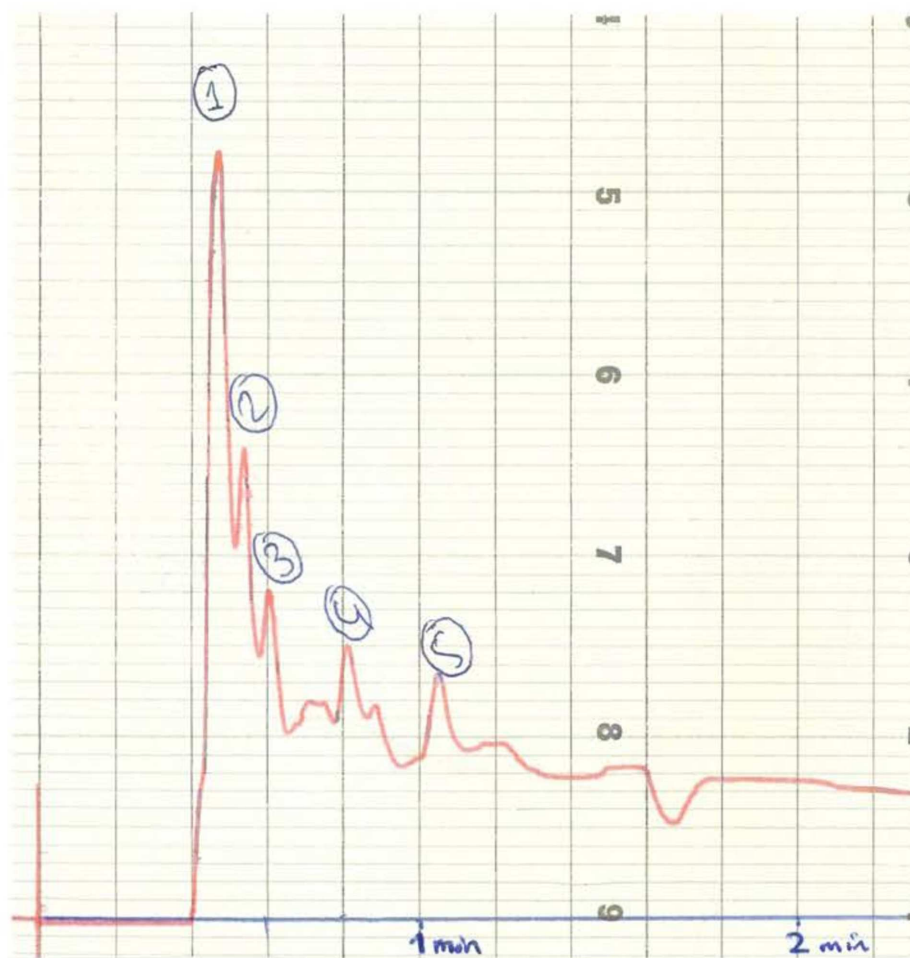
Fig. 4 Cl_2 in gas form
         Packing material   =   SE-30
         Tc = 150°C
         Fc: 24 ml/min.
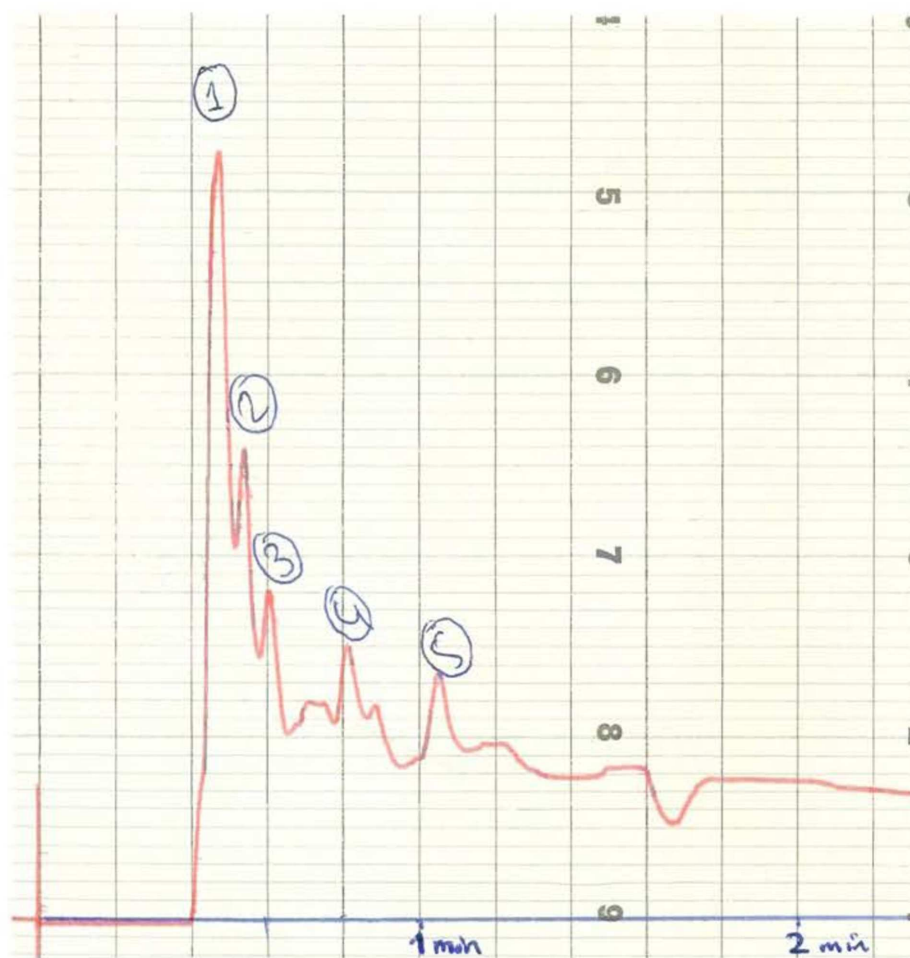
Fig. 4   Cl₂ in gas form
          Packing material = SE-30
          Tc = 150°C
          Fc: 24 ml/min.
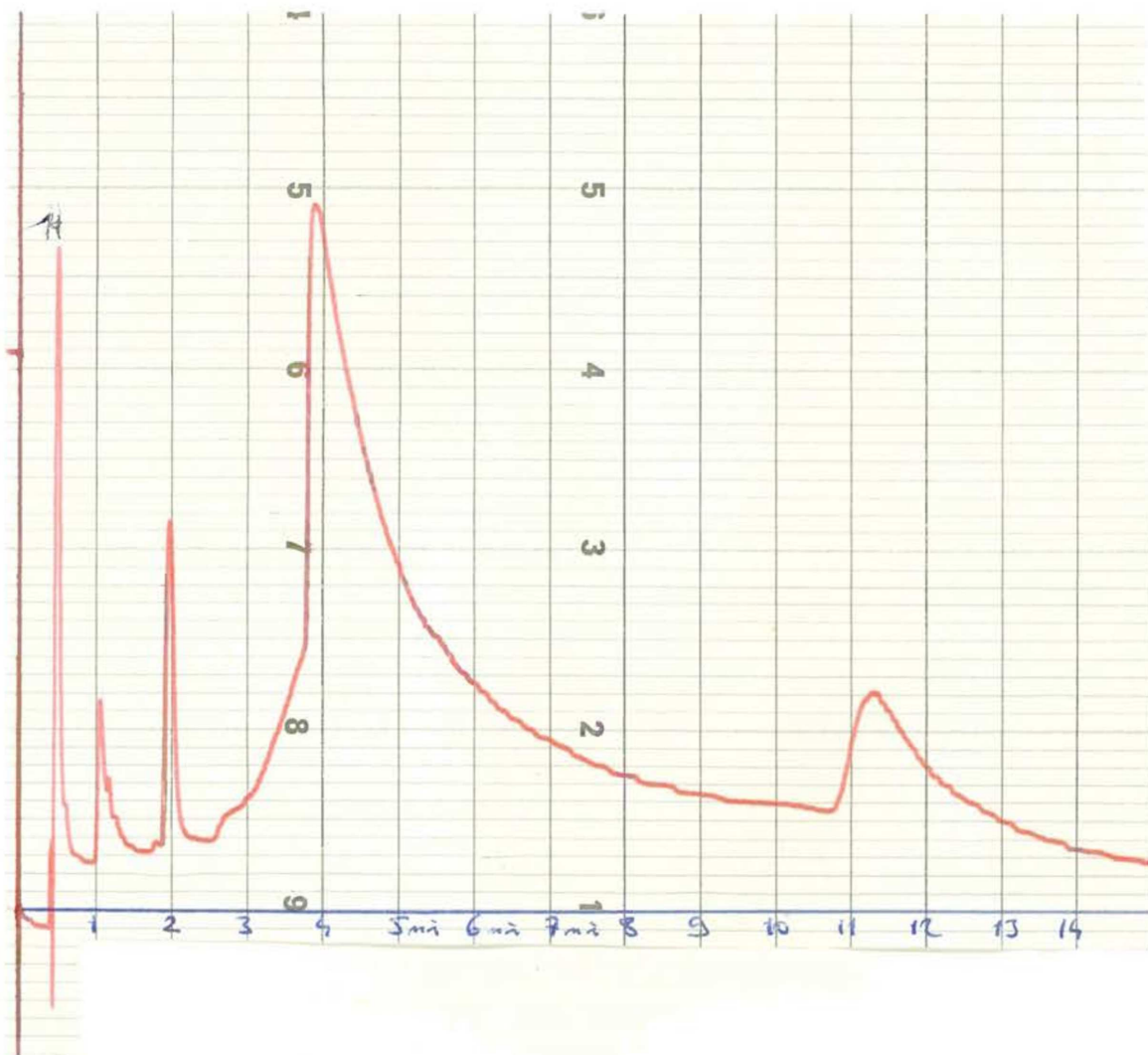
Fig. 5   AsCl$_3$

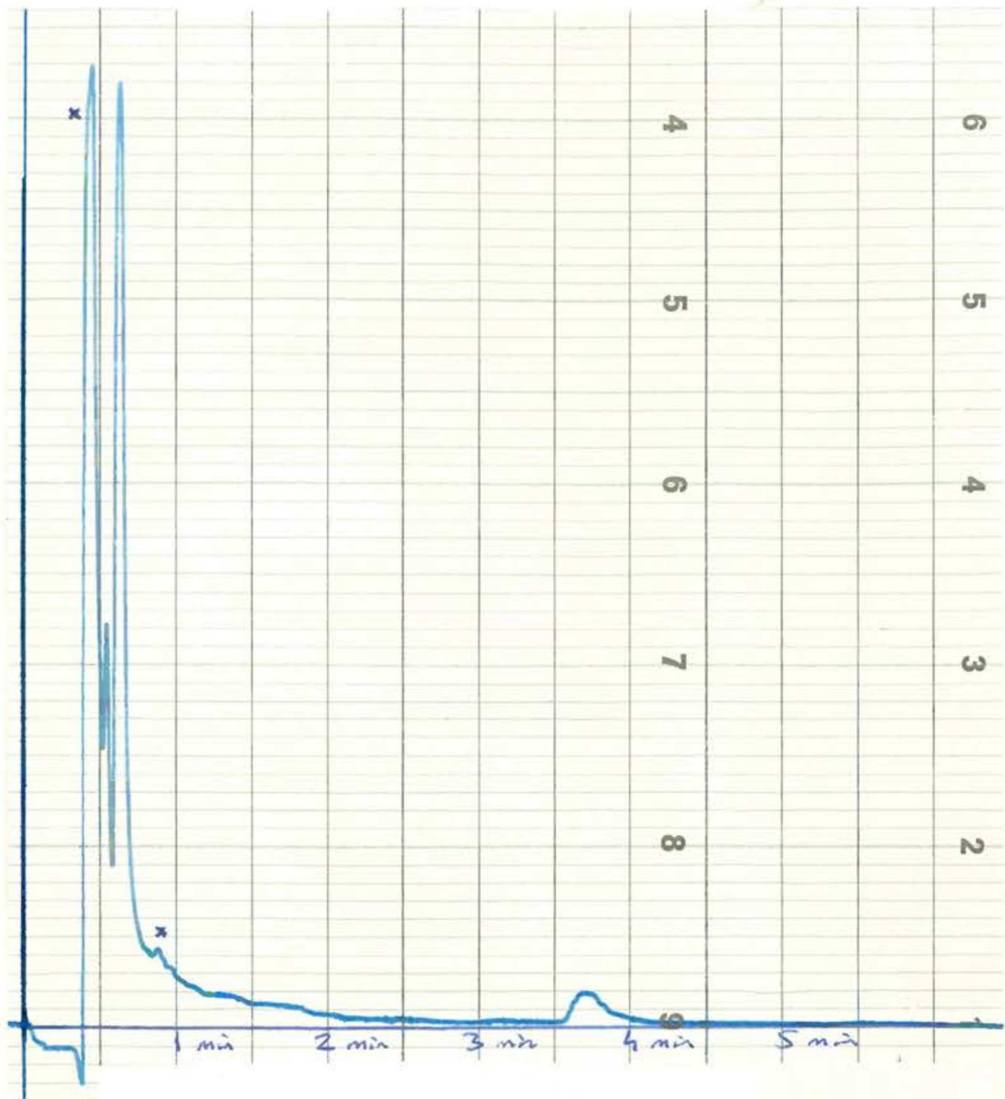Packing material = SE-30

Tc = 125°C

Fc: 24 ml/min.
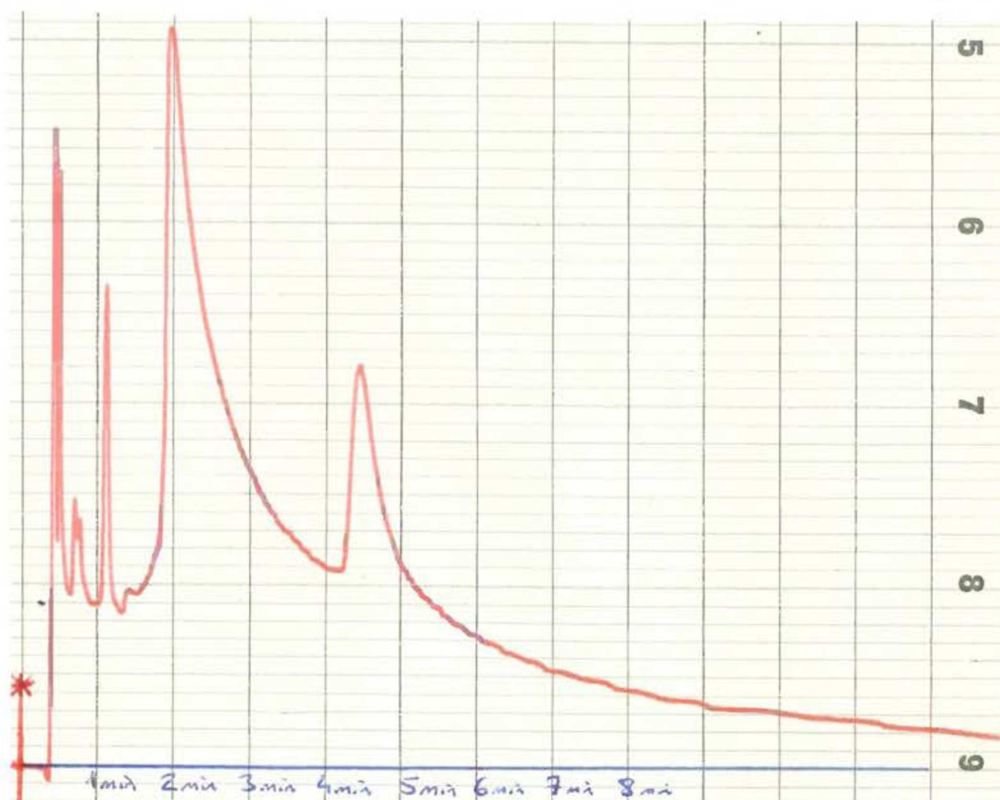
Fig. 6   AsCl$_3$
          Packing material = SE-30
          Tc = 150°C   Fc: 24 ml/min.
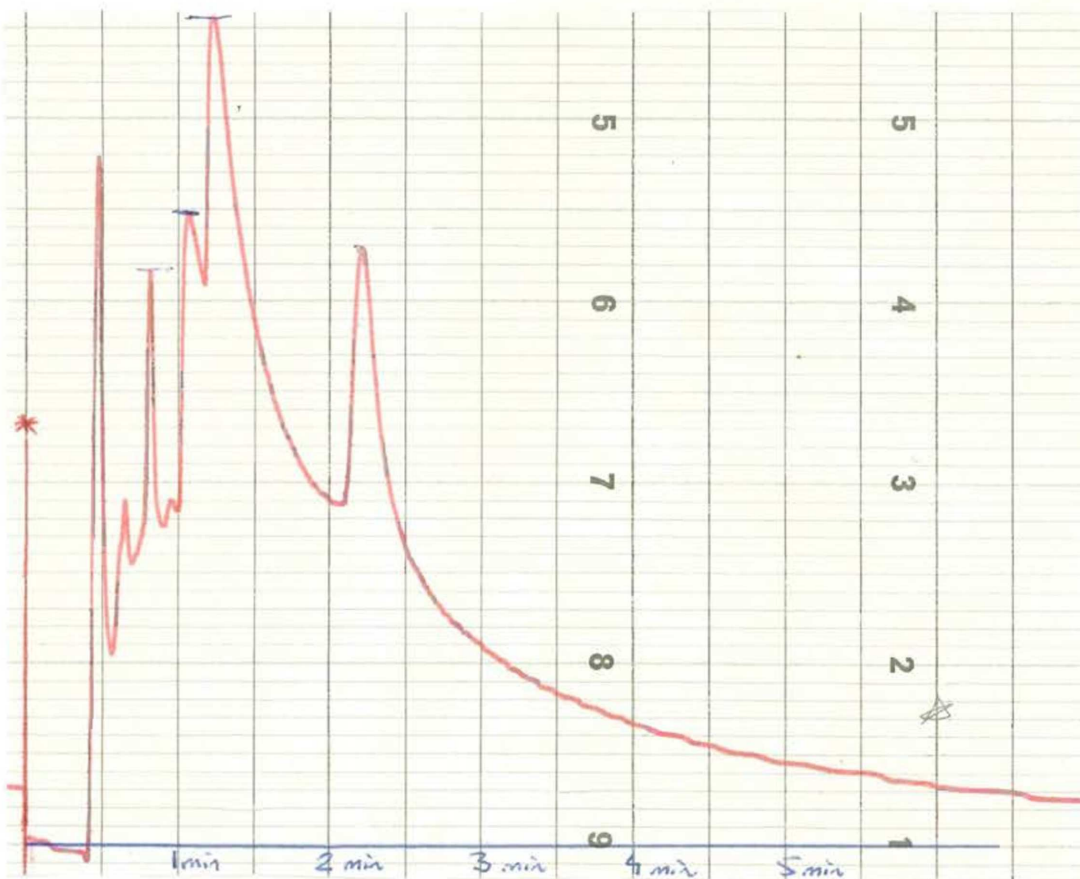
Fig. 7   AsCl$_3$
          Packing material = SE-30
          Tc = 175°C   Fc: 24 ml/min.
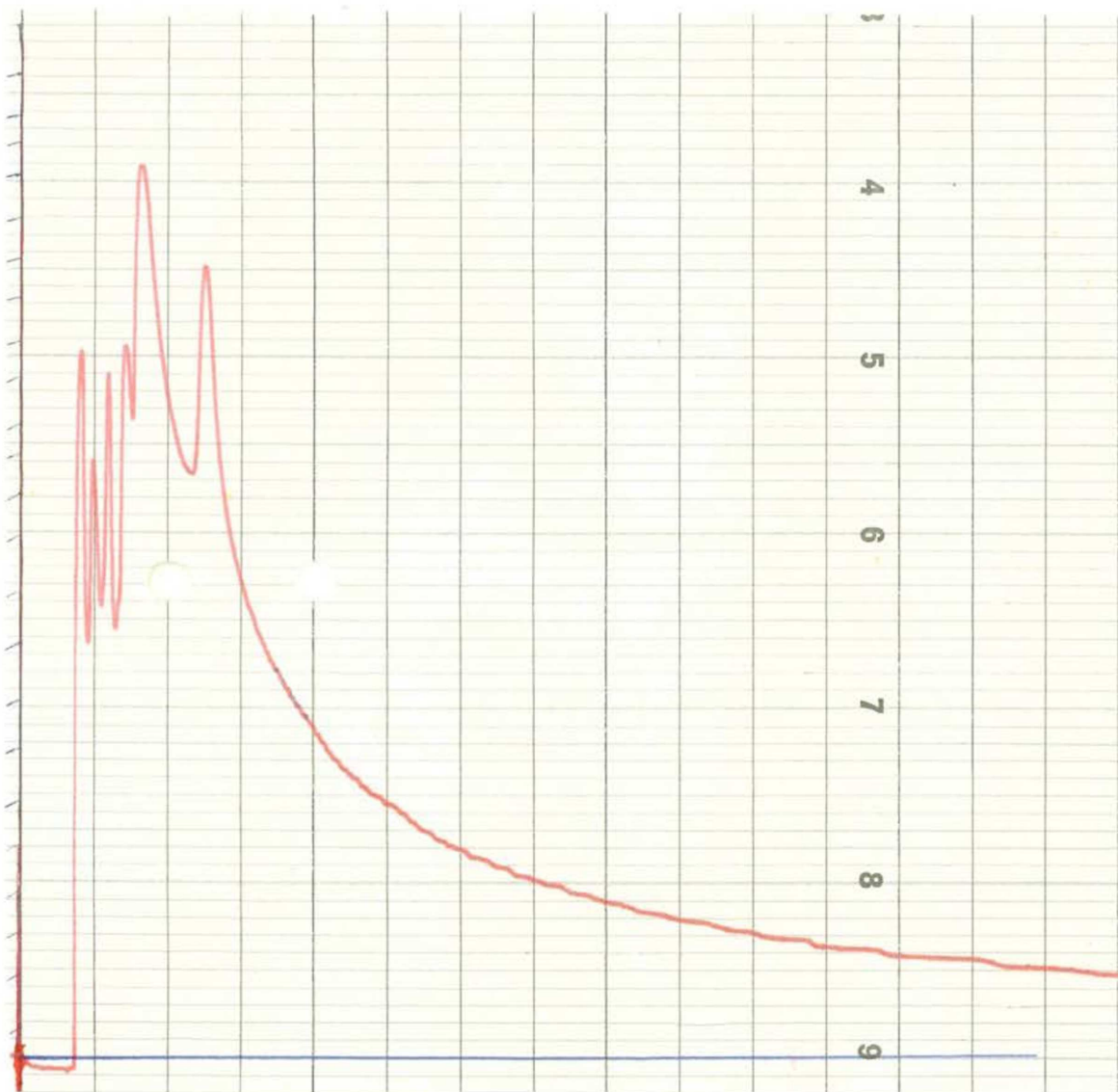
Fig. 8   AsCl$_3$
          Packing material: SE-30
          Tc = 200°C
          Fc: 24 ml/min
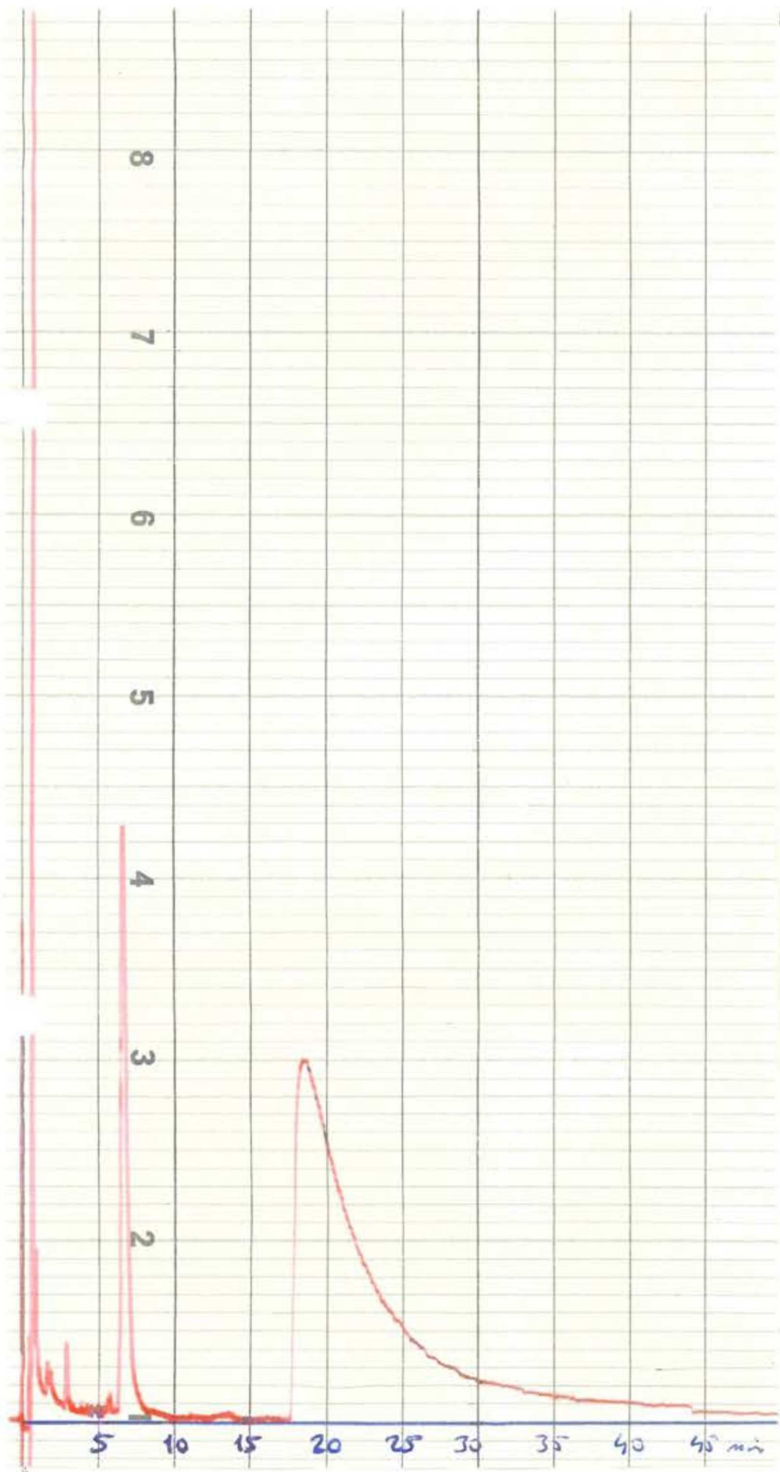
Fig. 9   AsCl$_3$

Packing material: SE-30

Tc = 90°C

Fc: 24 ml/min
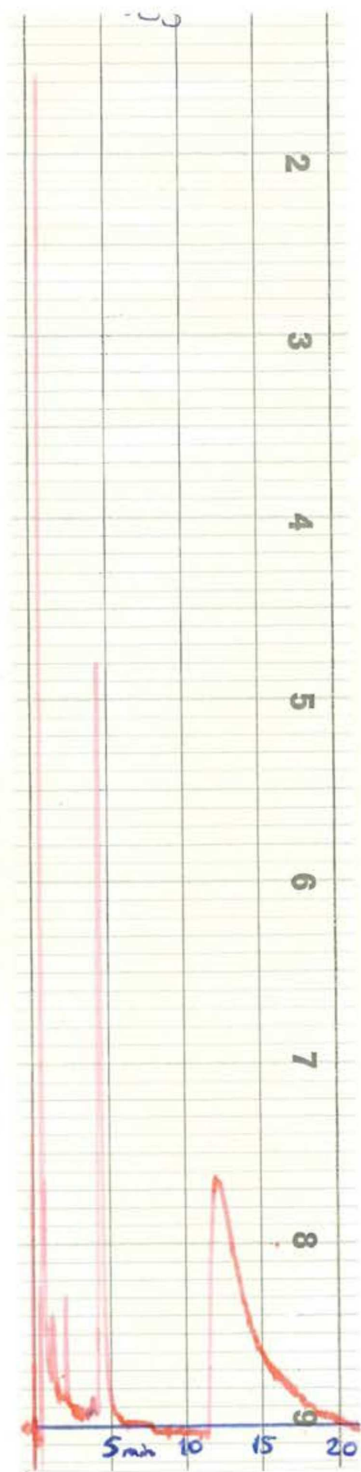
Fig. 10   AsCl$_3$

Packing material:
          SE-30

Tc = 100°C

Fc: 24 ml/min
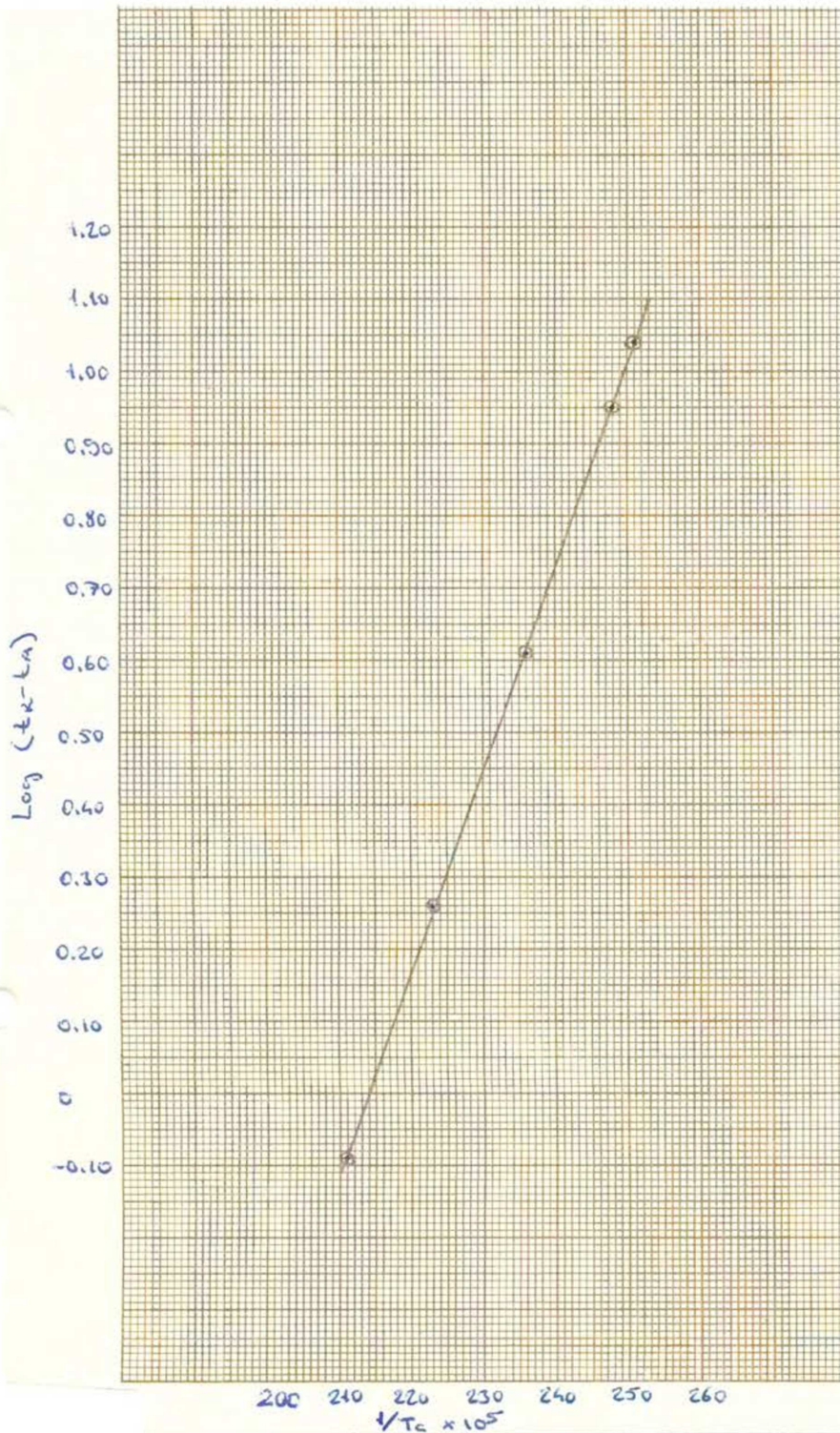
Fig. 12   Log $(t_R - t_A)$ vs T^{-1} for
AsCl$_3$ on SE-30
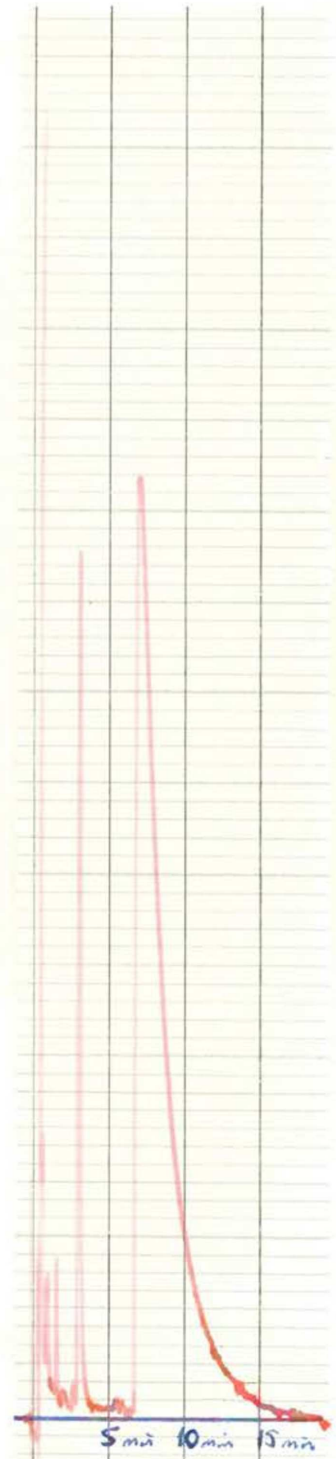
Fig. 11   AsCl$_3$

Packing material
SE-30

Tc-110°C

Fc: 24 ml/min.
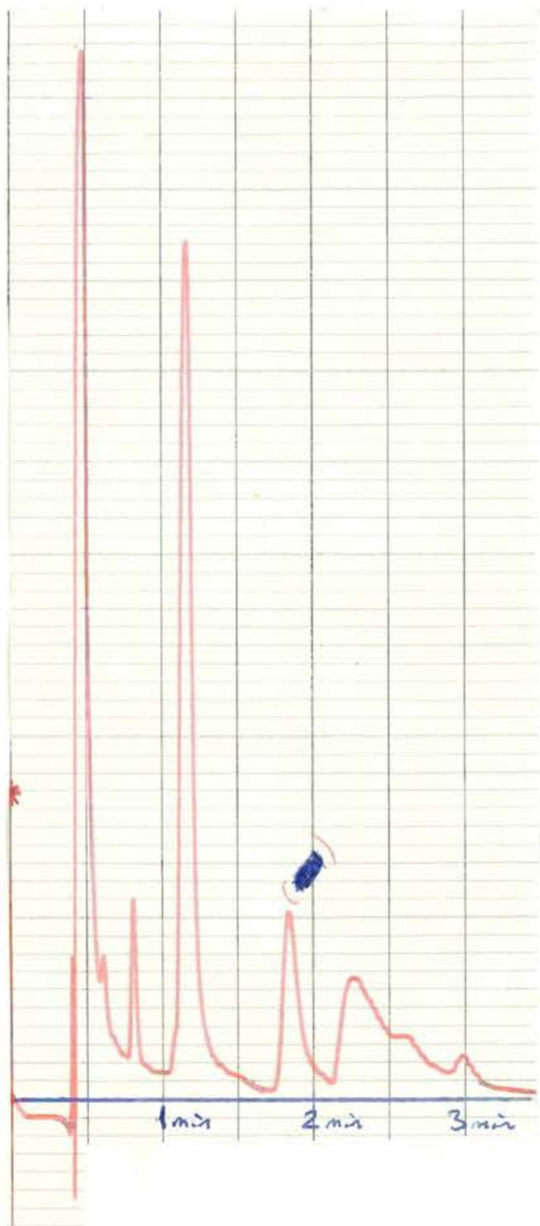
Fig. 13   TiCl$_4$
Packing material:
SE-30
Tc = 150°C   Fc = 24 ml/min.
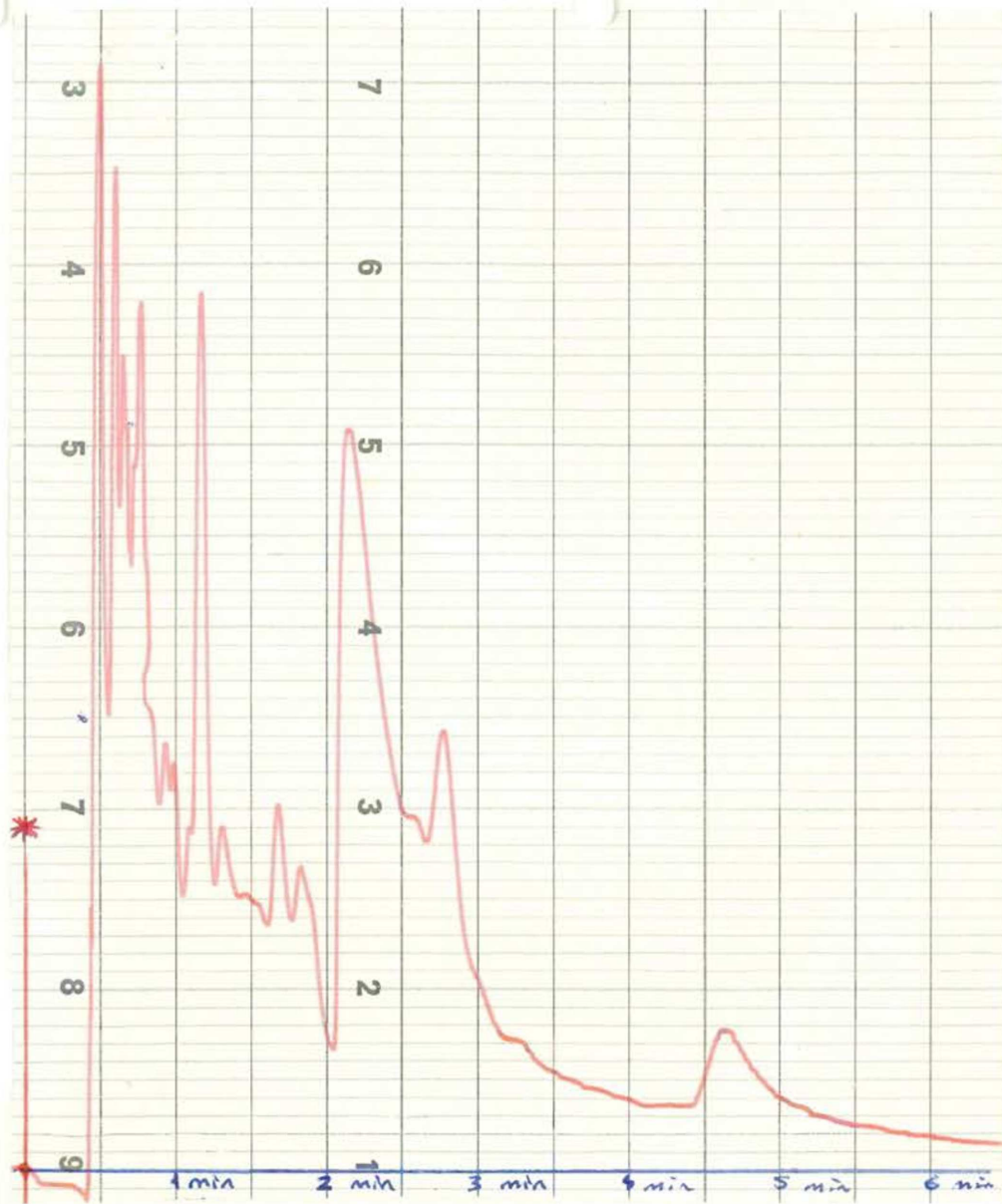
Fig. 14   AsCl$_3$ (more concentrated)
Packing material: SE-30
Tc = 150°C   Fc: 24 ml/min

Fig. 15   SnCl$_4$

Packing material = SE-30
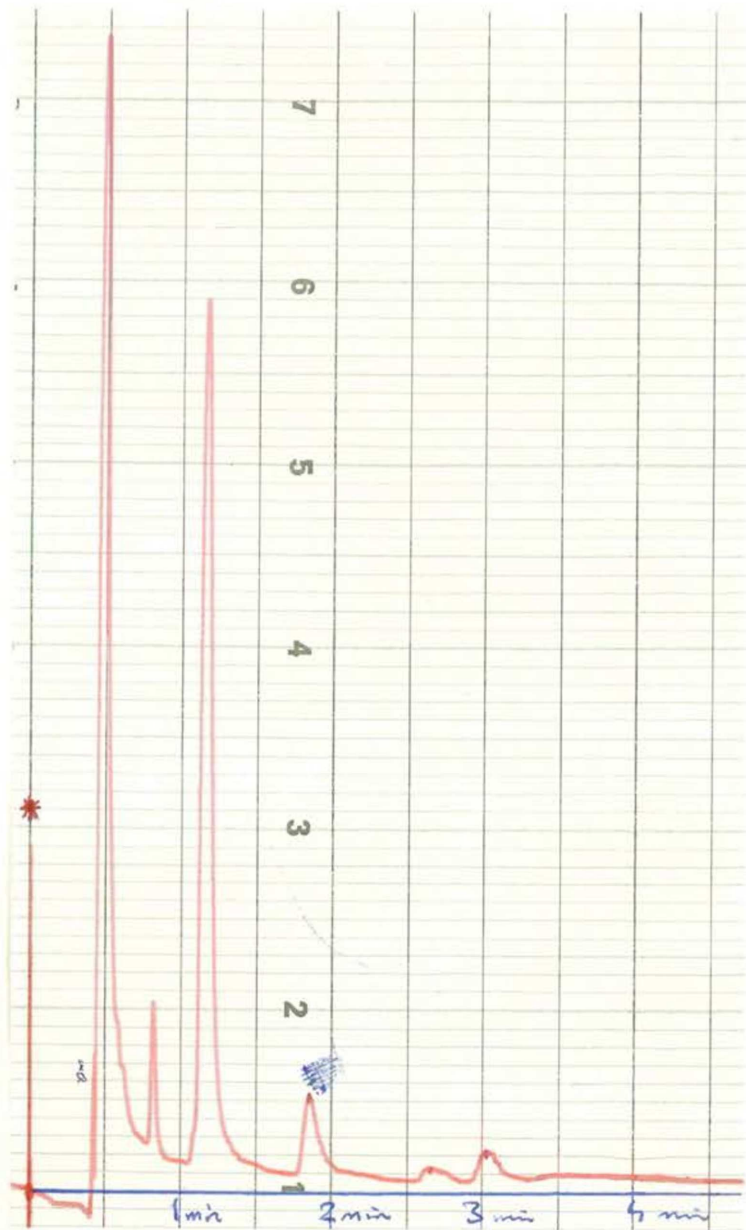
Tc = 200° C

Fc: 24 ml/min

Fig. 16   SbCl$_5$

Packing material = SE-30
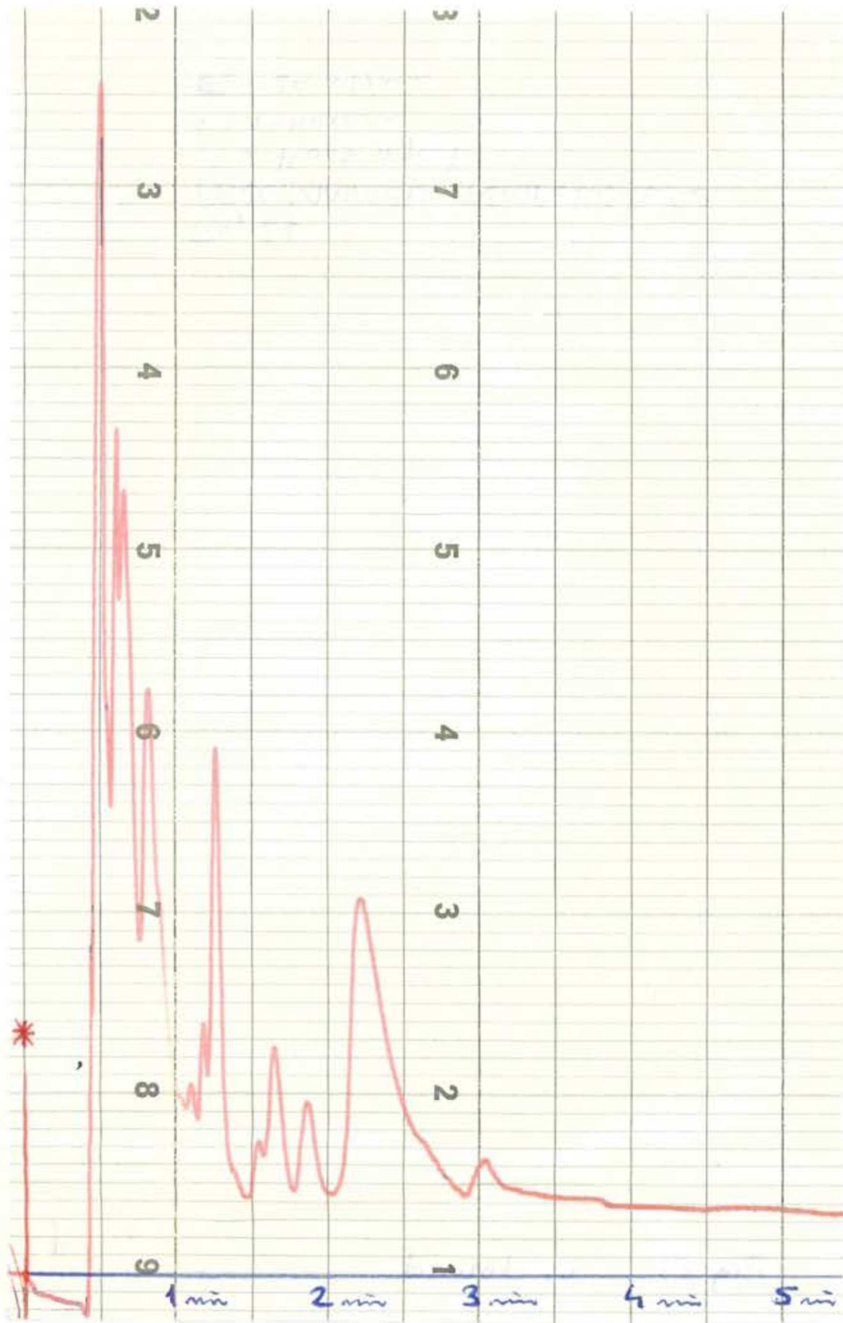
Tc = 150° C   Fc: 24 ml/min.

Fig. 17   SbCl$_5$
          Packing material = SE-30
          Tc = 150°C
          Fc = 24 ml/min.
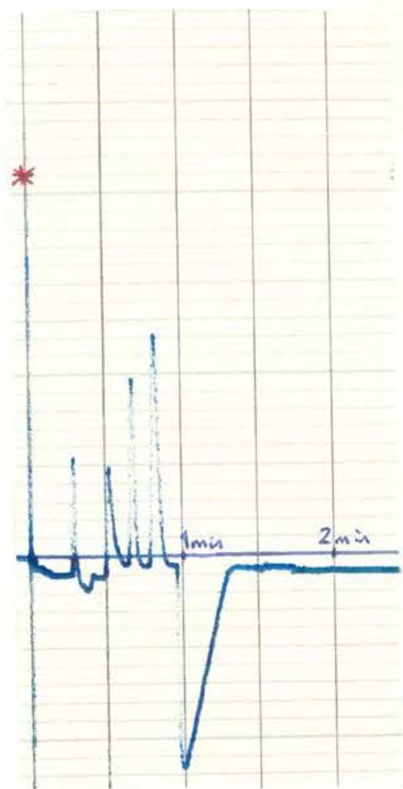
Fig. 18   n-Hexane

   Packing mat.: Carbopack A

   Tc = 200°C
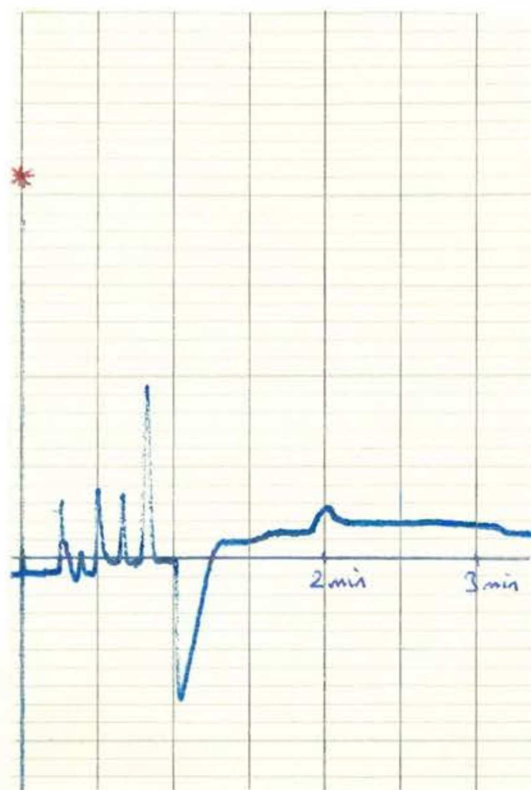
   Fc = 24 ml/min.

Fig. 19   n-Hexane

   Packing mat.:   Carbopack A

   Tc = 200°C
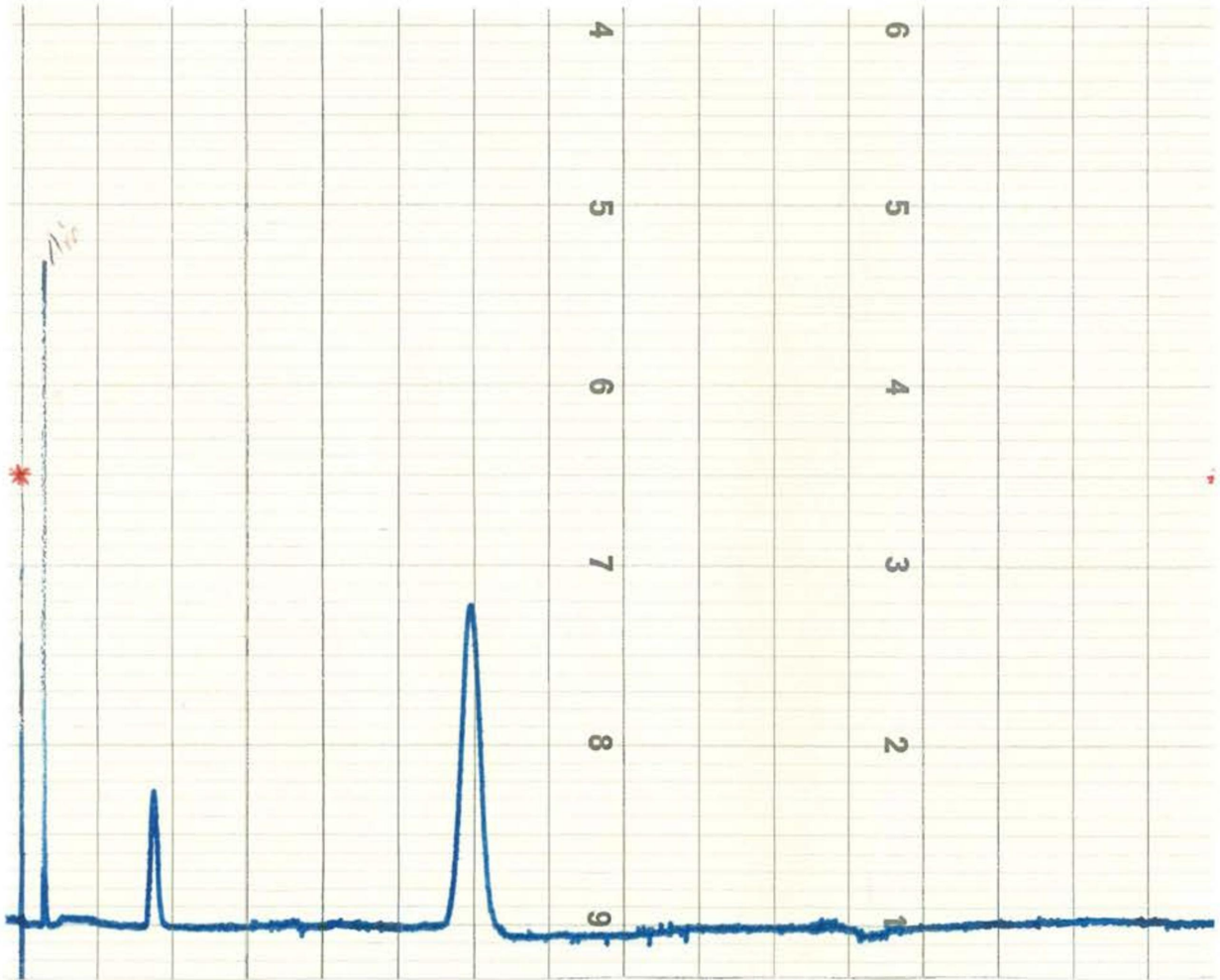
   Fc = 24 ml/min.

Fig. 21   n-Hexane

Packing mat.:   Carbopack A

Tc = 60°C

Fc = 24 ml/min.
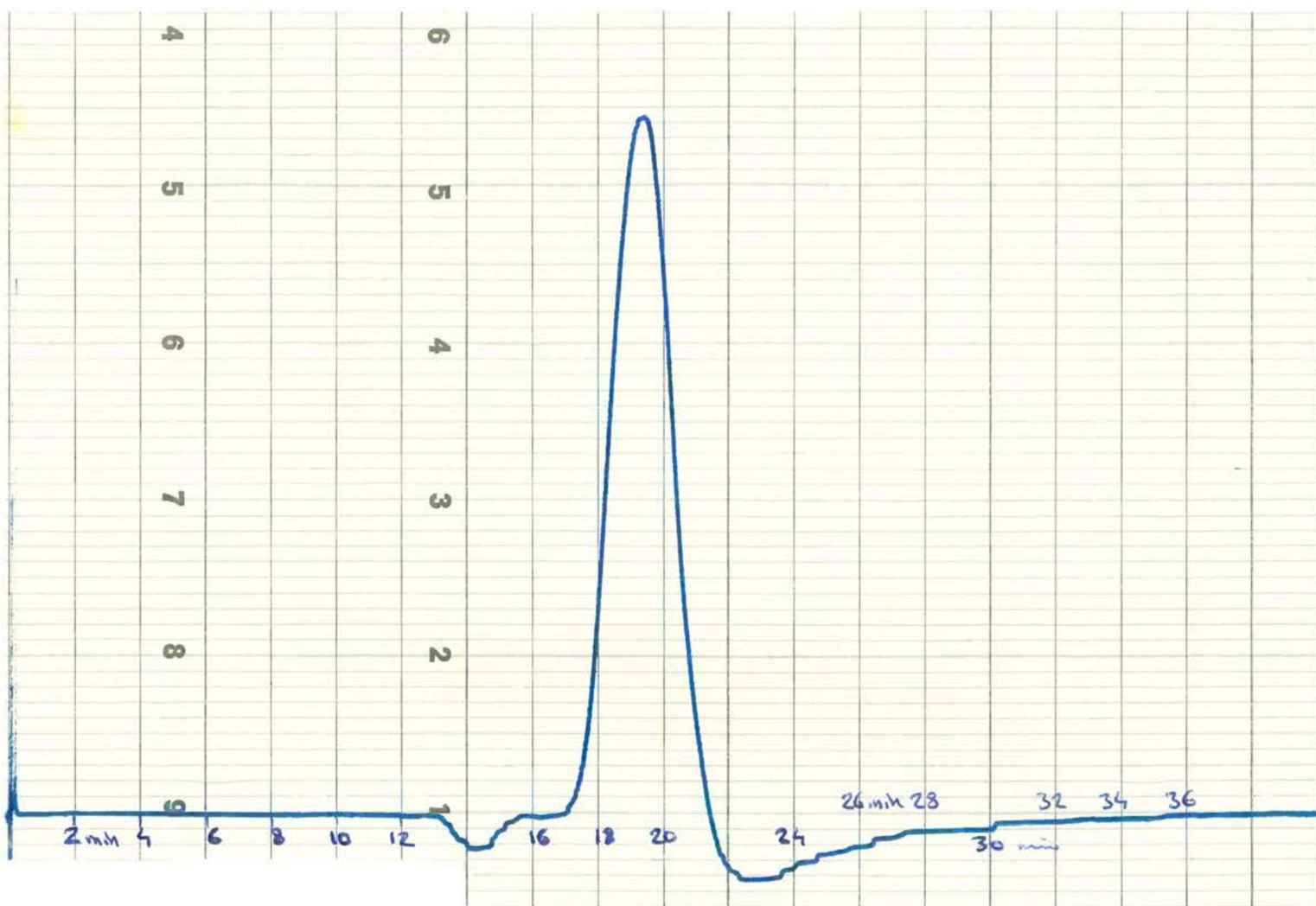
Fig. 22   n-Hexane

Packing mat.: n-Hexadecane

Tc = 40°C
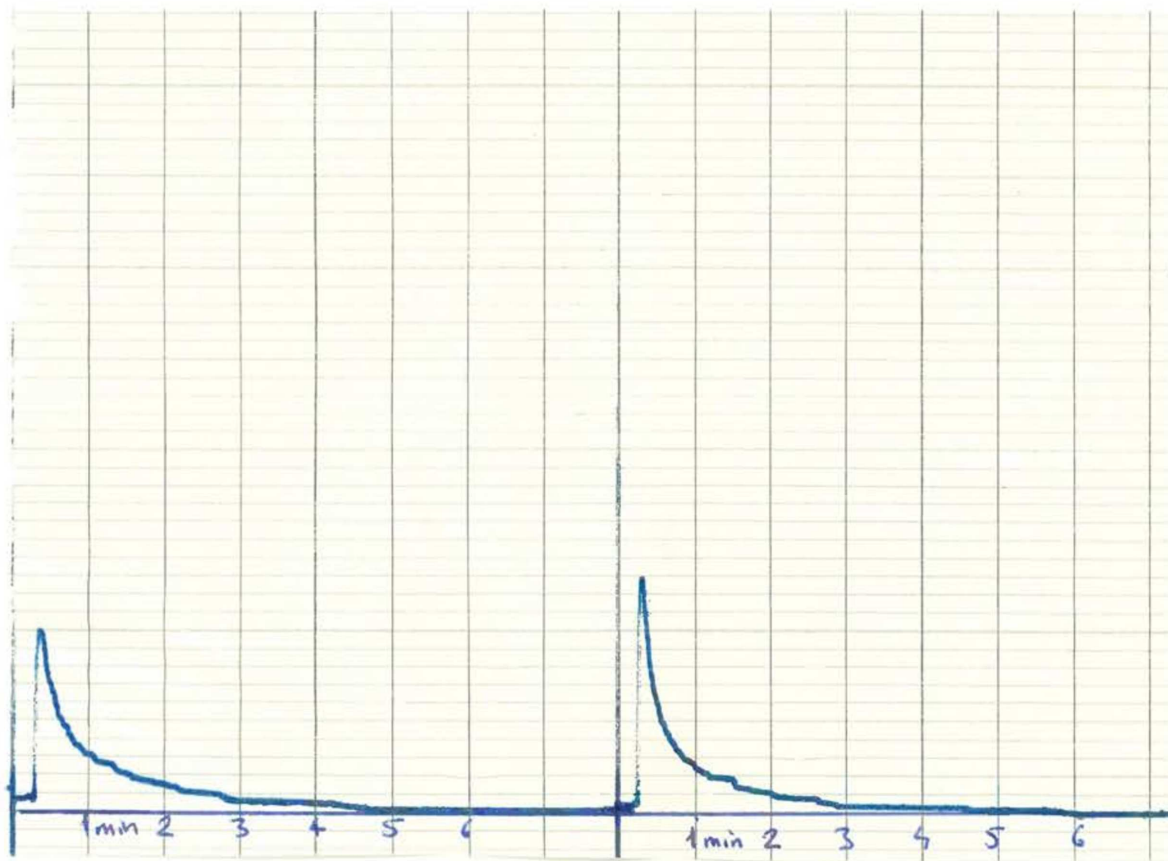
Fig. 23 Cl_2 gas
Packing mat.:
n-Hexadecane

Tc = $40^{\circ}C$

Fig. 24 HCl gas
Packing mat.:
n-Hexadecane

Tc = $40^{\circ}C$

Fig. 25   n-Hexane

Packing mat.:   Carbopack B-HT
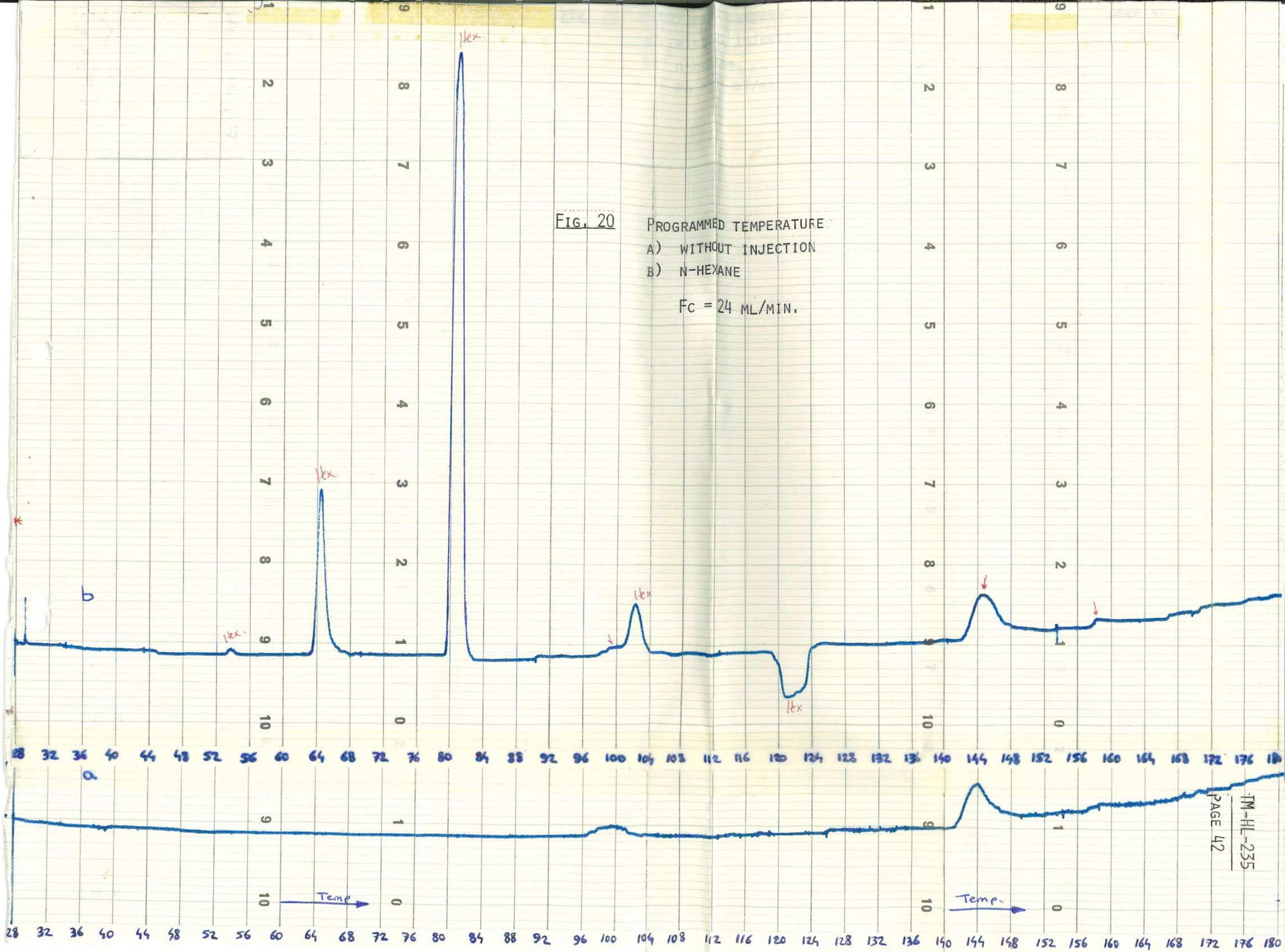
Tc = 100°C

Fc = 48 ml/min.

FIG. 20   PROGRAMMED TEMPERATURE
A) WITHOUT INJECTION
B) N-HEXANE

$F_C = 24$ ML/MIN.