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ADVANCED RESEARCH PROJECTS AGENCY

Contract ARPA SD-88

Technical Report No. ARPA-26

SYNTHESIS OF SILICON COMPOUNDS

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June 1966

By
Eduard Krahé

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SYNTHESIS OF SILICON COMPOUNDS

By

Eduard Krahé

Technical Report No. ARPA 26 Contract ARPA SD-88

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June, 1966

Submitted to:

Advanced Research Projects Agency
The Department of Defense

Mallinckrodt Laboratory

Department of Chemistry

Harvard University

Cambridge, Massachusetts

ABSTRACT

There is only one binary alloy system of silicon which is liquid below the temperature of decomposition of methyl chloride, alcohol, and ether: the gold-silicon system. The possibility of using a liquid eutectic form of silicon as starting material for the direct synthesis of organosilicon compounds was so inviting, because of the constant exposure of fresh surface to the stream of organic reagent, that experiments were undertaken. It was expected that no gold would be consumed or transported, and so the high price of the gold would represent only capital investment, the cost of which might be overbalanced by operational advantages.

The experiments reported here show that methylchlorosilanes (intermediates for making silicone polymers) are indeed produced from methyl chloride and gold-silicon alloy, but that the gold enters into the reaction in such a way as to be transported as fine dust. The chemical change was studied intensively, along with reactions of methanol and ethers. The report concludes with some work on organoboran chlorides.

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SYNTHESIS OF SILICON COMPOUNDS

by

Eduard Krahé

I. INTRODUCTION

The direct synthesis of organosilicon halides (the Rochow reaction) has become the key to the large-scale production of silicone polymers. For the most important product, dimethyldichlorosilane, the method consists in effecting reaction of an intimate mixture of powdered elemental silicon and copper with methyl chloride at about 280°C. The crude reaction product is a very complex mixture, and isolation of dimethyldichlorosilane by distillation is cumbersome although feasible. The dimethyldichlorosilane is then converted into dimethylsiloxane by hydrolyzing it with water. The initially-generated silanols are not stable and condense to high-molecular polysiloxanes:

$$(CH_3)_2SiCl_2 + 2H_2O \longrightarrow (CH_3)_2Si(OH)_2 + 2HCl$$

$$n(CH_3)_2Si(OH)_2 \longrightarrow \left[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}} - O - \right]_n + nH_2O$$

The hydrolysis presents difficulties in that the reaction proceeds rather violently, liberating considerable heat and large quantities of troublesome hydrogen chloride. Organoalkoxysilanes are equally well suited for hydrolytic preparation of polysiloxanes, but react less vigorously with water, thus facilitating control of the reaction. Furthermore, there is no formation of hydrogen chloride; the only other hydrolyzation product is an alcohol. Therefore the question arises as to whether organoalkoxysilanes can be made by direct

synthesis with ethers (instead of organohalides) as starting materials. The problem has been investigated by several authors, as listed in a summary report.[1] No encouraging results could be obtained, however. A patent by Yamada and Yasunaga[2] claimed that ethers react directly with silicon under certain specialized conditions, but this result could not be confirmed on reinvestigation.[3]

The aim of the work here presented was to check some reactions already investigated in the past, and to try to find new methods to overcome the inherent low reactivity of ethers in the direct synthesis with elemental silicon.

2. USE OF LAMINAR SILICON

Kautsky[4,5] describes an unusually reactive form of elemental silicon obtained by treating $CaSi_2$ with $SbCl_3$ at elevated temperature:

$$3CaSi_2 + 2SbCl_3 \longrightarrow 6Si + 2Sb + 3CaCl_2$$

One way of removing the unwanted antimony is to oxidize it with iodine and remove the SbI_3 with hot benzene. Removal of the $CaCl_2$ is more difficult. Alcohol not only acts as a solvent for $CaCl_2$ but also reacts with the silicon; a brown powder results, which catches fire after moderate warming in the open air. The brown powder also reacts violently with water.

---

[1] J. J. Zuckerman, Adv. in Inorg. Chem. and Radiochem., Vol. 6, p. 407, (1964).

[2] S. Yamada & E. Yosunaga, Japanese Patent 286(1951); Chem. Abstr. 47 3334(1953)

[3] J. J. Zuckerman, Thesis, Harvard University, Cambridge, Mass., 1960.

[4] H. Kautsky and L. Haase, Z. Naturforsch. 8b, (1953) 45.

[5] H. Kautsky and L. Haase, Chem. Ber. 86, 1226 (1953).

Kautsky[4,5] assumes that the layer structure of $CaSi_2$ remains unchanged when it is treated with $SbCl_3$. In his view the ionic silicon layers are reduced to elemental silicon, the electrostatic attraction to the positively charged calcium ions vanishes, and the stack of layers breaks down, leaving extremely finely-divided silicon of very great surface and high reactivity. This so-called laminar silicon has already been examined by Zuckerman,[6] but he was not successful in bringing about a reaction with ethers. Since Zuckerman did not prepare the laminar silicon himself, but used a sample obtained from the General Electric Company instead, and since he performed only a single run with methylphenyl ether (anisole), we thought it might be of interest to make Kautsky's silicon on a larger preparative scale and to try it out under different reaction conditions and with different ethers.

Following Kautsky's procedure we got a product matching the properties described in the literature, except that it stubbornly retained considerable amounts of SbI_3 despite repeated washing with benzene. Orientational experiments were carried out in sealed tubes with suspensions of laminar silicon in a) ethanol, b) anisole (methylphenyl ether), and c) acetone. The tubes were kept at 210°C for 60 hours. After this time the alcohol and acetone had reacted completely, but anisole did not react at all. The reactions with alcohol and acetone gave quite complex reaction mixtures which were not investigated further.

---

[6] J. J. Zuckerman, Ph. D. Thesis, Harvard University, Cambridge, Mass. 1960.

Since we were not successful in getting pure laminar silicon, free of SbI_3 and halide impurities, and since there is strong possibility that SbI_3 acts as a Friedel-Crafts catalyst and obscures the results, the experiments with laminar silicon were discontinued.

3. ACTIVATION OF SILICON AND SILICIDES BY GRINDING IN INERT ATMOSPHERE OR IN VACUO

When ordinary elemental silicon is milled in an inert atmosphere or in vacuo, its reactivity is greatly enhanced by virtue of breaking up the oxide film on its surface. For example, ordinary silicon does not react with ammonium hydroxide, but upon lengthy grinding under the surface of ammonium hydroxide, strong hydrogen generation occurs.

A convenient all-glass ball mill which may be used either for grinding in vacuum or in inert atmosphere is described by E. Zintl and W. Morawietz (see Houben-Weyl "Laboratoriumspraxis" I/2, p. 449). Such a device was made of Pyrex and mounted in felt-lined bearings so it could be rotated about its horizontal axis. Steel balls were used to accomplish the grinding (see Fig. 1).

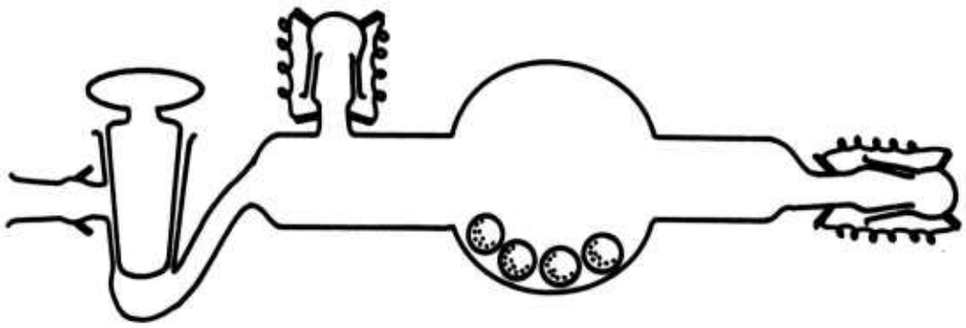


Figure 1.

Silicon and $CaSi_2$ were ground in this mill in vacuo, and then were used in the following experiments:

(1) Anhydrous acetone and vacuum-ground silicon were sealed into a Carius tube and then kept at 150°C for 70 hours. No change could be noticed. Similarly, silicon was treated with a variety of ethers at about 250°C for periods of 12 hours, again without any reaction taking place.

(2) In an anologous, manner, vacuum-ground $CaSi_2$ and several aliphatic ethers, e. g., di-n-hexyl ether, di-n-butyl ether, and also di-naphthyl ether, were heated in sealed tubes, but no reaction occurred.

4. NaSi AS A POTENTIAL SILICON CARRIER IN THE DIRECT REACTION WITH ETHERS

It is well known that ethers are split upon treatment with metallic sodium. For example, anisole reacts according to the following equation:

$$C_6H_5OCH_3 + 2Na \longrightarrow C_6H_5ONa + CH_3Na$$

Up to 1948 alkalimonosilicides were unknown, except for a compound Li_6Si_2 described by Moissan. Then Hohmann[7] prepared silicides by heating very finely powdered silicon with distilled alkali metals in fused alumina crucibles which were inserted into small iron bombs under argon. The monosilicides are for the most part well-crystallized brittle substances of metallic luster. They display a remarkable reactivity towards water, oxygen, diluted acids, etc. Mostly they ignite explosively upon contact with above mentioned reagents. The reactivity increases from NaSi to CaSi.

We were interested in whether a reaction would take place between NaSi and ethers, and if so, what the reaction products would be. The procedure given by Hohmann requires that in an argon atmosphere very finely powdered

[7] E. Hohmann, Z. Anorg. Chem. 257, 113 (1948).

silicon along with three or four times the stoichiometric amount of distilled sodium be placed into a crucible of fused alumina, the latter being inserted into a small iron bomb which can be closed tightly with a screw cap and a copper gasket. Then the bomb is heated to 700°C for 24 hours and slowly cooled down over a period of 72 hours. The upper end of the bomb is then almost turned off on a lathe and opened in an argon current. It then takes several days to distill off the excess sodium at 300°C. NaSi remains as dark shining needles. Hohmann reports in his paper that according to Geiersberger and Orlamunder (unpublished), the reaction between potassium or sodium and silicon can be brought along in a particularly simple manner; after heating the components in an ordinary iron crucible under nitrogen to several hundred degrees and cooling to room temperature, it appears that the mixture immediately catches fire in the air, a property not shown by either alkali metal or silicon alone. We repeated this experiment with pretty much the same result. When we tried to clean the crucible with methanol, the residue sticking to the walls ignited explosively..

All attempts to carry out Hohmann's procedure in detail were unsuccessful. This is due to the fact that I could not obtain fused alumina crucibles, but had to use porous "Norton" alundum thimbles which did not confine or contain the molten sodium. Furthermore, it proved to be difficult to seal the bombs appropriately. A Parr bomb which was used throughout these experiments could not be sealed tightly enough with either commercially available hollow copper gaskets (filled with asbestos) or with a specially-made plain copper gasket. Each time some leakage occurred, causing the

sodium to escape, with the result that the threads froze and had to be cut open in the machine shop. It was necessary then to replace the lid and the screw cap by new parts which are rather expensive. The major obstacle to the use of bombs of the Hohmann type is that they have to be specially made and therefore are very expensive, at least in the U.S.A., and all the more so since they can be used only once.

A very nice way to carry out the reaction would be to use sealed Pyrex tubes. The most serious drawback is that Pyrex resists sodium only up to 300°C(see C. B. Jackson and R. M. Adams, "Liquid Metals Handbook", Navexos P-733 (Rec.). Wash., D. C., U.S. Govt. Printing Office (1952)). Nevertheless, we tried this way taking care not to go higher than 300°C. It turned out, however, that at this temperature no reaction happened, even though the glass walls were considerably attacked. Experiments carried out in sealed tubes using 1) a mixture of metallic sodium, vacuum-milled silicon and di-n-hexyl ether, and 2)metallic sodium and silicon powder previously heated under nitrogen to several hundred degrees, then mixed with di-n-hexyl ether. The tubes were kept at 260°C overnight, then cooled and opened. Neither showed any reaction, and the vapor-phase chromatography analysis and infrared spectra were negative.

It is certainly worth the effort to carry through the Hohmann procedure and do experiments with pure NaSi in the necessary kind of bomb. The author intends to do this after his return to Germany, where the crucibles and bombs are available.

5. THE GOLD-SILICON SYSTEM

The gold-silicon system has been investigated by C. DiCapua[8], E. R. Jette and E. B. Gebert[9] and W. Loskiewicz[10]. These authors showed that the system behaves like a simple binary system, showing little or no mutual solubility of gold and silicon in the solid state (see Figure 2).

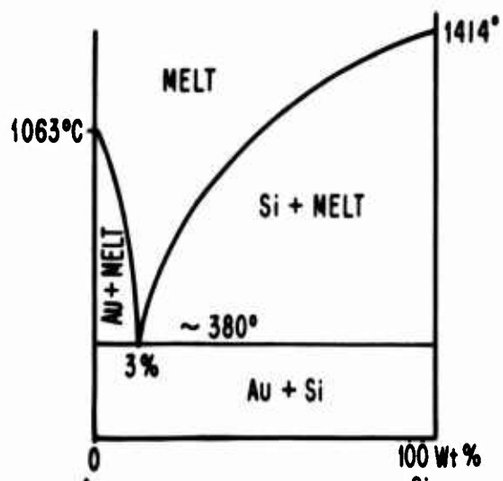


FIGURE 2

Its main characteristic is that it has an unusually low-melting eutectic, which in the early papers was graphically determined by extrapolation and was reported to have a composition of around 6% Si and 94% Au by weight, melting at about 300°C according to Berezhnoi[11] and at 370°C according to Gmelin[12].

---

[8] DiCapua, Att. accad. naz. Lincei 29, III (1920).

[9] E. R. Jette and E. B. Gebert, J. Chem. Phys. 1, 735 (1933).

[10] W. Loskiewicz Prezglod Gorniczy-Hutniczy 21, 583 (1929).

[11] Berezhnoi, "Silicon and its Binary Systems", Cons. Bureau, N. Y. 1960.

[12] Gmelins Handbook d. anorg. Ch. Band 8, Gold, Auflage, 1954, p. 727.

A recent investigation by E. G. Heath[13] using semiconductor grade silicon and a new technique involving gravity segregation confirmed most of the already-known facts, including a m. p. between 370° and 380°C for the eutectic, but the composition of the eutectic was found to be 3.15 ± 0.05% Si by weight (or 18.6 ± o.3 atomic %). Heath points out that the gold-silicon eutectic therefore falls in the large group of binary eutectics in which the atomic percentage of the atom of smaller diameter lies between the values of 17 and 19 (Hume-Rothery and Anderson 1960).

Although copper and silver are extensively used as catalysts for the direct synthesis of alkyl- and aryl-halosilanes, gold has never been checked in respect to its suitability as a possible catalyst. This is partly understandable, since the quantities required in large-scale production would be tremendously expensive. On the other hand, the gold-silicon eutectic has the unique advantage of being liquid at relatively low temperatures, which would make it possible to keep a clean surface continually in contact with the organohalides. We desired to find out first of all whether gold shows catalytic activity in the eutectic, and whether it leads to a smooth reaction of the silicon with, for example, methyl chloride.

In the beginning we encountered considerable difficulty in preparing the eutectic alloy. Two ways chosen by the early workers consisted in 1) heating mixtures of the components in refractory porcelain crucibles in a hydrogen atmosphere beyond the melting point of silicon, and stirring with a porcelain rod, or 2) heating the mixture in an evacuated quartz tube beyond the m. p. of silicon, and subsequently chilling the charge. Heath reports

[13] E. G. Heath, J. Electronics and Control 11, 13 (1961).

that he prepared the eutectic by melting and chill-casting in vacuum, but does not mention to what temperature he heated the mixtures (although it seems that he too went beyond the m. p. of Si). Adopting the technique of working in evacuated quartz tubes, we tried to make the eutectic in Vycor tubes. We were not able to reach the m. p. of Si, not to mention going beyond that temperature. Keeping the tube at the m. p. of gold gave no satisfactory results. We decided then to work in an ordinary alundum crucible, and not to care about keeping the air off. At this point of our work we were happy to be able to use the facilities of the Gordon McKay Laboratory Metallurgical Department. But again we could not attain the m. p. of Si, although working with a "Heavy-Duty" furnace. The best we could do was to melt the gold, take the crucible out of the furnace, and add the calculated amount of Si while stirring with a graphite rod. This technique actually was successful; and the resulting alloy could conveniently be remelted over an ordinary Bunsen burner.

The eutectic Au-Si alloy had the color of freshly-melted tin, although the lower side of the ingot had a gold color. The eutectic alloy was very brittle. After several days in the open air the color had turned to yellow. When brought to the melting point, the surface of the alloy became covered with a dull grey skin, which developed again when it was removed. At the melting point both the melt and the skin are of tin color, but these change to gold color upon solidifying. The melt sticks tenaciously to Pyrex glass, and since it expands upon soldifying, it causes the glass to break into small pieces. The melting point was found to be around 380°C. The alloy and its melting point varied somewhat with each ingot, since complete dissolution of the calculated amount of Si was difficult, and since excess silicon arbitrarily was added when too much skin had been formed.

The following way of preparing the alloy was finally developed: massive gold was placed in a porcelain crucible, covered with silicon and then heated with a Meker burner. Then, with a graphite rod, part of the silicon was "rubbed" into the gold surface, which resulted in local alloy formation and liquefaction. Once liquid alloy was generated the conversion of the whole mass into alloy went rather smoothly. Care was taken to stir thoroughly. This procedure, though time consuming, gave better yields than the previous method.

Recovering the gold out of used alloy was conveniently done by treating with aqua regia, evaporating to a small volume, and repeating these two steps once or twice. After this the nitric acid was removed as completely as possible by treating with hydrochloric acid and evaporating. Finally the resulting concentrated $HAuCl_4$ solution was diluted with distilled water and the gold precipitated with hot oxalic acid, filtered, washed, and melted in a porcelain crucible.

Gravimetric determination of gold in samples of the alloy was done following the procedure by G. Spacu and M. Kuras, Z. anal. Ch. 104, 88 (1936), consisting in precipitating the gold with 2-mercaptobenzothiazole in alcoholic solution. Silicic acid also precipitated during the step of removing the nitric acid with hydrochloric acid. Therefore the filter containing the mixture of silicic acid tris (2-mercaptobenzothiazole)-gold and free 2-mercaptobenzothiazole was carried over into a platinum crucible, and after incineration was treated several times with hydrofluoric acid until its weight was constant.

6. PRELIMINARY EXPERIMENT WITH METHYL CHLORIDE

Methyl chloride was passed through gold-silicon eutectic alloy in the device of Fig. 3 for one hour at 390°C, and the products were led through a trap held at 0°C. No condensable products could be obtained. The exit gases did not smell of methylchlorosilanes or hydrogen chloride. Probably

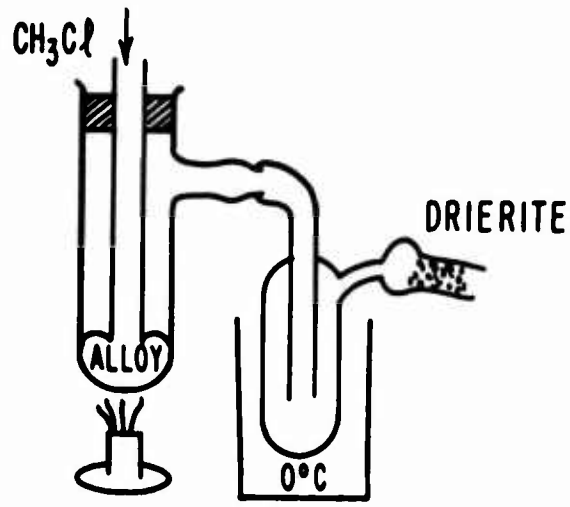


FIGURE 3

the way the methyl chloride ran through was to short to lead to a noticeable reaction. Therefore we set up an apparatus which permitted shaking the alloy, thus assuring closer and more extensive contact of the alloy surface with the methyl chloride (see Fig. 4).

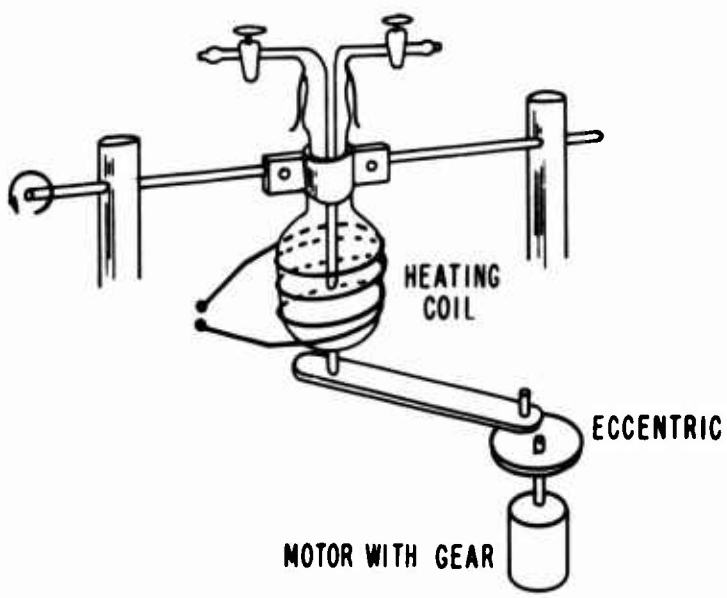


FIGURE 4

The flask was lined with a NORTON "Alundum" Crucible, since we observed that the alloy did not stick to this material (see Fig. 5). Heat was furnished

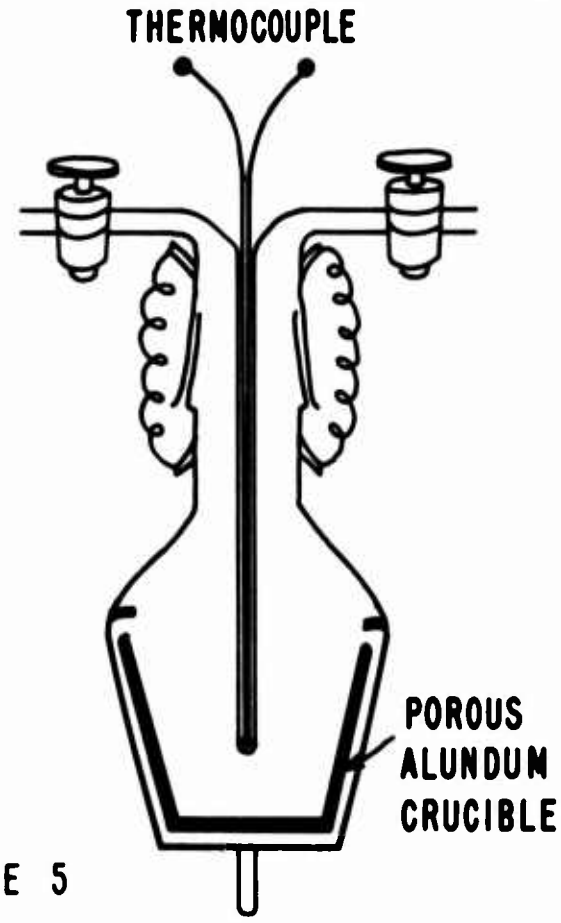


FIGURE 5

by a Nichrome coil wound around the flask, and the temperature was measured by a thermocouple. Stopcocks at the inlet and outlet tubes (see Fig. 4) allowed the enclosure of definite quantities of methyl chloride. In the first experiment CH_3Cl was passed through the apparatus while the alloy was kept at 390°C. The exit gases contained much of what we thought to be hydrogen chloride. It was believed that this was due to catalytic degradation of the alumina surface. In the next experiment the reaction flask was filled with a defined amount of methyl chloride, closed and then shaken

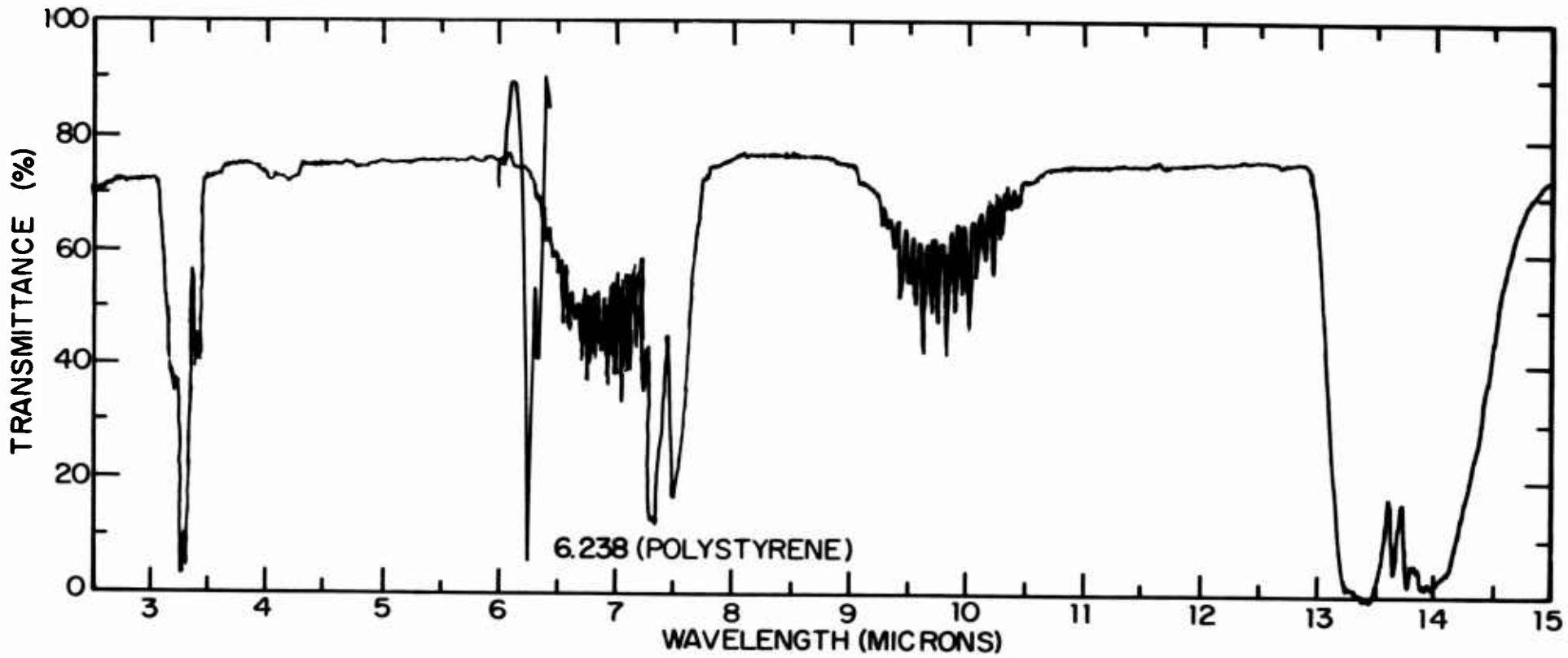
at 390°C over a period of one hour. First, formation of a skin on the surface could be observed, then the skin gradually disappeared, followed by a deposition of reddish brown dust which covered up the entire surface of the inner walls of the flask. Towards the end some white deposit was also generated. After cooling down the flask and opening it, air streamed into it, giving white smoke. The contents of the flask had a choking odor of hydrogen chloride and probably also methylchlorosilanes. The original purpose of this experiment had been to control the pressure change which should take place during a reaction, but this attempt failed because the Tygon tubing connecting the outlet tube to a manometer proved permeable to methyl chloride. The manometer was then replaced by a trap maintained at -30°C. and a slow methyl chloride current was passed over the agitated alloy at 390°C for 2 hours and 30 minutes. Upon evaporation of the trapped exit products, no liquid condensate was left.

Since up to this point it had not been possible to establish clear evidence for the formation of methylchlorosilanes, it was decided to follow the reaction by infrared techniques. Again the flask was charge with a defined amount of methyl chloride, and the outlet tube was sealed with a serum stopper. Previously some silicon powder[14] had been added to the alloy. After 30 minutes reaction time at 390°C the first sample of 8 cc was taken out of the flask with a syringe and transferred into a 50 mm gas cell. In addition to the methyl

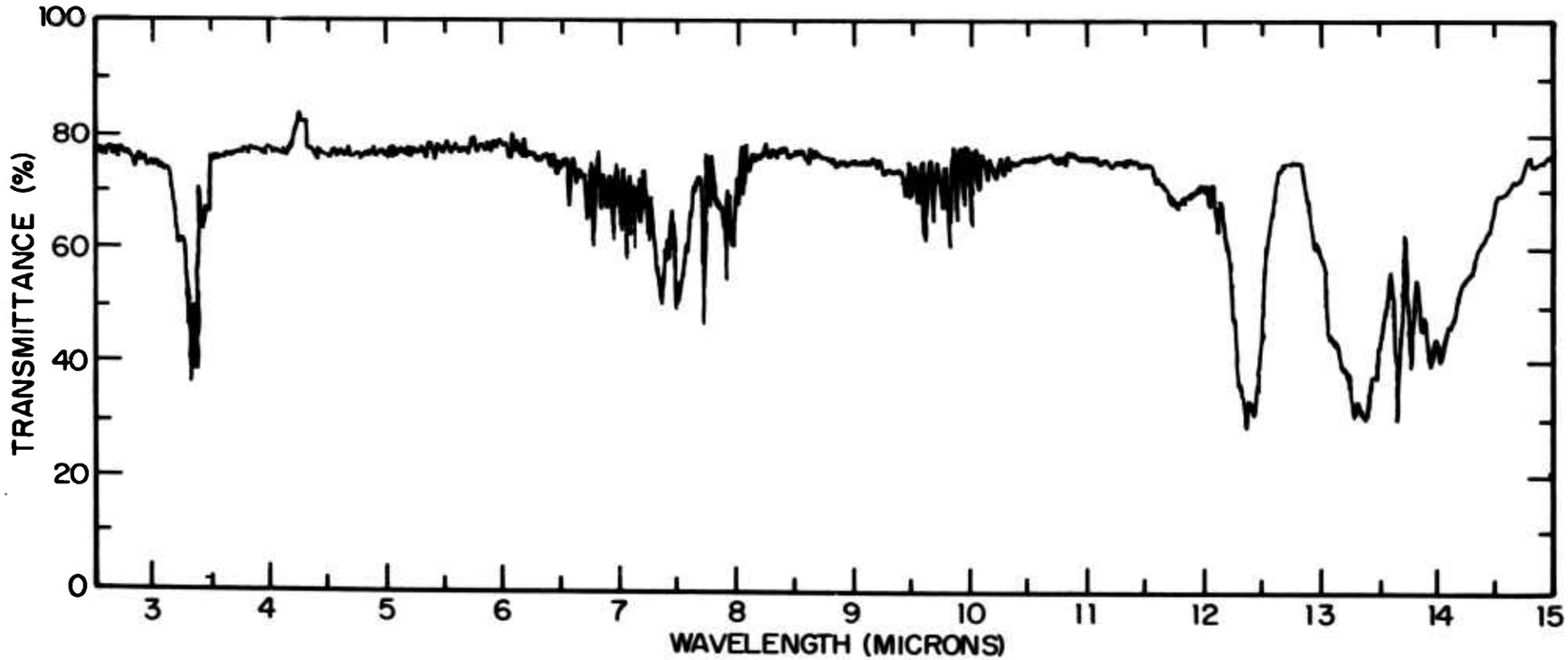
[14] The silicon used throughout the experiments described in this report was: Silicon 99.86% pure, 80 mesh, A. D. MacKay, Inc., 198 Broadway, New York 38, N. Y.

chloride spectrum there were absorption bands which in part might be assigned to methyl groups on silicon, particularly in the 12.4μ region. The narrow band which lies very close to 8.0μ belongs to the CH_4 spectrum (see Spectrum #21) whose most characteristic band is located at 7.7μ . The most interesting fact is that methane is generated at the comparatively low temperature of 380-390°C, and this will be discussed in a later portion of this report.

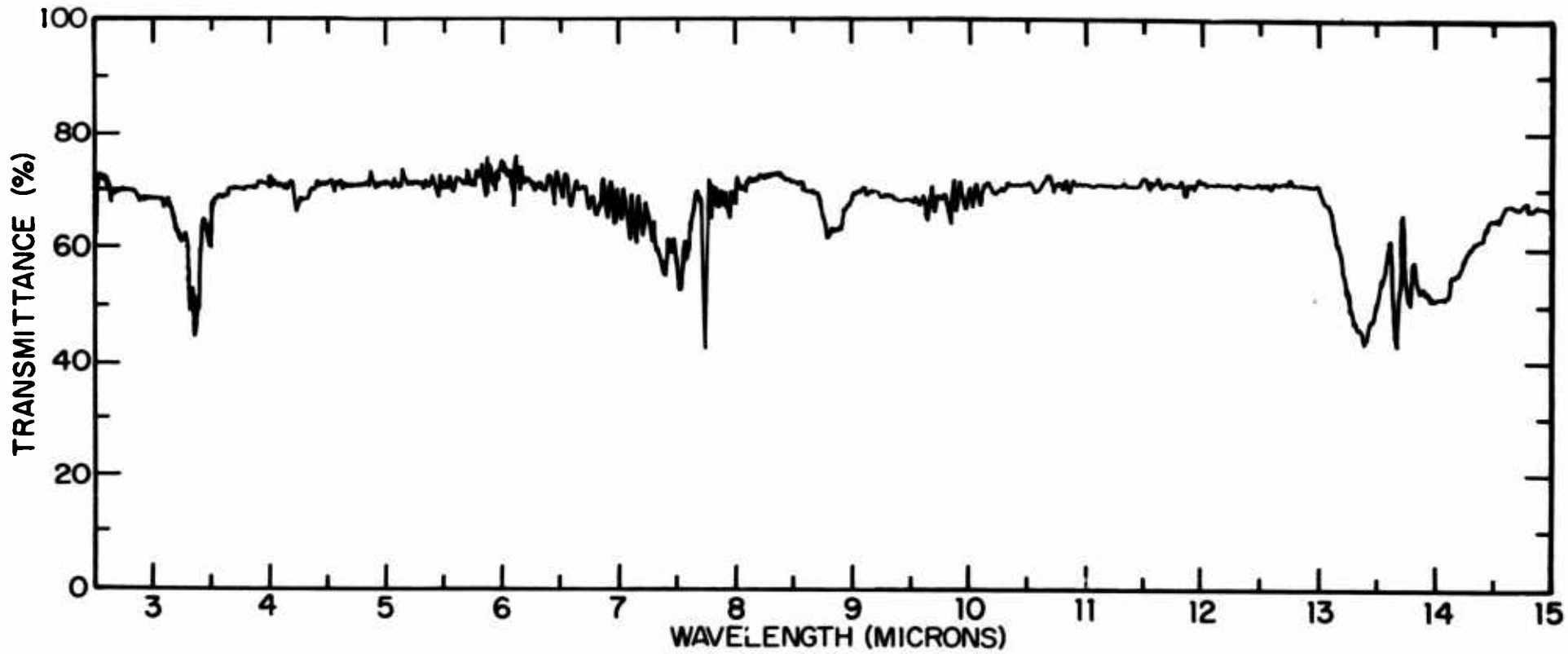
Samples taken after 45 minutes and 60 minutes, respectively, from the start of the experiment gave essentially the same spectra. At the end of the experiment the walls of the flask were again covered completely with reddish brown dust. It is interesting to note that after about a month during which time the last sample had been kept in the gas cell the band at 12.4μ (see Spectrum #a29) had disappeared. This suggests some kind of interaction with the walls of the cell, probably due to adsorbed atmospheric moisture; this would be in agreement with the presumption that this band was caused by methylchlorosilanes. Although no conclusive evidence for the formation of methylchlorosilanes could be gained, two interesting features of the interaction of methyl chloride with the gold-silicon alloy were established: on the one hand the occurrence of methane, as mentioned above, and on the other hand the formation of extremely finely-divided reddish brown dust particles which had been deposited all over the walls of the flask. Part of this powder was collected, no special care being taken to protect it from exposure to the air. A small quantity was treated with aqua regia and a test for gold was performed with $SnCl_2$ (Cassius) with positive result. Whether silicon also was



NO. 16 CH_3Cl (MATHESON LECTURE BOTTLE)



NO. 21 8 ml. OF REACTION VESSEL CONTENTS



NO. a 29 CELL FROM 3/6/65, AFTER STANDING. ONE GROUP OF BANDS IS MISSING NOW.

present could not be established. Another small sample was brought into an X-ray capillary and a powder diagram was taken. Comparison with a diagram obtained from pure gold powder showed that the brown deposit was mainly gold with a little silicon (see Fig. 6). (This is understandable, since some silicon had been added).

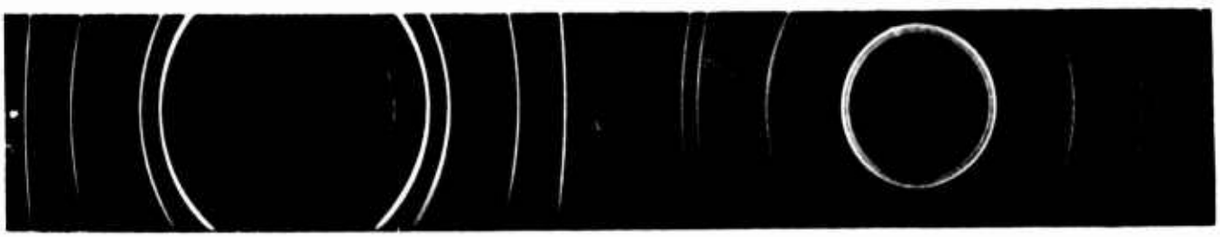


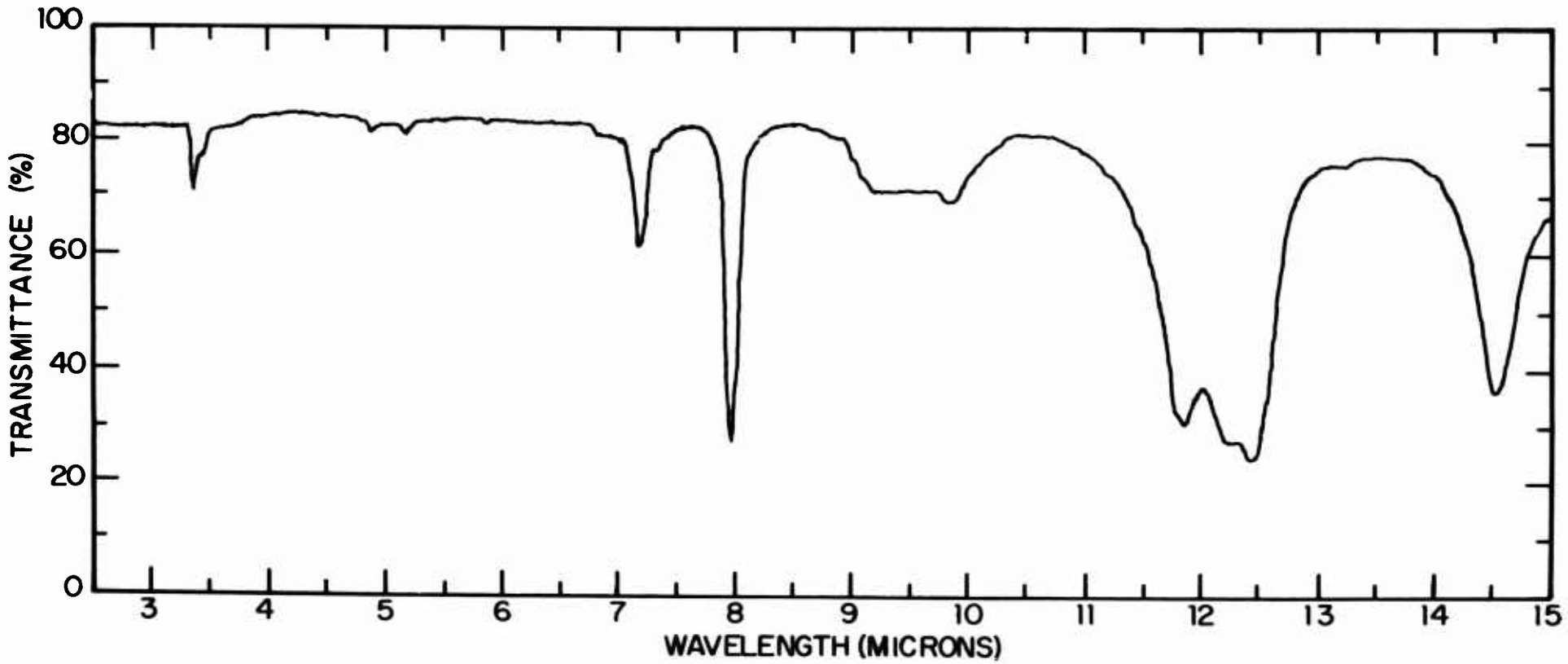
FIGURE 6

For working on a preparative scale the shaking device was abandoned because it was too difficult to clean after each run, and especially the liner, which could not be replaced. Instead, an apparatus was chosen which permitted stirring the alloy with a Pyrex stirrer (see Fig. 7). This time cylindrical Pyrex glass liners were used instead of Alundum crucibles, because they were cheaper and more available. Furthermore, we feared that aluminum oxide might interfere catalytically. After each run the glass liner had to be replaced due to breakage. After some powdered silicon had been added to freshly prepared alloy, a reaction was carried out over a period of 45 hours at a temperature of 385°C. A methyl chloride current of about 50 bubbles per minute, roughly corresponding to 2 mmoles per hour, was passed over the alloy

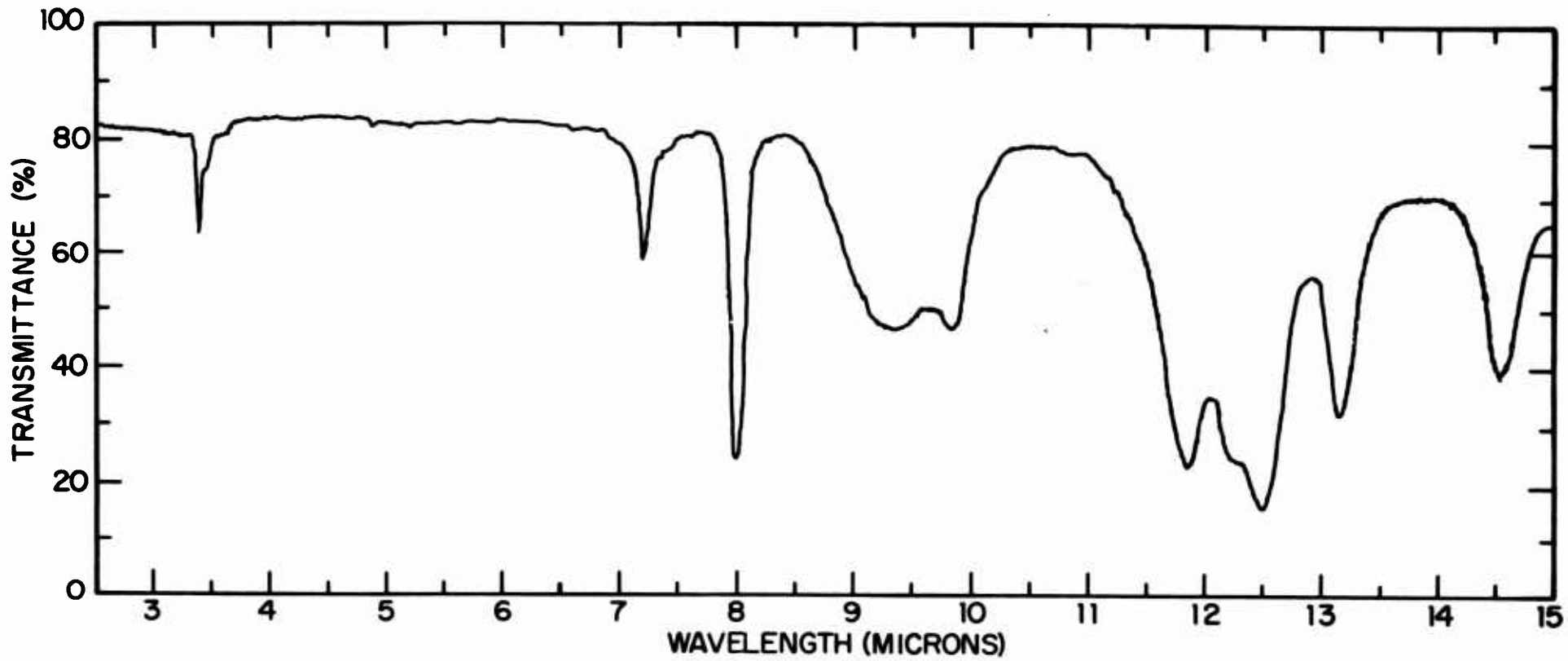
with a mixture of nitrogen. Trap I was kept at 0°C, trap II at -30°C and trap III at -70°C. After the experiment no condensate at all was found in trap I, upon evaporation of the lower boiling products; these also were condensed into a small bomb and checked by infrared, which showed only methyl chloride. In traps II and III about 0.5-1.0 cc of a clear liquid was left having the characteristic smell of methylchlorosilanes. The infrared spectrum was the same as that of an authentic sample of $(CH_3)_2SiCl_2$ (see #34, #22) except for the absorption band at 1.131μ[15]. Here again the walls of the reaction vessel were covered with a thick deposit of reddish brown powder. There was no such deposit right over the blade of the stirrer. Only a few centimeters away from the blade, deposit could be found, getting thicker the greater the distance from the blade (see Fig. 7). The alloy was covered with a relatively coarse brown powder mixed with unchanged silicon granules. It seemed that a considerable part of the silicon had been dissolved during the reaction time.

Analysis of the liquid product by gas chromatography could not be performed, because at this stage of the work no appropriate equipment was available. NMR spectra provided no useful information because they were too complex. All material having been used up in the meantime, this experiment was repeated. Some experimental details are recorded in the following: the glass liner was charged with 53 grams of gold-silicon alloy, and 2.4 grams of 80 mesh silicon were added. Two traps were connected to

[15] Due to $(CH_3)_3SiCl$ and CH_3SiCl_3 (see A. L. Smith, Spectrochimica Acta, 1960, Vol. 16, p. 87).



NO. 34 $(CH_3)_2SiCl_2$ FROM G.E. (CAPILLARY)



NO. 22 REACTION PRODUCT -70° (CAPILLARY)

the outlet, and both were kept between -50 and -60°C. Temperatures during the experiment varied between 381°C and 387°C. Methyl chloride was passed over the alloy at an approximate rate of 8 mmoles/hour. Two hours after reaction started the walls were already covered with considerable brown deposit. After 70 hours the reaction was stopped and the traps were disconnected. The weight loss of the glass liner and contents was 15.8 grams. Most of the elemental silicon which had been added seemed to have dissolved during the reaction. After evaporation of the methyl chloride about 1.5 grams of methylchlorosilanes remained. Much of the methylchlorosilane product was carried away by the methyl chloride, so that by more careful evaporation the yield would certainly have been higher. This time the mixture of methylchlorosilanes was examined by gas chromatographic techniques. For our purpose we used an F & M Flame Ionization Gas Chromatograph, Model 609, and an 8' 1/4" column of 20% Silicone (Fluoro) FS1265 (QF-1) (also furnished by the F & M Scientific Corporation) on 60-80 mesh support (probably Diatoport). After trying several column packings we chose this one for its excellent separating properties for methylchlorosilanes. The following set of data was used to obtain the chromatograms #B - H:

Injection Port	178-180°C
Block Heater	196-198°C
Column Temperature	50-55°C
Sample size	1μl
Chart Speed	0.5"/min.
Attenuation	E = 4
Flow Rate Helium	~70 ml./min. (Rotameter reading 6.1)
Flow Rate Air	>800 ml./min. (Rotameter reading 12.4)
Flow Rate Hydrogen	~60 ml./min. (Roatameter reading 8.2)

Chromatogram A was run under similar conditions, but the sample size was much greater, about 30 to 50μl being injected. It (Chromatogram A) has been included to show that the crude organosilicon product obtained by direct synthesis contains a small proportion of various high-boiling compounds whose nature was not established during this work. Chromatogram I differs from the rest of the chromatograms only in that the attenuation was E = 2, and the sample size 10μl. In Chromatogram B the peak areas of the three methylchlorosilanes were counted out on graph paper and, as a rough standard to go on, the total was set equal to 100. From this the percentage of the individual components are about 28% $(CH_3)_3SiCl$, 24% CH_3SiCl_3 and 48% $(CH_3)_2SiCl_2$. The chemical identity of the compounds in question was secured by admixing standard samples of $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, and CH_3SiCl_3 made available through the courtesy of the General Electric Company's Silicone Products Laboratory at Waterford, N. Y. These standard samples were not absolutely chromatographically pure, but are as pure as can be obtained by distillation. Gas chromatograms made by General Electric on the samples are included in this report. In spite of their impurities, the standard samples were well suited to identification purposes. Chromatogram I made with pure MATHESON lecture bottle methyl chloride proves that the reaction product still contained disssolved methyl chloride.

The work with methyl chloride and gold-silicon alloys established that 1) gold acts catalytically to help effect reaction between methyl chloride and silicon, since pure silicon alone in the same apparatus under the same conditions produced no methylchlorosilanes whatever, 2) the reaction consumes

silicon from the surface of the liquid alloy, and hence the liquid must continually be stirred to bring fresh surface into reaction, 3) a mixture of products is obtained, but $(CH_3)_2SiCl_2$ predominates, and 4) the gold does not all stay confined to the reaction zone but becomes scattered and appears some distance away as a red powder. The last point adds even more doubt concerning the feasibility of using gold-silicon alloy as a practical reaction medium, but for the purposes of laboratory investigation the unique behavior of the Au /Si system encouraged us to try it on preparative reactions which have not been successful under more ordinary conditions.

7. REACTION OF GOLD-SILICON ALLOY WITH METHANOL

The same apparatus (see Fig. 7) was used for this experiment. The

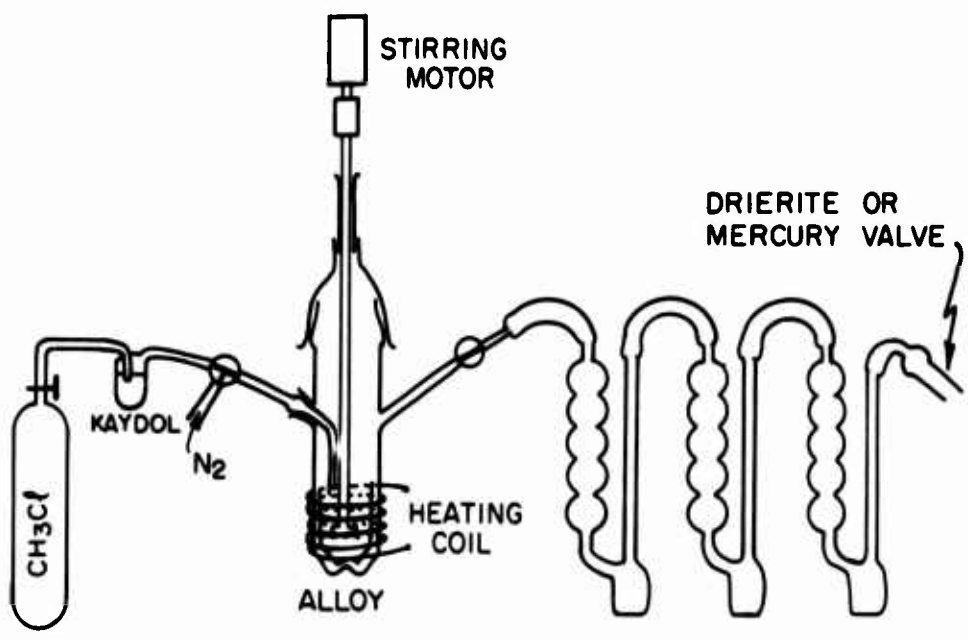


FIGURE 7

glass liner was charged with 48 grms of freshly prepared gold-silicon alloy and 2 grms of 80 mesh silicon. Two traps were connected to the outlet tube

and cooled with crushed ice. Prepurified nitrogen was bubbled through anhydrous methanol (Fisher Certified Reagent) held at room temperature, and then passed over the alloy. About one hour after the start of the experiment, some deposit could be observed on the walls of the reaction vessel. However, it was of an entirely different appearance from that seen before. It was coarser than the deposit formed during reaction with methyl chloride, and was of a pure pink color rather than brick-red. After approximately 2 hours and 30 minutes the clean shining alloy surface had disappeared under a thick layer of pink-colored powder. On reducing the stirring speed the alloy again became visible. It could be observed that here again the pink deposit was carried over considerable distances, settling down (for example) in the outlet tube at a distance of about 15 cm from the liner. This was just what we had observed in the case of the experiments with methyl chloride.

After 18 hours the experiment was stopped. By then the layer of deposit on the walls had grown considerably, and remained of pure pink color. A film of liquid substance could be noticed in parts of the vessel. About 14 grams of methanol had been carried along with the nitrogen. Trap I contained roughly 5 cc of a cl r colorless liquid, and trap II about 0.3 cc of clear colorless condensate on the surface of which floated a thin solid white skin. Of the alloy nothing was left in the liner. It had been completely converted into a pink powder mixed with much unchanged silicon. Furthermore, a very striking volume increase had occurred. Aqua regia did not wet a sample of the pink powder; only on repeated boiling was the sample attacked by it, and white spongy foam separated on the surface of the solution. X-ray powder

diagrams made of the wall deposit and of the powder in the liner showed exclusively the pattern of elemental gold.

FIG. 8 POWDER PATTERN OF THE POWDER IN THE LINER

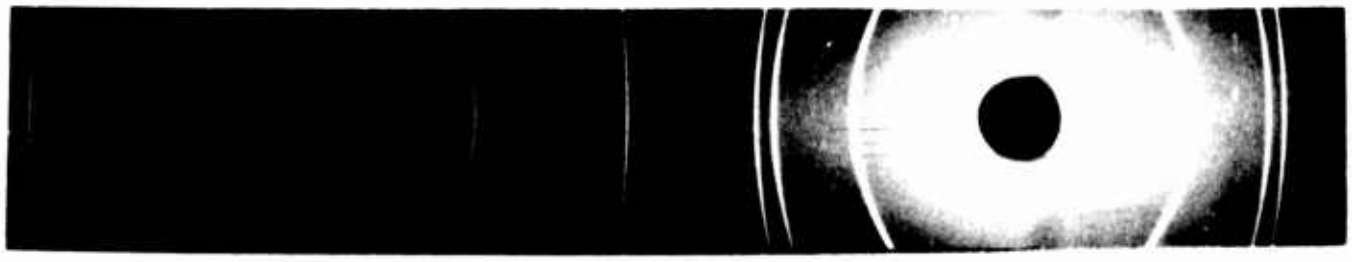


FIG. 9 POWDER PATTERN OF ELEMENTAL GOLD

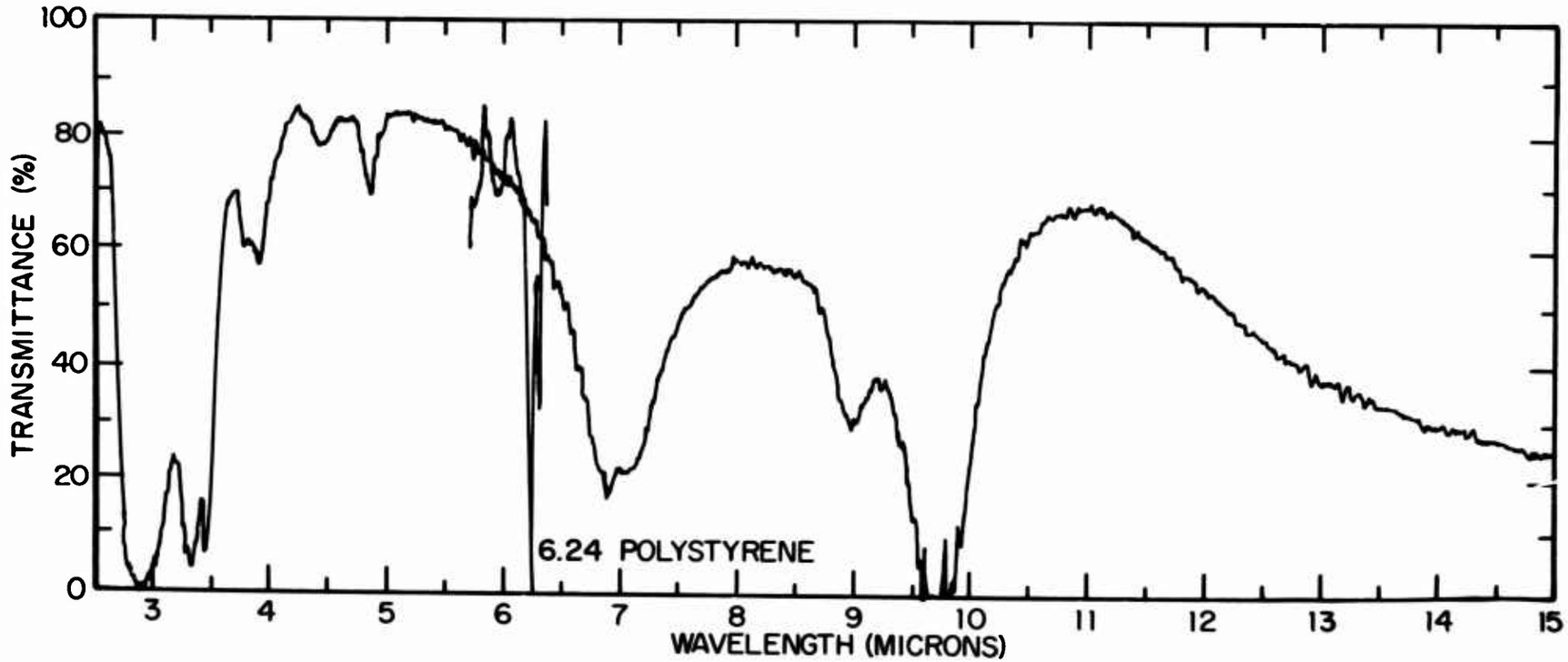
When treating a sample of the pink powder with 10% methanolic KOH solution, most of the bulky powder dissolved, leaving a little gold powder of the true yellow gold color. The supernatant alcoholic solution was then of the same pink color, and did not fade on standing (at least for one day). The liquid condensate in both traps had a very peculiar choking and irritating odor. In a sample sent to Schwarzkopf Microanalytical Laboratory no silicon could be detected. Gas chromatographic examination did not reveal the nature of

the reaction products. Samples of tetramethoxysilane and dimethyldimethoxysilane were synthesized according to procedures described in the literature[16]. These samples were not absolutely pure by gas chromatographic standards, but it was possible nevertheless to show that the reaction products in question were not identical with either one of the above-mentioned reference substances. (See the following chromatograms[17].) The infrared spectrum of the reaction products showed several peaks in addition to those of methanol (see #65,#66).

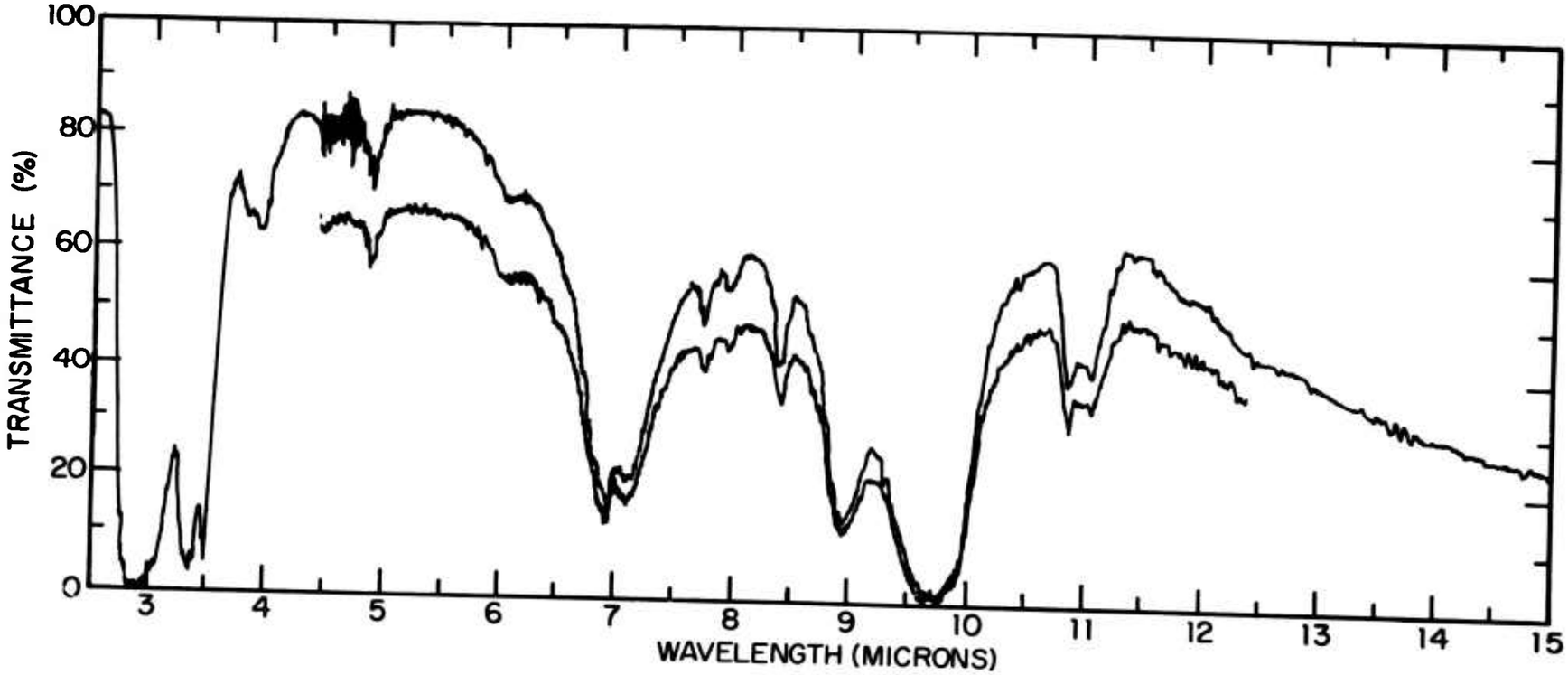
APPARATUS FOR THE PREPARATION OF TETRAMETHOXYSILANE

[16] For $(CH_3O)_4Si$ the method given in Brauer "Handbuch der praparativen anorg. Chemie" Vol. 1, p. 623 was modified and simplified: anhydrous methanol (Fisher Certified Reagent) was used without further drying. A 100 cc. Erlenmeyer flask was charged with 0.4 moles of methanol and a magnetic stirring bar, then sealed with a serum stopper. A little less than 0.4 moles of $SiCl_4$ was slowly added under constant stirring by means of a syringe. The hydrogen chloride evolving during the reaction escaped through a hypodermic needle plunged into the serum stopper. Cooling was done by immersing the flask into a Petri dish filled with crushed ice. Then it was stirred for 30 min. while warming up, until HCl evolution was over. Finally the product was fractionated: b.p. 117°C, reported lit. value 121°C. Refractive index nD/23 = 1.366, reported lit. value nD/20 = 1.3683. For $(CH_3O)_2Si(CH_3)_2$ a similar technique was used, following the indications given in JACS 75 (1953) 2712, b.p. 80-82°C, nD/25 = 1.369, reported lit. value nD/20 = 1.3708.

[17] From Chromatogram P it seems as though a reaction took place between the reaction products and the $(CH_3O)_2Si(CH_3)_2$.



NO. 65 CH_3OH, SUCH AS WAS USED IN THESE EXPERIMENTS (CAPILLARY)



NO. 66 PRODUCT OF DIRECT SYNTHESIS, CH_3OH + Au/Si (CAPILLARY)

8. REACTION OF GOLD-SILICON ALLOY WITH ETHERS

1) Anisole: One experiment was carried out in a similar fashion as that with methanol. Nitrogen was bubbled through anhydrous anisole (methyl phenyl ether) heated to 140°C (b. p. 155°C). During the experiment considerable dark brown deposit settled down on the walls. The powder pattern of this substance was essentially identical with the gold pattern (see Fig. 10).

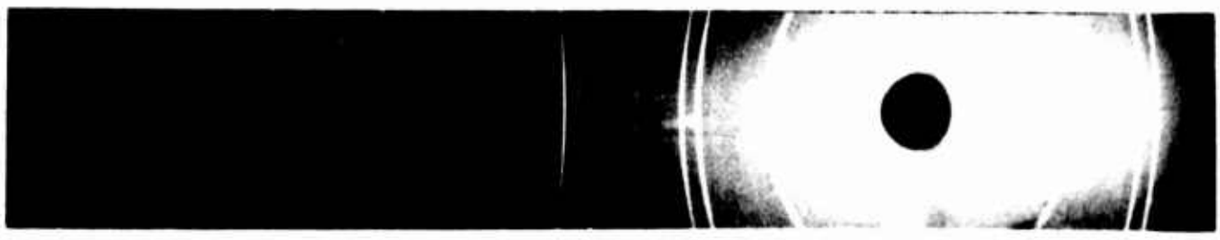


FIGURE 10

The major part of the alloy in the liner had again been converted into a brown coarse powder.

A second experiment was carried out somewhat differently. This time the anisole was dripped into the reaction zone. A reflux condenser was inserted to assure recycling of the ether. This had the inconvenience that liquid anisole came into contact with the molten alloy, which then began to solidify. After discontinuation of the run the anisole showed positively no signs of any change, according to its spectrum.

2) Dimethyl ether: Over a period of 40 hours MATHESON lecture cylinder dimethyl ether was passed over the molten alloy in the same apparatus as

used throughout these experiments. Again two traps were lined up next to the outlet tube and cooled with methanol/dry ice. After the end of the reaction the walls of the vessel were covered again with the all-too-well known deposit, this time of dark brown color. The X-ray pattern was that of gold (see Fig. 11). Trap I was filled to capacity with mainly dimethyl ether, which

FIGURE 11

also contained considerable quantities of brown powder. Infrared spectra taken from the gas in the reaction vessel and from pure dimethyl ether were identical.

After evaporation of the dimethyl ether out of trap I, a little bit of a colorless jellylike substance was left over, which became solid, white and opaque upon standing in the air. Apart from this, one of the bulbs of the trap was coated with a white layer. Trap II, which did not contain anything, showed some white spots (as though some liquid had evaporated leaving a solid residue). The white material in the bulb was examined somewhat closer: it had a pungent, irritating odor (similar to formaldehyde) and was of waxy consistency.

It dissolved smoothly in 10% methanolic KOH solution. The substance was collected and sent to Schwarzkopf Microanalytical Laboratory. The results showed that the substance in question contained silicon in a proportion of 0.48%. This is a very small but promising result to start with, and further work on this interesting problem should be done. At first this experiment should be repeated under the same conditions and the product examined more closely.

9. THE SEARCH FOR VOLATILE GOLD COMPOUNDS IN THE DIRECT SYNTHESIS OF METHYLCHLOROSILANES WITH A GOLD-SILICON ALLOY

At an early stage of the experiments it was found that during the reaction of methyl chloride with the molten eutectic mixture of gold and silicon a considerable amount of gold is transported over substantial distances as a red-brown dust of very small particle size. At the same time, infrared spectra show the generation of considerable quantities of methane (see page 11 of this report). Now, it is well known that organohalides undergo thermal degradation above certain limiting temperatures. For methyl chloride this particular decomposition temperature is reported in the literature to be 500°C in the absence of a catalyst[18]. Trambouze[19] found that copper lowers this

[18] R. J. Voorhoeve, De Synthese van Methylchloorsilanen: Proces en Mechanisme. Dissertation Tech. Hogeschool Delft, 1964.

[19] P. Trambouze, Bull, soc. chim. France 1956, 1756.

temperature down to 300°C by catalytic action. (See also Voorhoeve[18] and Rochow and Hurd[20]. The products of the decomposition are reported to be hydrogen, carbon, hydrogen chloride, intermediate methyl- and chloromethyl radicals, and methane[18, 19, 20].

We undertook a series of experiments to examine whether the smooth methane formation during our direct synthesis experiments was mainly due to pryrolytic decomposition of the methyl chloride, or to some other cause.

10. ELEMENTAL SILICON AND METHYL CHLORIDE

80 mesh silicon along with finely powdered silicon of the same grade was used for charging a glass liner in the same apparatus employed for the direct synthesis experiments. The outlet tube was connected to a straight tube mercury manometer. The apparatus was evacuated and then charged with methyl chloride. The silicon was stirred during 120 minutes at a temperature of 384°C. Not even traces of methane could be found in the infrared spectra. Neither could the smell of hydrogen chloride be noticed.

In the second run the duration was extended to 17 hours at 386°C[21]. The results were identical.

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[20] D. T. Hurd and E. G. Rochow, JACS 67, 1057 (1945).

[21] A third experiment was undertaken with preparative aims. Silicon powder was inserted into the glass liner, heated up to 380°C and methyl chloride was then passed over the silicon for 20 hrs. Surprisingly, the silicon powder was carried along and deposited on the walls very much the same way as it was the case with gold in the gold-silicon runs. There was even deposit in the Tygon tubing going from the outlet to the first trap. Very little liquid was found in trap I in form of small droplets which had strong acidic reaction. Infrared showed the characteristic spectrum of water. The condensate resulted probably from adsorbed atmospheric moisture. Its acidic reation possibly arose from the thermal decomposition of methyl chloride. Trap I had been kept on 0°C; Trap II, which had been cooled with methanol/dry ice, contained pure methyl chloride. The contents evaporated without leaving any residue.

11. ELEMENTAL GOLD AND METHYL CHLORIDE

Twenty-three grams of gold powder were stirred for 24 hours at 390°C with 620 mmHg methyl chloride. After this time the reaction vessel contained hydrogen chloride, which was detected with ammonia. Yet no methane could be found in the infrared spectrum.

12. APPARATUS BLANK

The apparatus was thoroughly cleaned, evacuated and charged with methyl chloride. At a temperature of 380°C it was stirred for 3 hours. The odor of the gas at the end of this time indicated a considerable amount of hydrogen chloride, but this could not be detected in the infrared spectrum. The latter showed exclusively the methyl chloride bands. No methane could be seen.

A second run was carried out over a period of 18.5 hours. The results were exactly the same.

From these experiments it seems that under the reaction conditions the methane generation was not due to methyl chloride pyrolysis, but was in some way characteristic of the gold-silicon alloy. In one case, for example, a strong methane peak at 7.7 was found in a sample collected 30 min. after the start of the experiment (see page 10). On the other hand, the remarkably small particle size of the red-brown gold powder deposited throughout the experiments strongly suggested the formation of some labile volatile gold alkyl compound. This would be in agreement with the work of Hurd and Rochow on

copper methyl in connection with the mechanism of the reaction between methyl chloride and silicon-copper (see literature reference on the preceding page[22]).

It was hoped that a potential gold alkyl compound might be trapped on a cold finger and prevented from decomposing. Therefore a modified version of the apparatus which had been used before was constructed for the following experiments (see Fig. 12). The only difference was that the middle part of the reaction vessel had to be made larger in diameter in order to fit a cold finger. The cold finger itself had evacuated and silvered double walls to ensure thermal insulation. The tip was in direct contact with the cooling agent, of course.

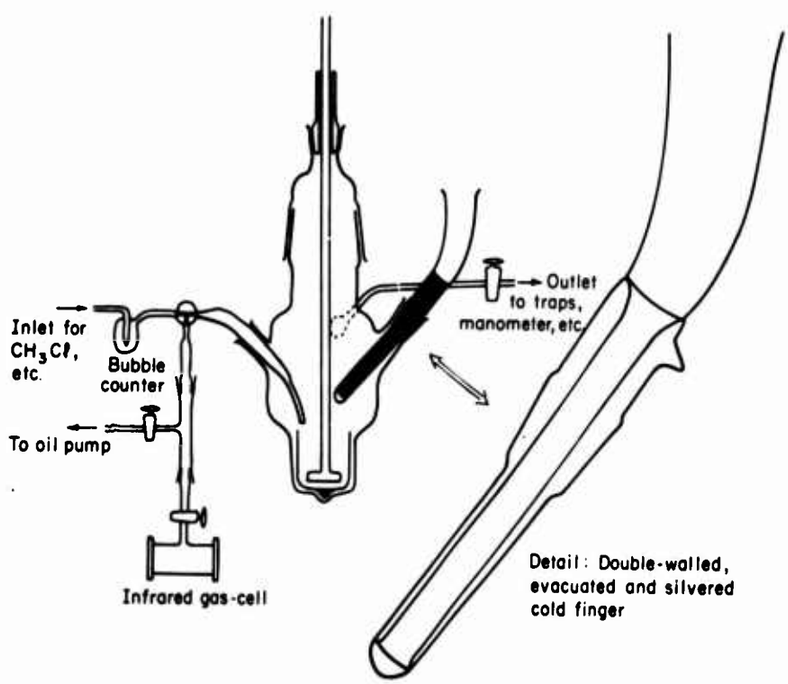

FIG. 12

[22] Recently the formation of copper methyl in the copper-catalyzed direct synthesis has been contested: R. Muller and H. Gumbel, Z. anorg. allg. Ch. 327, 302 (1964).

1) In the first experiment 47 grams freshly prepared gold-silicon alloy were heated to 360°C, at which temperature melting occurred. A moderate nitrogen current was passed over the alloy during this time. Two traps of the same type as used in the direct synthesis were connected to the outlet tube. A vigorous stream of about 200 bubbles/min. of methyl chloride was then passed over the alloy. The temperature had risen meanwhile to 380°C. Stirring was also vigorous. The cold finger was filled with methanol-dry ice, and the temperature reading in the upper part was -30°C. The cold finger tip almost immediately covered up with a red brown coating, but the silver of the double-walled part next to the tip still showed through, however. Now the cold finger temperature was lowered to -60°C. After 15 minutes from the start of the experiment reddish-brown dust could be noticed all over the reaction vessel. After 20 minutes the cold finger tip was completely covered with a rather thick opaque chocolate-brown layer. Below -62°C refluxing of the methyl chloride set in. This is of course not the true boiling point which is only -24°C. After 30 minutes the experiment was brought to an end. On taking the cold finger out of the vessel, atmospheric moisture condensed on the tip. The tip was then rinsed in some acetone. The brown powder seemed to be of extremely small particle size, since the suspension in acetone was of blue-violet color when looking through. This indicates a particle size in the range of about 10^{-2} mm.[23]

[23] According to H. B. Weiser, Inorganic Colloid Chemistry, Vol. 1, New York 1933, p. 82, cited in Gmelins Handbuch der anorganischen Chemie, 8. Auflage Gold, System #62, 1954, page 386.

Before continuing the experiments, it had to be taken into consideration whether apart from gold alkyl compounds other gold compounds might be responsible for the transport of gold and for the occurrence of methane. A possibility would be the formation of gold (I) chloride, AuCl, according to the following reaction scheme:

$$CH_3Cl + Au \longrightarrow AuCl + CH_3$$

The AuCl could be carried away in part out of the hot reaction zone into colder parts of the apparatus, there remaining intact for a certain time until disproportionation sets in according to:

$$2AuCl \longrightarrow 2Au + Cl_2$$

or

$$3AuCl \longrightarrow AuCl_3 + 2Au .$$

With these equations the transport of gold onto the walls of the reaction vessel can be explained as well. Another part of the AuCl would disproportionate in the reaction zone itself, and cause a chlorination of elemental silicon:

$$Si_x + Cl_2 \longrightarrow 2SiCl$$

$$AuCl_3 + Si_x \longrightarrow Au + 3\,SiCl$$

Or, simply, the life time of the AuCl under the reaction conditions might be so small that all the AuCl generated disproportionates right in the reaction zone. The gold transport would then be purely mechanical in that the small gold particles would be carried along by the methyl chloride current. Now, when a cold finger is used it ought to be possible to trap part of the AuCl. It might be recognized then by its yellow color, although at the temperature

of liquid nitrogen it turns to colorless. But on taking the cold finger out of the apparatus and exposing it to atmospheric moisture, disproportionation according to

$$3AuCl \longrightarrow 2Au + AuCl_3$$

should proceed rapidly. When treating with water a colored solution should be obtained. If this is not so because of too small quantities, at least a test for chloride ions should be positive. The methyl radicals of course yield methane by stripping off a hydrogen atom from another methyl chloride molecule.

In one experiment which was run without a cold finger, some of the gold dust on the walls was collected, treated with nitric acid, and tested for chloride ions. The result was negative, however. But this test should be repeated later on, using condensate resulting from a cold finger experiment.

Two more experiments similar to the first one were performed:

2) The apparatus was repeatedly evacuated and filled with nitrogen. The alloy was brought to 390°C and the cold finger cooled down to -74°C. Methyl chloride was then passed over the alloy. After a while the cold finger was taken out. The white deposit was scratched off with a spatula. There it liquefied, evaporated, and left a brown powdery residue.

3) Eighty-three grams of freshly prepared alloy were used this time in an experiment of the same nature. The temperature varied between 370° and 387°C. After 7 minutes from the beginning of methyl chloride addition, there was still no noticeable deposit on the walls. On thawing the deposit on the cold finger, no brown residue was left on the tip. After 12 minutes the cold

finger was taken out of the vessel. A little bit of brown dust could be detected on the silvered part of the cold finger upon close examination. A peculiar leek or garlic-like odor originated from the cold finger and the reaction vessel. Fourteen minutes after the experiment started the cold finger was cooled again. After 18 minutes a distinct brown deposit could be noticed on the walls. After 30 minutes the experiment was ended. During thawing the following was observed: The purely white crystalline layer was getting shiny due to melting methyl chloride, and turned to brown, getting darker as the methyl chloride liquefied. When the methyl chloride started to drip down, the brown film broke. It could not be seen whether the underlying solid methyl chloride also changed its color to brown on liquefaction.

These experiments seemed to confirm our point of view that some unstable gold compound occurred in these reactions. From Gilman's work it is known that trimethyl gold can be prepared.[24] It is made by reacting gold tribromide with methyllithium in ether solution at -65°C. The free trimethyl gold is highly unstable and begins to decompose at about -40 to -35°C. The products of this thermal decomposition are gold, methane and ethane. It can be stabilized by adding ethylenediamine, 2-aminopyridine, or benzylamine. Aside from quite a range of other reagents it is cleaved by hydrogen chloride to form dimethylgold chloride and methane:

$$(CH_3)_3Au + HCl \longrightarrow (CH_3)_2AuCl + CH_4 .$$

This cleavage takes place readily at -65°C. Thiophenol also causes cleavage at this temperature:

$$(CH_3)_3Au + HSC_6H_5 \longrightarrow (CH_3)_2AuSC_6H_5 + CH_4 .$$

[24] H. Gilman and L. A. Woods, JACS 70, 550 (1948).

When the ethereal solution is allowed to warm up slowly to room temperature, at about -40 to-35°C a gold mirror begins to form on the walls of the flask. The evolved gas consists of about 77% ethane and 19% methane.

Next it was desirable to find out whether the volatile gold compound was identical with trimethylgold, by preparing the condensate on the cold finger at the temperature of liquid nitrogen and then dissolving it

a) in anhyrous ether cooled to -76°C, or

b) in a saturated solution of hydrogen chloride in anhydrous ether cooled to -76°C, or

c) in anhydrous ether cooled to -76°C and adding a solution of thiophenol in ether held at the same low temperature.

In case a, upon warming the deposit, the formation of a gold mirror could not be observed. The experiments carried out under b and c likewise never led to the desired cleavage products, although Gilman's procedures were closely observed. It must be concluded from this that either formation of $Au(CH_3)_3$ does not occur at all under those circumstances, or that the quantities formed were too small, or that we were not successful in preventing the substance from decomposing before undergoing the various chemical tests. In every experiment of this kind, finely divided gold powder again was left over, which might be a hint in the direction just mentioned. Besides, it must be kept in mind that it is not possible to prevent the methylchlorosilanes from condensing simultaneously with the hypothetical gold compound right on the same spot, which might lead to chemical reactions between them. That we are dealing with a compound other than $Au(CH_3)_3$ is supported by the fact that we never found ethane in the infrared spectra. This is not an absolutely reliable proof

because the characteristic bands of ethane almost coincide with those of methyl chloride. We think it to be worth the trouble in future experiments to check the occurrence of ethane besides methane by gas chromatographic techniques.

Nevertheless, some interesting and even puzzling results came out during the search for trimethylgold. As a quite general rule, for example, it could be stated that the formation of transported gold was pretty low when using freshly-made alloy. Only after a certain time the rate increased. This looks as if the fresh alloy first needs to be activated. The fact that the alloy in almost every experiment was converted more or less to a brown powder, in which the particle size covered all the range from relatively coarse to extremely small, was puzzling. The cause of this phenomenon could not be found. The stirring speed certainly plays an important role, but unfortunately no numerical values can be given, since throughout the experiments the stirring was adjusted quite arbitrarily. The time needed to transform the alloy into powder varied considerably. The rate of the methyl chloride addition might be of equal importance. We will come back to this point later on in this report.

Kinetic reasons, as well as the experimental results just reported, make it seem highly improbably that $Au(CH_3)_3$ is formed under the conditions of our experiments. To find another explanation of the phenomena we have to turn out attention to the hypothetical monomethylgold, CH_3Au. So far as we know, nothing is reported about it in the literature, but it is more reasonable to assume the formation of this compound than that of $Au(CH_3)_3$. If it exists, it should be possible to stabilize it with ligands such as amines, phosphines and so on.

Some experiments were carried out in which the only change from the previous experiments lay in an addition of ammonia. The ammonia was condensed onto the cold finger tip, either before or after the experiment. The condensate was then allowed to react with the ammonia for a while, but on evaporation no definite residue was left except some brown gold powder which might have been there right from the beginning.

In order to distinguish between gold deposit transferred to the cold finger tip just by mechanical transport in the methyl chloride current, and gold resulting from decomposition on the tip, the cold finger was replaced by a new device (see Fig. 13).

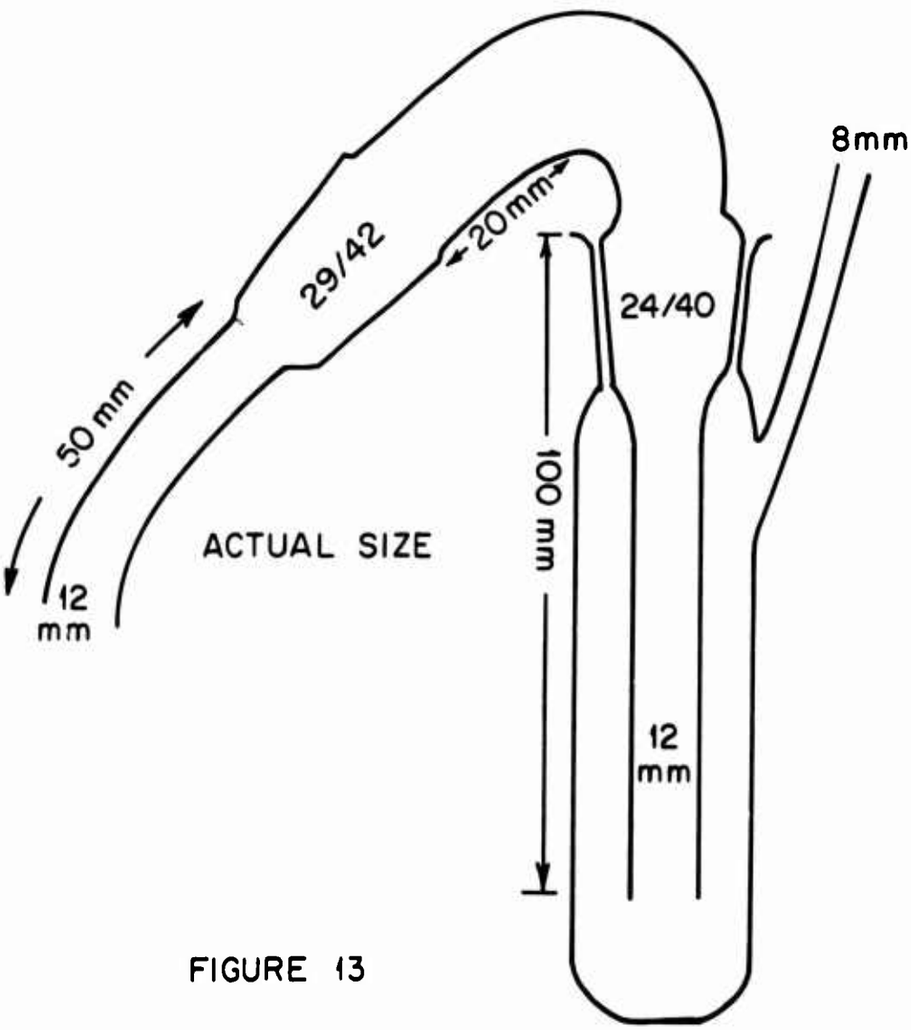

FIGURE 13

The idea was to pump off the reaction products over a distance as short as possible into a trap cooled down to liquid nitrogen temperature. This presented some advantages over the cold finger arrangement. First, the products were no longer exposed to the hot reaction gases coming up from the reaction zone. Next, it was possible to separate the gases from gold dust being carried along, simply by putting glass wool stoppers into the inlet tube of the trap. The contents of the trap could then be checked for unstable compounds. In the beginning a water pump was connected to the outlet tube of the trap and the pressure was adjusted so that it was about 100 mm. Later on the outlet tube was simply connected to a straight-tube mercury manometer, since the liquid nitrogen cooling the trap maintained a reduced pressure which sucked the products into the trap. In order to give an idea of what went on, the following experiments are given in some detail:

4) Alloy which had been used previously for the preparation of methylchlorosilanes was placed in the apparatus. Then, at 380° to 390°C a vigorous stream of methyl chloride was passed over the alloy which was stirred during this time. The inlet tube of the trap had been blocked with a glass wool plug. During reaction time the glass wool became brown at the side facing the apparatus. After 70 minutes the experiment was brought to an end. On thawing and evaporating the contents, some brown residue was left in the trap, undoubtedly gold (but this result is not unequivocal, since the glass wool might have been not sufficiently tight).

5) The experiment was repeated with the same alloy. This time two glass wool plugs were inserted, one in each end of the inlet tube of the trap. Methyl chloride was added over a period of two hours. After this time only the first

glass wool plug, the one in the reaction vessel, showed brown color. No brown deposit was found in the space between the two glass wool plugs. On disassembling the apparatus, it was found that the alloy had been converted meanwhile into a brown powder.

6) Again this experiment was repeated with freshly prepared alloy. Some elemental silicon had been added previously. After one hour the lower part of the first glass wool stopper had become dark. After 2 hours there was still no deposit in the space between the two stoppers, the second stopper still being clean. Since by this time only little deposit had been formed in the reaction vessel, it was assumed that the alloy, being fresh, was not yet sufficiently activated. The experiment was therefore discontinued. The color on the glass wool stoppers indicated that mainly silicon had been carried along. On evaporation the methyl chloride had a leek or garlic-like odor. Some dark residue was left in the trap.

7) In a new attempt, after about one hour the first stopper was entirely colored by brown powder, and the second one slightly (at the end facing the apparatus). This time the trap was cooled with dry ice. A tiny bit of brown film was floating on the liquid methyl chloride, which apparently was gold.

8) With the same alloy the experiment was repeated again. The trap was cooled this time with liquid nitrogen. The alloy seemed to be highly active, since formation of methylchlorosilanes could be noticed right after the reaction started. Unfortunately the experiment had to be discontinued after 30 minutes, since the alloy had been converted completely into brown powder.

9) With freshly made alloy the results were again doubtful. Only little deposit could be found in the reaction vessel, and similarly the glass wool stoppers were only slightly colored. Here, after running over a period of 6 hours, the fresh alloy was again converted completely into brown powder. This is strange after so short a time.

10) Some more experiments were carried out, with no clearer results, however. For instance, freshly prepared alloy was treated the same way as in the preceding experiments. After 4 hours a considerable part of it had again been converted. Then for a while the stirrer went out of control, the stirring speed increasing rapidly. After half an hour much more deposit had been formed than in all the time before in this experiment. Simultaneously, the alloy was now completely transformed into brown powder. No brown deposit was found between the glass wood stoppers when the run was ended. The evaporating CH_3Cl smelled again of garlic.

For the following experiments a new apparatus was used which allowed bubbling methyl chloride through the molten alloy (see Fig. 14). A "dust trap"

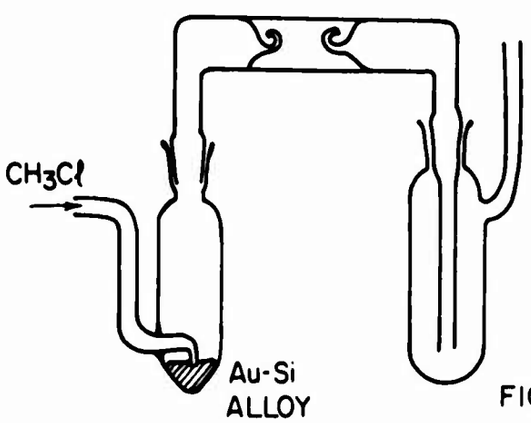

FIGURE 14

was built into the tube connecting the reaction vessel with the trap. After melting the alloy under streaming nitrogen, methyl chloride was bubbled through. Then the outlet tube of the trap was connected to a straight-tube

mercury manometer and the trap was cooled with liquid nitrogen. After 90 minutes the experiment was brought to an end. No visible brown deposit was found in the "dust trap". The contents of the condensation trap evaporated without a residue[25] worth mentioning. There was strong smell of methyl-chlorosilanes, which had apparently condensed in the inlet tube of the trap just below the taper. The only residue[26] left was two tiny dark dots. They turned out to be gold when tested with aqua regia, hydrochloric acid and tin (II) chloride (blue-violet color gradually becoming more intense). During the experiment a brown powder layer had formed on the alloy. This experiment was repeated once more. This time the walls of the reaction vessel as well as those of the connecting tube were covered with a thin layer of brown dust. This was also true, however, for the part of the tube on the right-hand side, behind the "dust trap". The condensed methyl chloride was perfectly clear and colorless. On evaporation it could not be established with certainty that a residue, however small, was left. But the tin (II) chloride test showed unequivocally the presence of gold.

The last experiment performed in this connection was to try to prove the existence of an unstable gold alkyl compound by the generation of methane upon decomposition. For this purpose the cold finger was used again. After 30 minutes reaction time at 380°C a gas sample was collected and an infrared spectrum was taken which showed the methane peak at 7.7μ. Then the apparatus was evacuated, the cold finger tip was thawed, again cooled down, and another sample was taken for infrared analysis. No methane peak could be found, however. In spite of the relatively short reaction time the major

[25] H. Gilman and L. A. Woods, JACS 70 550 (1948).
[26] H. Gilman and L. A. Woods, p. 552

part of the alloy had been converted again into a brown mixture of coarse and very small particles. It could well be seen how dust was carried along with the methyl chloride stream, settled down on the cold finger tip, and in turn was covered by condensing methyl chloride (which was not altered in color and looked perfectly colorless).

This final experiment would have been, in case of success, the most conclusive and compact proof for the presence of a gold alkyl compound. The failure must not be definitive, on the other hand. If one takes into consideration the large volume of the reaction vessel and the resulting low pressure and concentration of the evaporated cold finger condensate in the infrared gas cell, then the negative result is not surprising. This experiment should be repeated with the trap which replaces the cold finger. In this case it is easier to collect larger quantities of condensate, hence the infrared test should be more reliable.

The greatly varying times in which the alloy is converted into brown powder, still present a puzzling problem. One might be inclined to think that the melting point of the eutectic is very sensitive to changes in the composition, so that slight consumption of silicon would result in a sharp rise of the melting point. We do not think that this is the case, since in some experiments the conversion took place although free elemental silicon was still available. One of the clues to this problem might be the observation that it was not possible to remelt the brown powder to a lump of gold. When trying to do this the particles began to glow in the flame of the torch, as if an oxide had been heated. It might be that traces of moisture, along with the methylchlorosilanes, wrap up particles of the alloy during stirring with a film of

methylpolysiloxanes, and prevent them in this way from uniting with the alloy. But it remains strange that the same observations were made in the case of the reactions of anisole and dimethyl ether with gold-silicon alloy.

Concluding this chapter we would like to make some suggestions. The use of a gas meter would be of value in the experiments. The particle size of both the deposit and of what if left of the alloy in the liner would be of interest. Attention should be paid to the frequent occurrence of "garlic-odor" in the reaction vessel and the evaporating methyl chloride after an experiment is run. The question of what happens to the gold-silicon alloy, and why gold dust becomes deposited in all the passages, is decidedly secondary to the main problems of synthesizing organosilicon compounds, but is of considerable interest in the new field of organometallic compounds of the transition metals.

13. METHYLCHLOROBORANES

In connection with the work in the direct synthesis of methylchloroboranes and trimethylborane performed in this laboratory by Ratner and Weibrecht in 1963 and 1964, we repeated some of their experiments under somewhat different conditions. For example, we modified the arrangement of passing CH_3Cl over a heated mixture of cuprous chloride and elemental boron by adding anydrous aluminum chloride to the contact mass, according to observations by Müller and Gumbel on the catalytic influence of $AlCl_3$ or $FeCl_3$ on the reaction rate in the methylchlorosilane case[27].

[27] R. Müller and H. Gumbel, Z. F. anorg. allg. Chem. 327, 293 (1974).

The thoroughly mixed contact mass, suspended on glass wool, was gradually brought to 550°C while passing methyl chloride through the reaction tube. In the trapped exit gases no compounds containing direct boron-carbon bonds could be detected by spectroscopic means. Boron trichloride was present, on the other hand, in appreciable amounts. Large quantities of methane could be found in the infrared spectra as well.

In this connection we got interested in the NMR spectra of the methylchloroboranes. So far as we know, no work has been published in this field up to now. Preparative work was undertaken in order to obtain the two compounds CH_3BCl_2 and $(CH_3)_2BCl$. Various times it was tried to make these compounds following the method reported by Lengyel and Csákvári.[28] This consists in performing the reaction in the gas phase.

$$RAlCl_2 + BF_3 = RBCl_2 + AlF_3$$

The necessary aluminum compounds were made after a procedure given by Marsel, Kalil, Reidlinger and Kramer in Advances in Chemistry Series, Vol. 23, page 174/175. It was perplexing that the proton chemical shifts for the two methylchloroboranes were substantially the same. Finally, after much time had been spent on the preparative work, an authentic sample of trimethylborane made by the Grignard reaction showed itself to be chemically identical with the alleged methylchloroboranes. This fact is quite understandable from the way Lengyel and Csákvári performed the reaction. No time being left for further attempts, the work was discontinued.

Literature concerning the methylchloroboranes compiled from Chemical Abstracts for the period 1937 until 1965 (until page 4912 of Vol. 63) is listed below:

[28] B. Lengyel and B. Csakvari, Ibidem, 322, 103 (1963).

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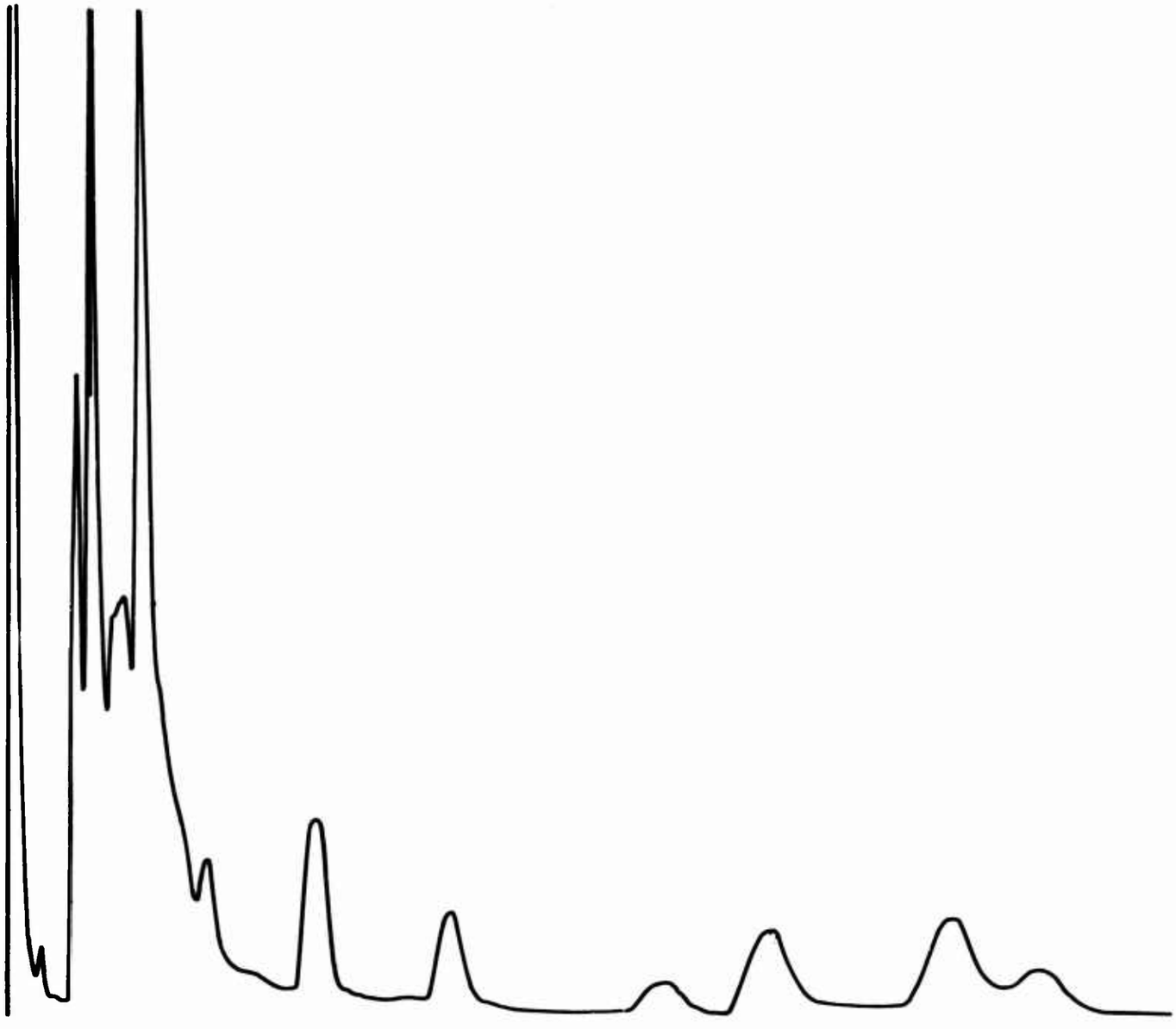
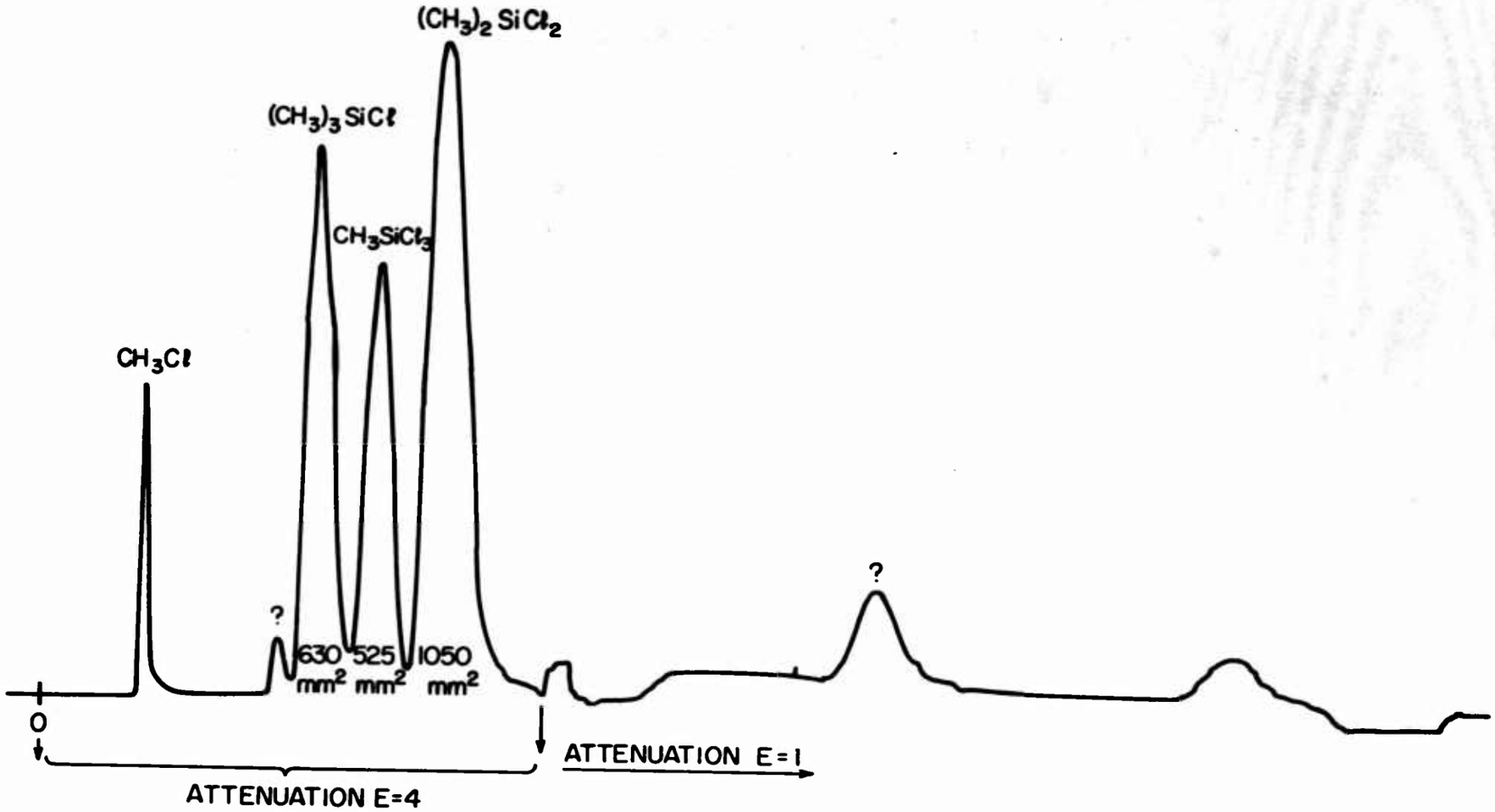
ACKNOWLEDGMENT

The author is grateful to the Advanced Research Projects Agency for the support of this work.

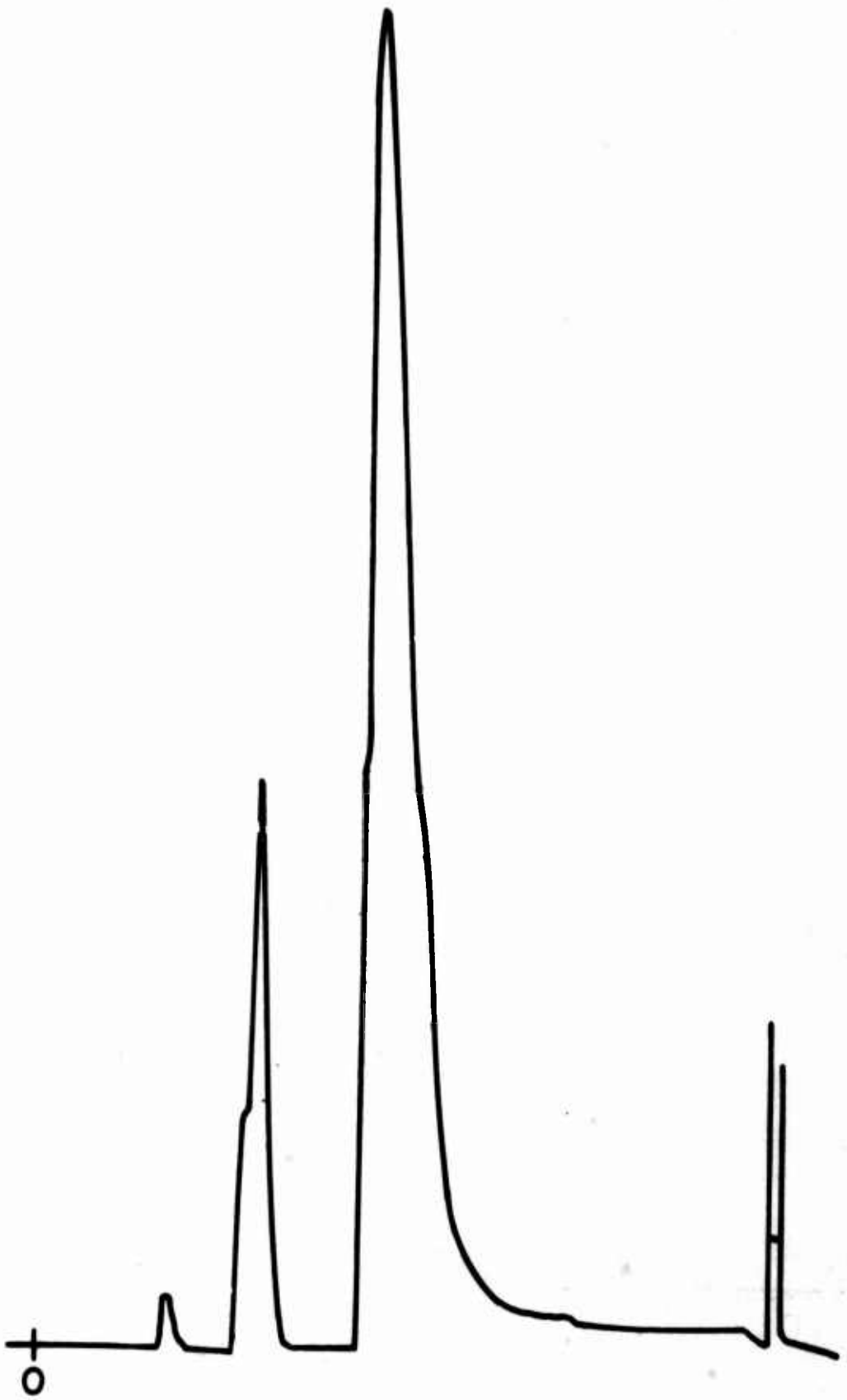
*To Chapter 13.



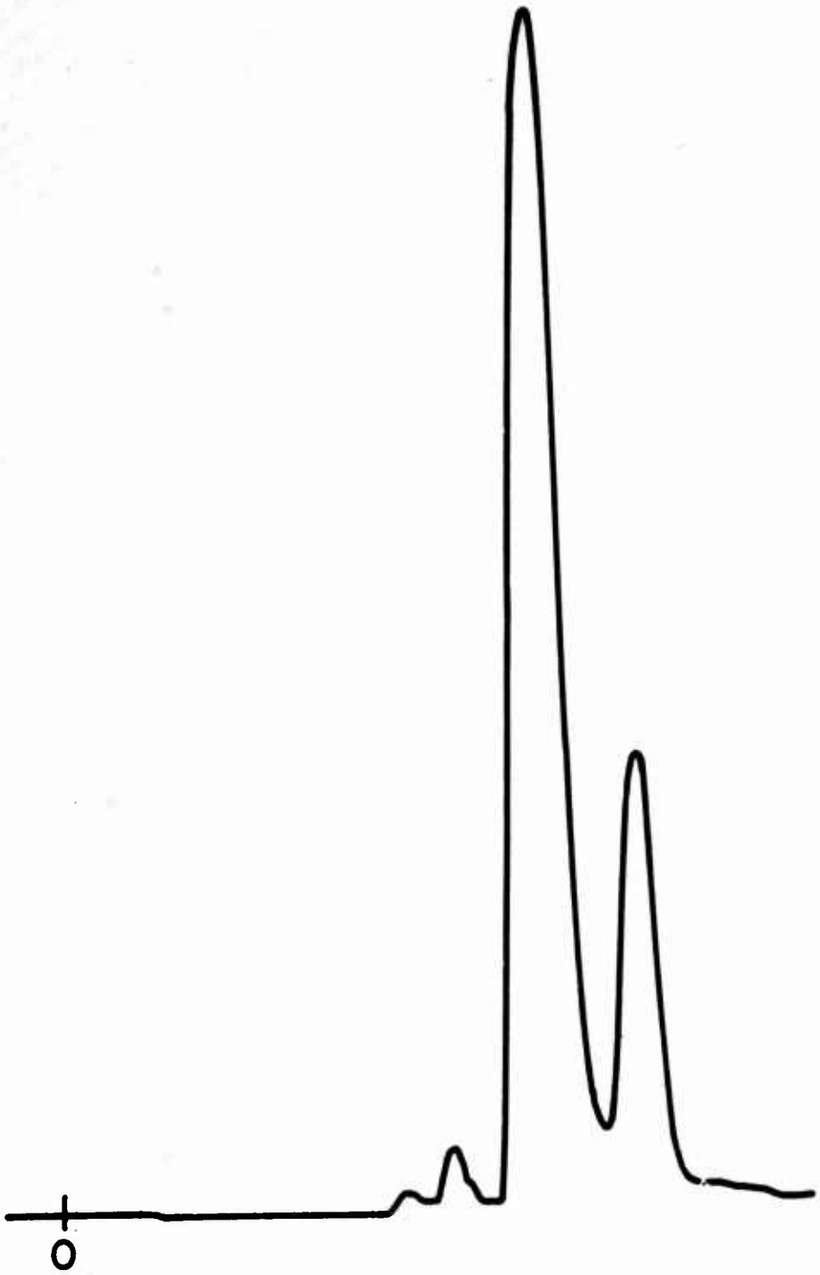
CHROMATOGRAM A REACTION MIXTURE, 1 MICROLITER (ATTENUATION E=4)



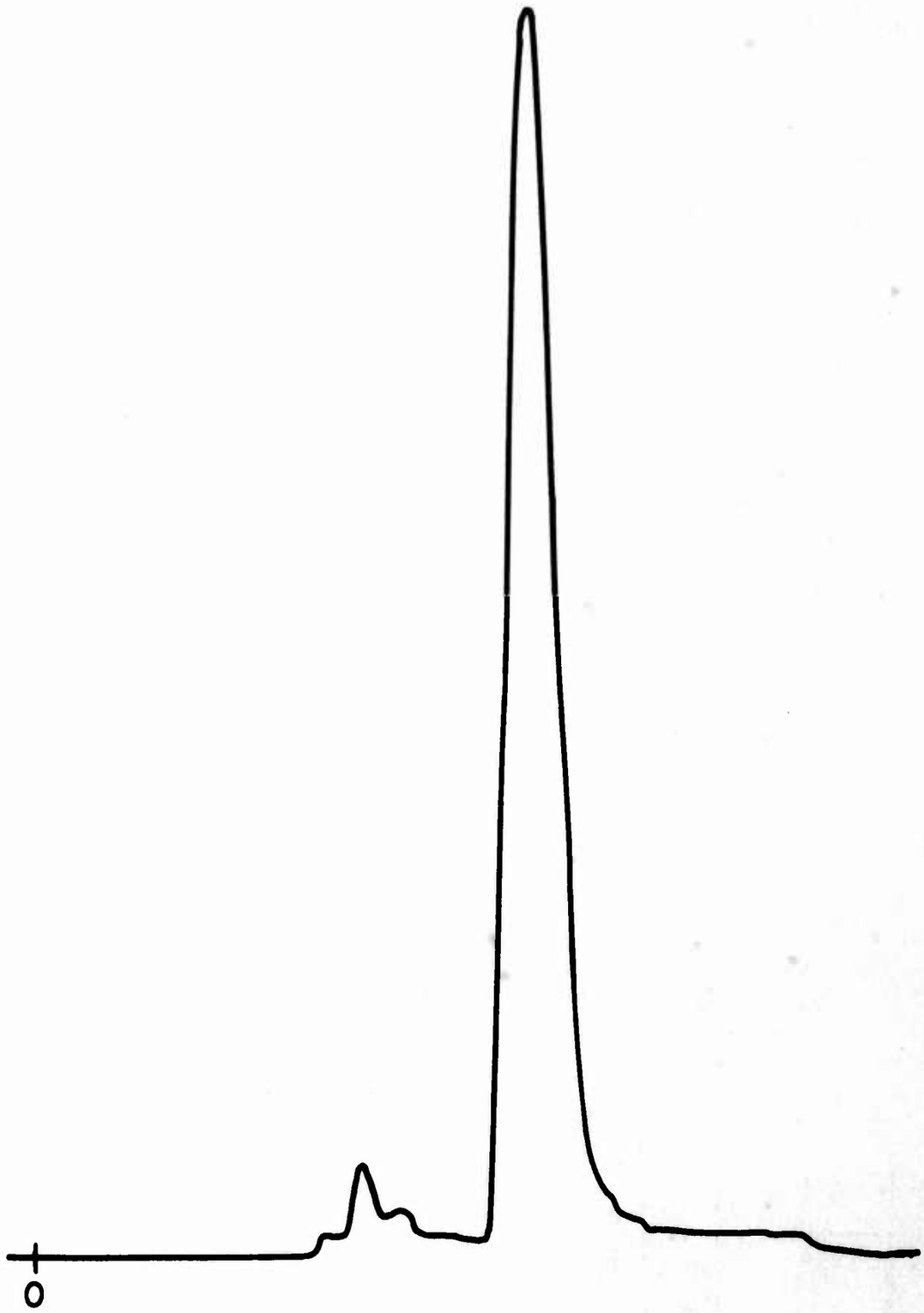
CHROMATOGRAM B REACTION MIXTURE FROM CH_3Cl + Au/Si



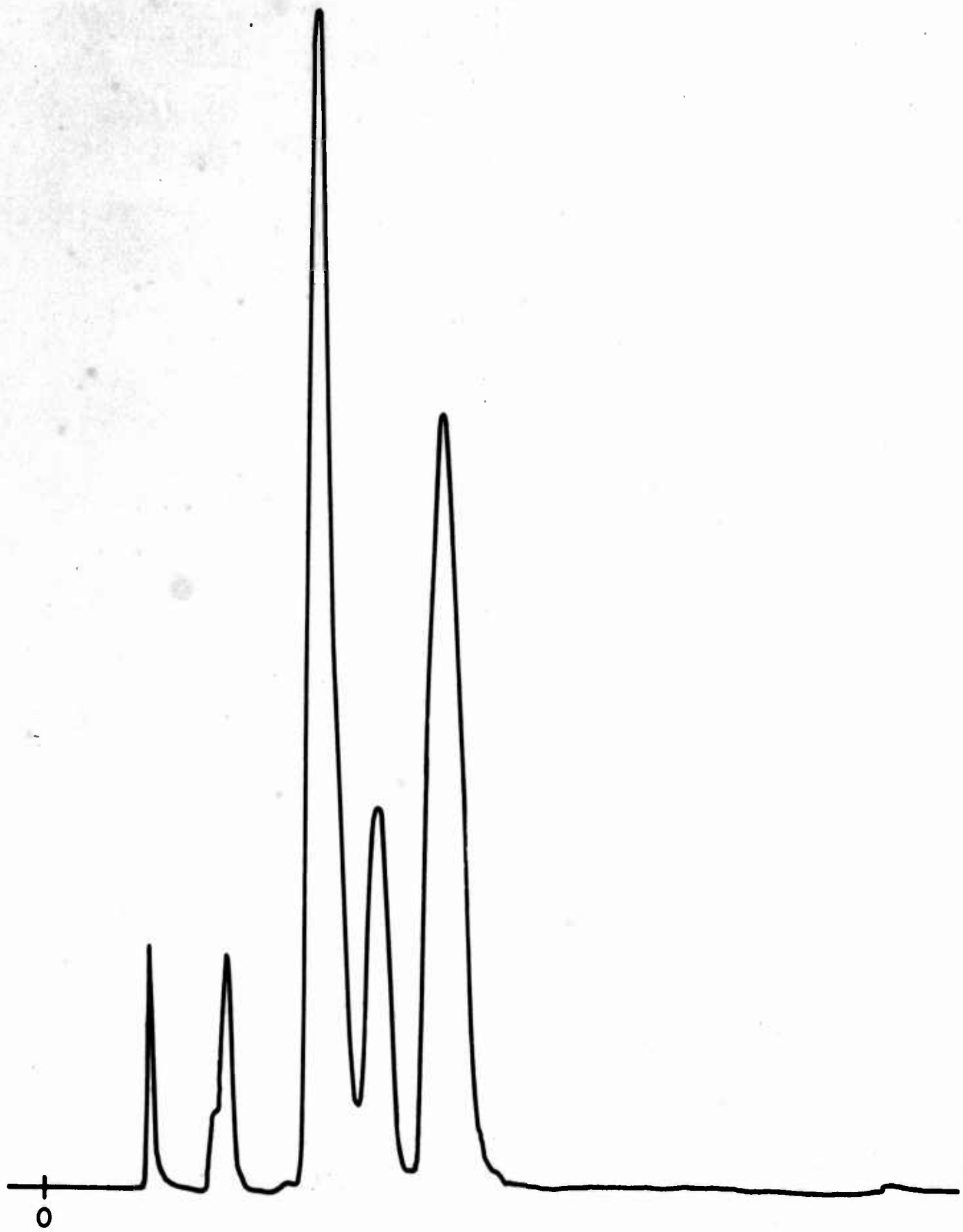
CHROMATOGRAM C $(CH_3)_3SiCl$ G.E. Vpc SAMPLE
COLUMN TEMP. 50-55°C



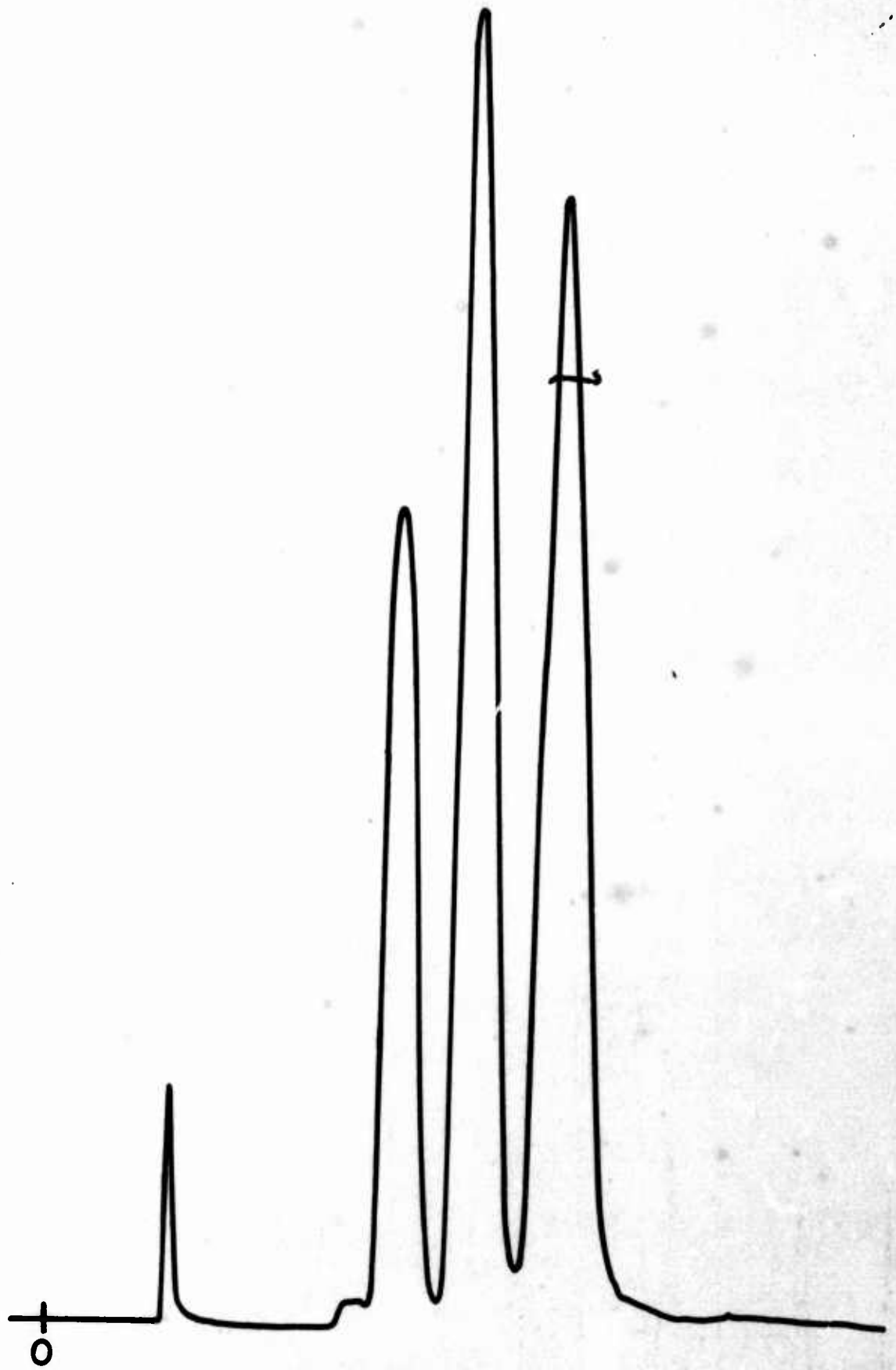
CHROMATOGRAM D CH_3SiCl_3 G.E. Vpc SAMPLE
COLUMN TEMP. 50-55°C



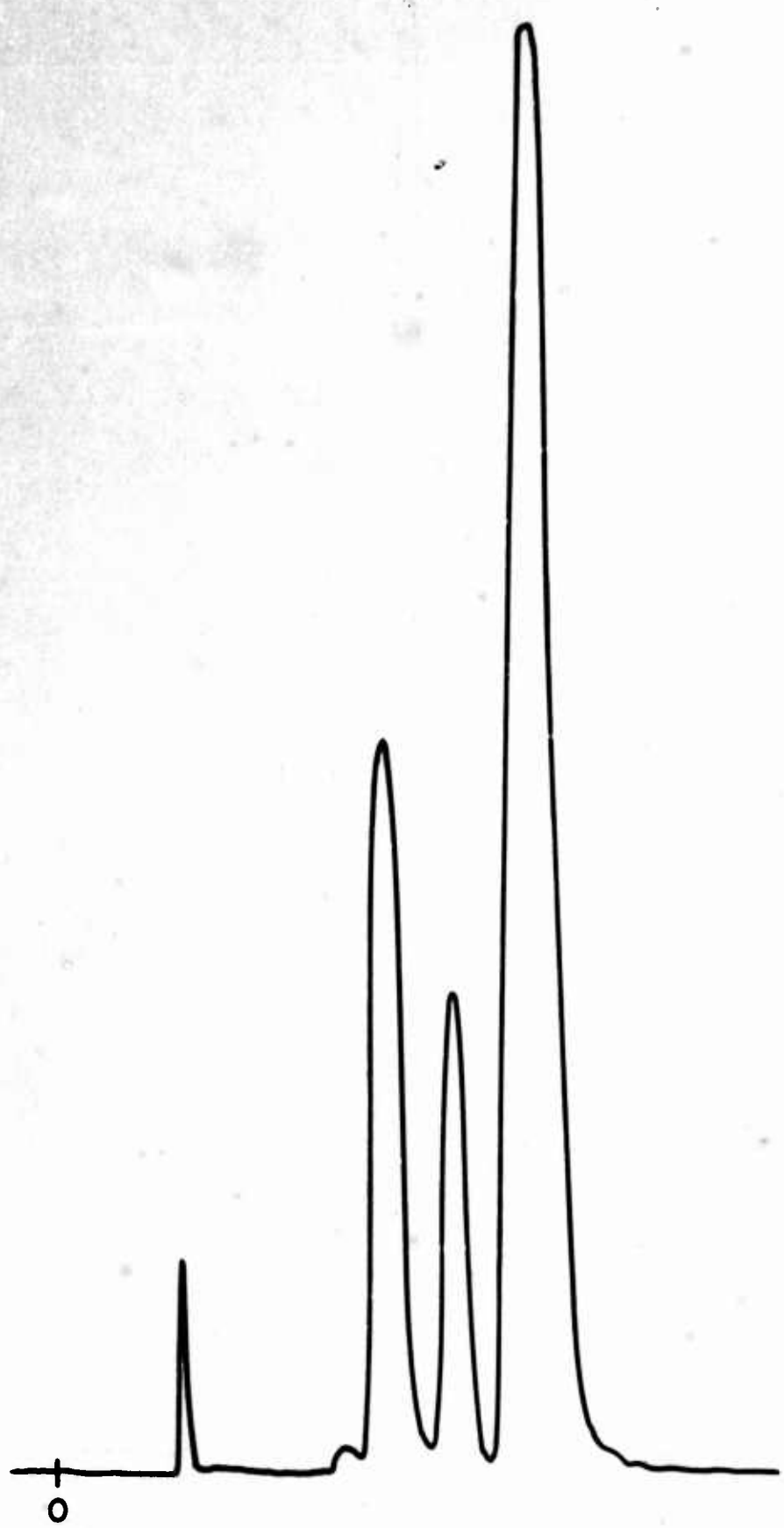
CHROMATOGRAM E $(CH_3)_2 SiCl_2$ G.E. Vpc SAMPLE
COLUMN TEMP. 50-55°C



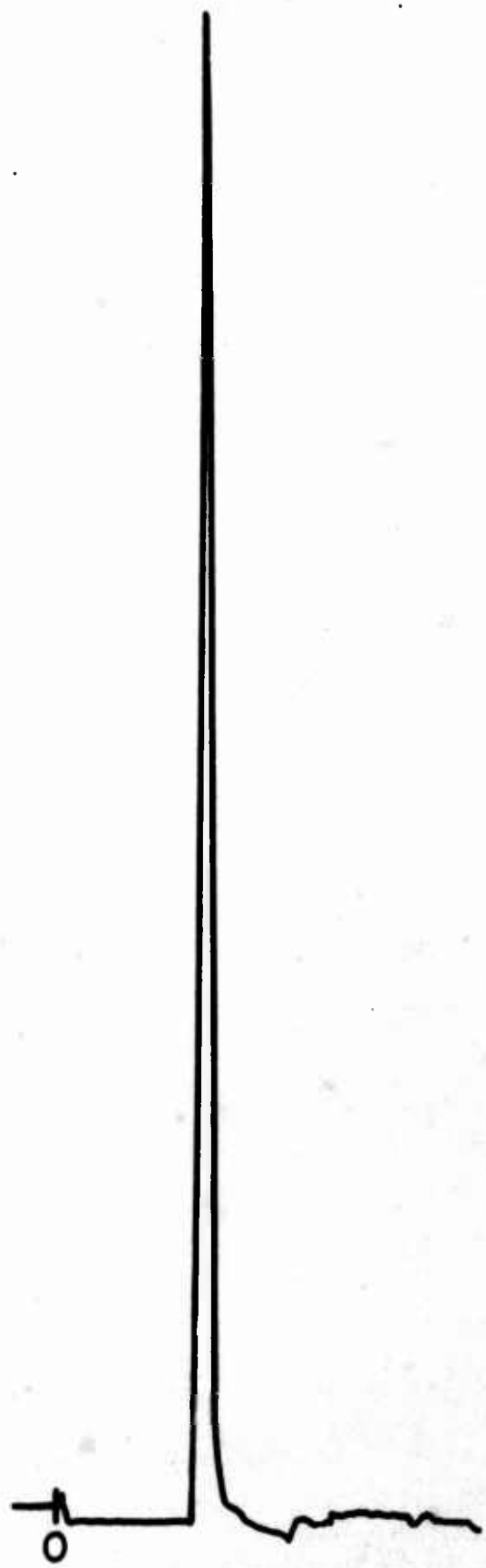
CHROMATOGRAM F REACTION MIXTURE CH_3Cl-Au/Si+$(CH_3)_3SiCl$
CT 50-55°C



CHROMATOGRAM G REACTION MIXTURE CH_3Cl Au/Si + CH_3SiCl_3
CT 50-55°C

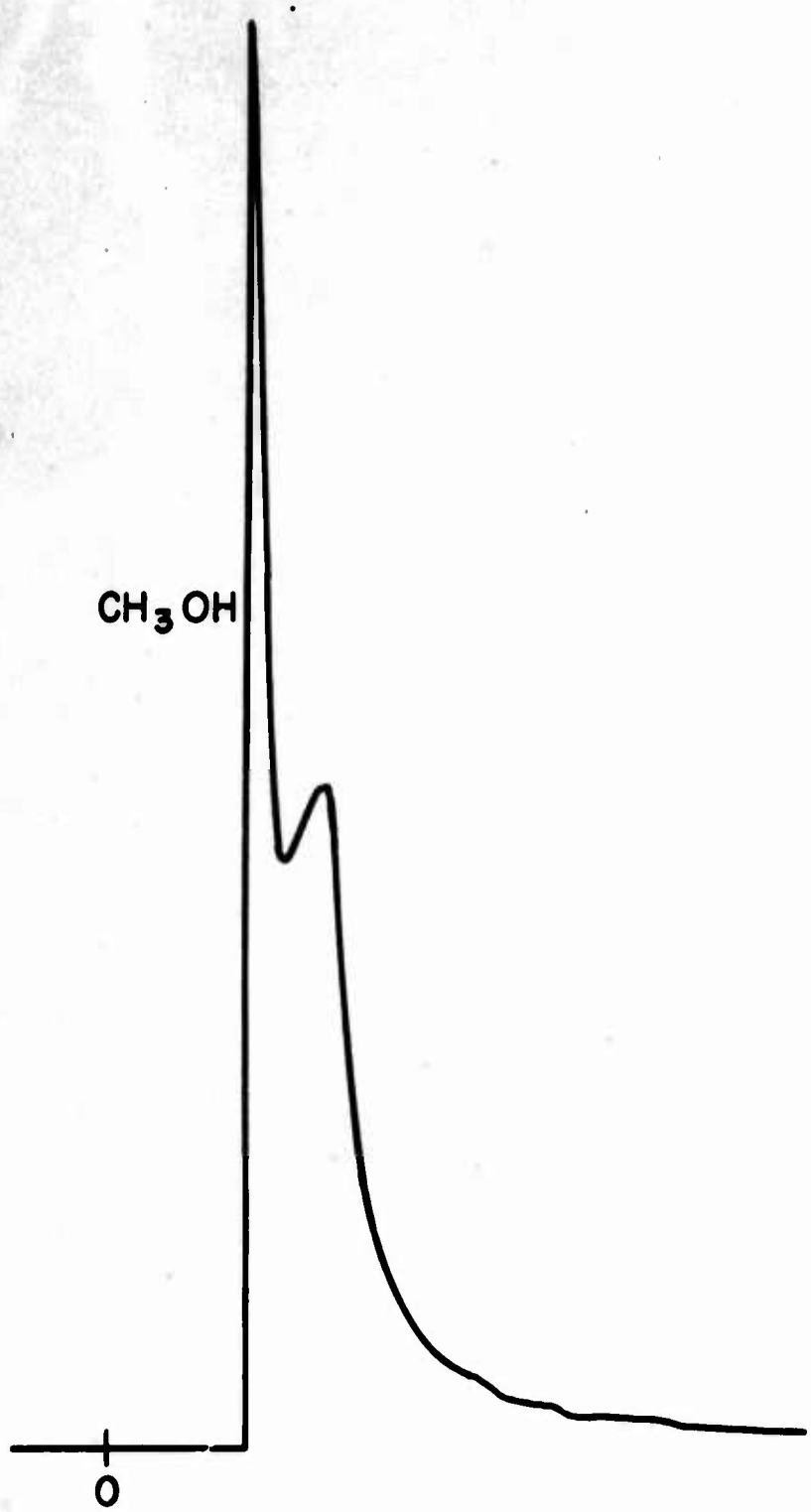


CHROMATOGRAM H REACTION MIXTURE CH_3Cl Au/Si + $(CH_3)_2SiCl_2$
CT 50-55°C



CHROMATOGRAM I CH_3Cl MATHESON

CT = 50-50°C



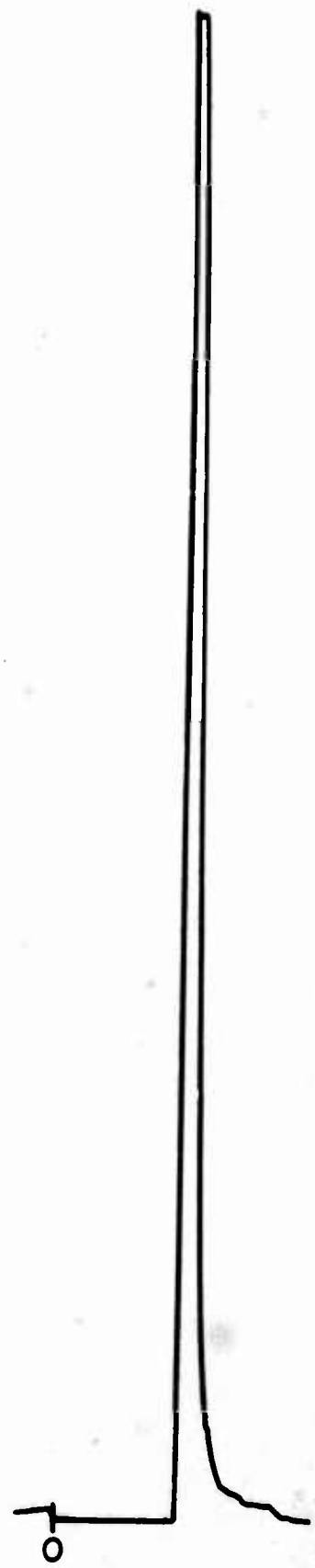
<u>CHROMATOGRAM J</u> COLUMN: 8' 5% SILICONE GUM, GE-XE 60 ON 60-80S

ATTENUATION: E = 8

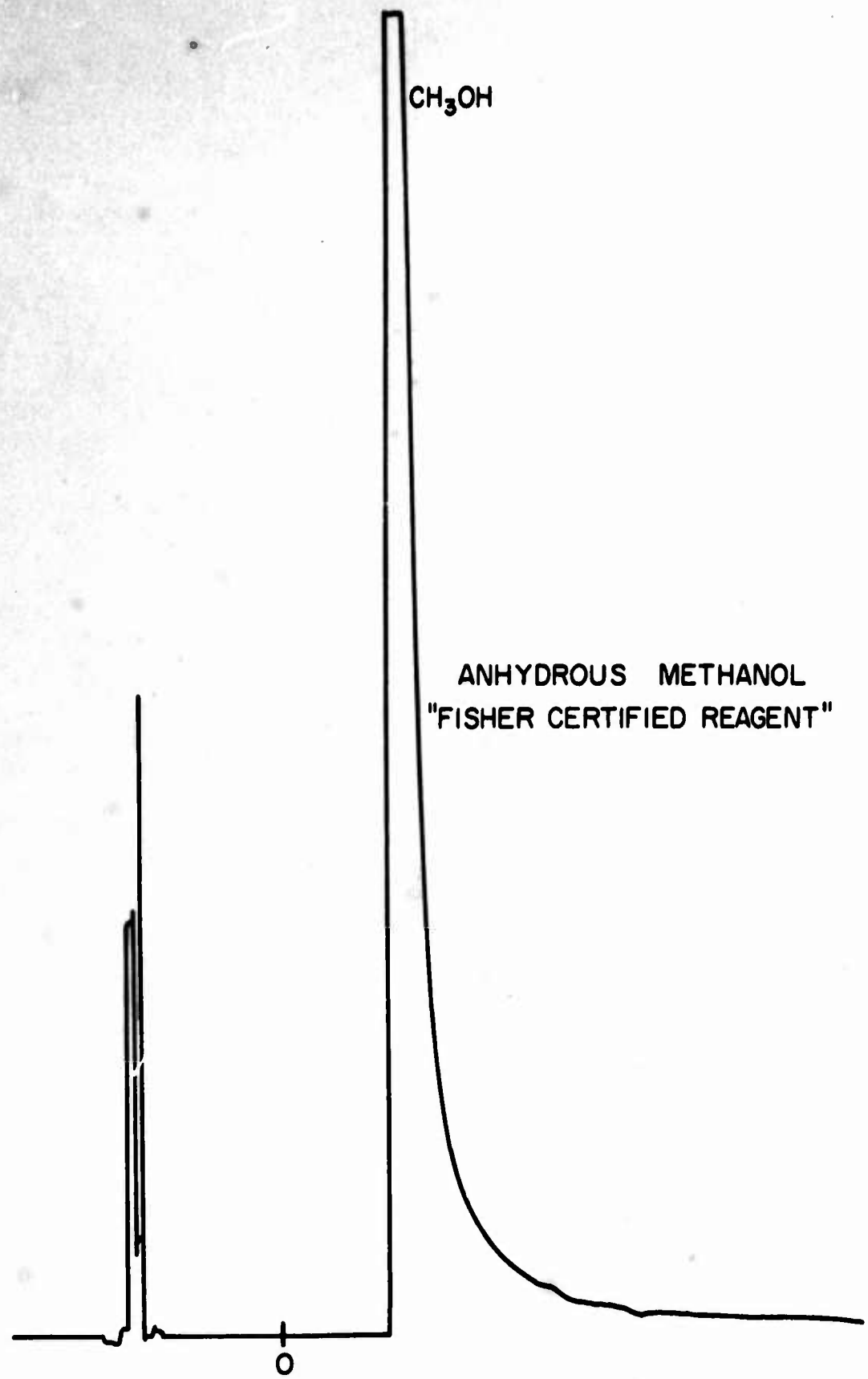
FLOW RATE HELIUM: 75 ml./min.

FLOW RATE H_2: 70ml./min.

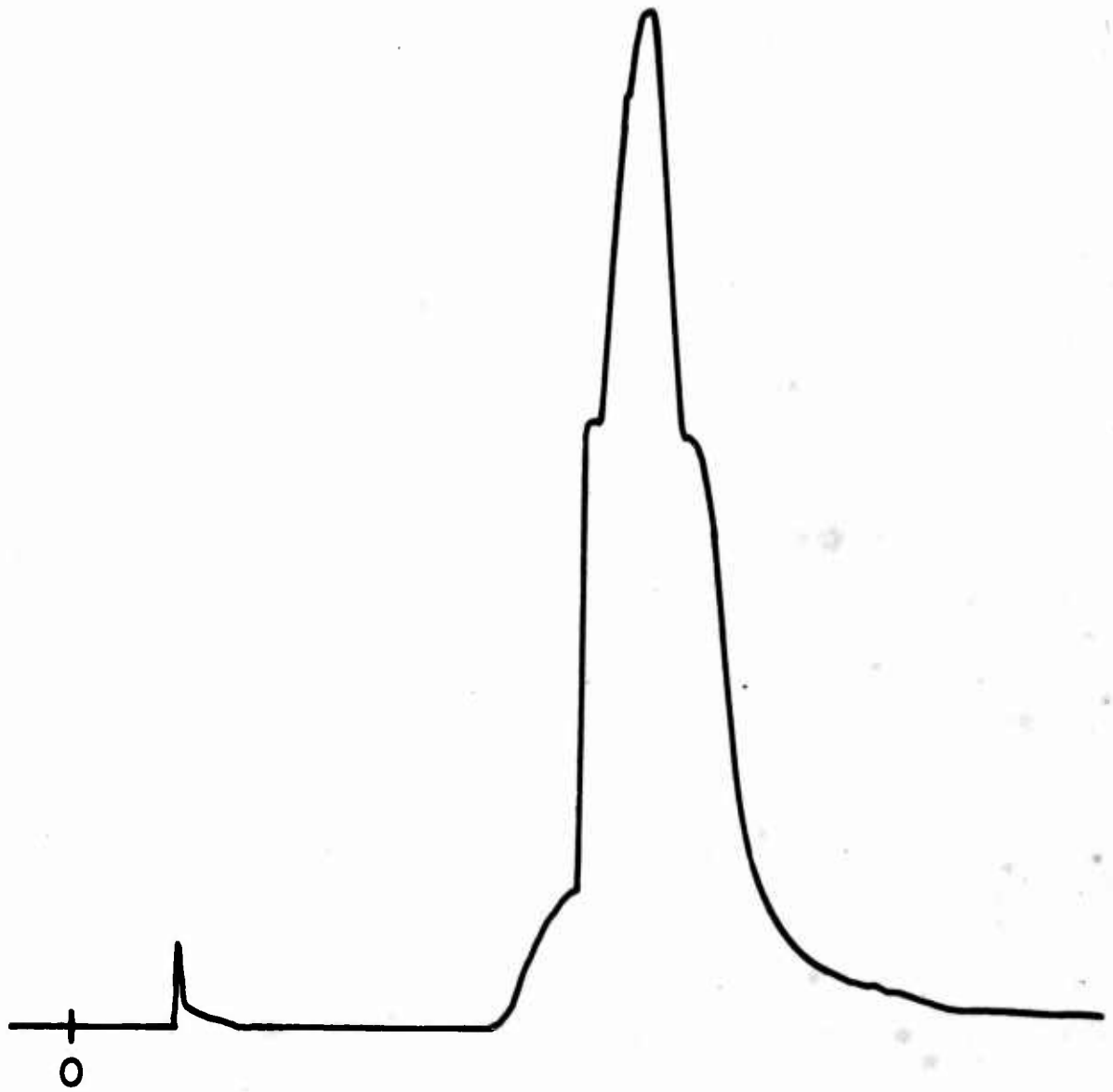
REACTION PRODUCT OF DIRECT SYNTHESIS Au/Si-CH_3OH



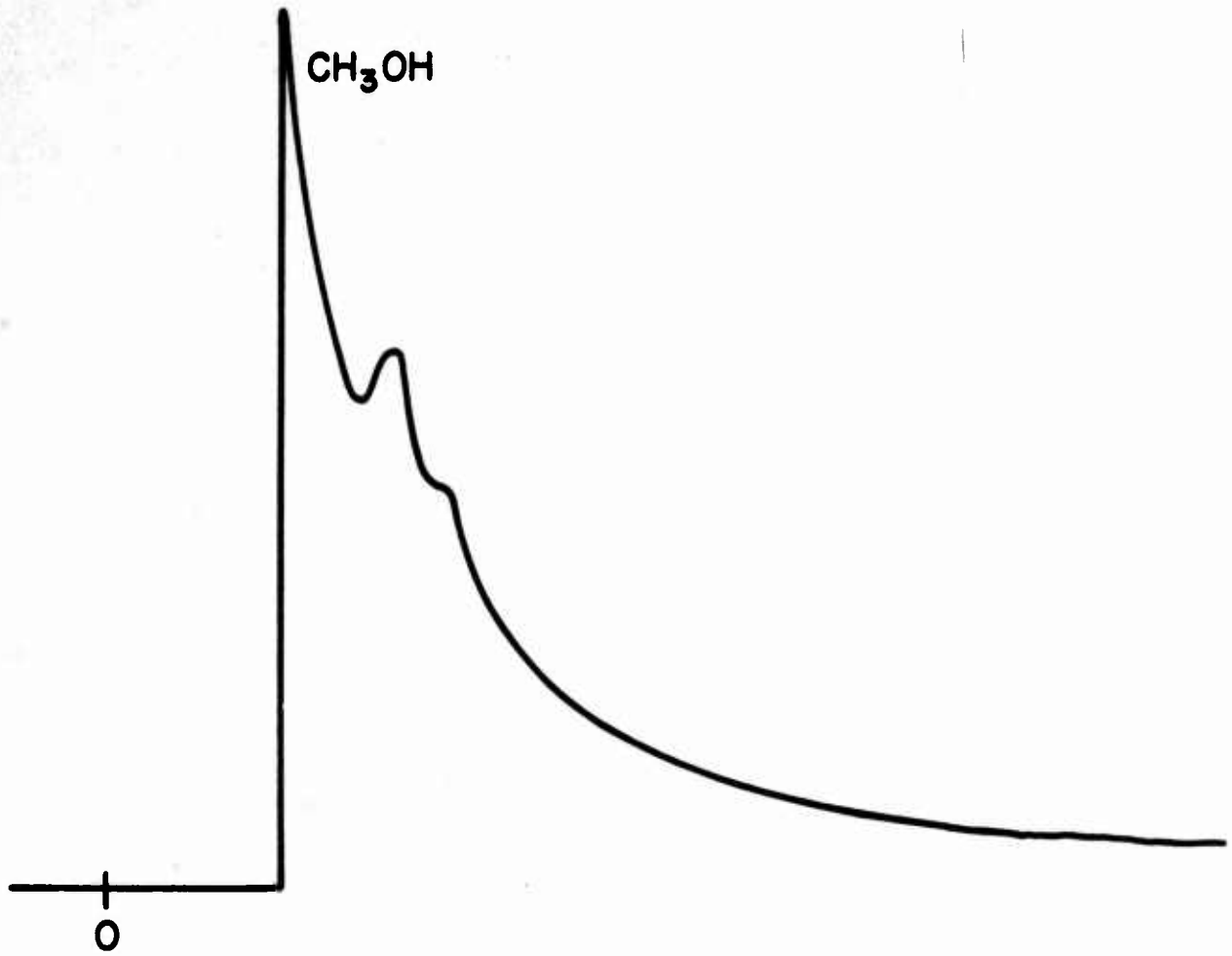
CHROMATOGRAM K FORMALDEHYDE
ATTENUATION: E = 2
10:1 VAPOR, DATA AS IN J



CHROMATOGRAM L COLUMN: COLUMN 8FT. 5% SILICONE GUM G.E.-XC 60 ON 60-80S, CT 50-55°
H_2 = 8.4~70ml./min., He = 6.2~75ml./min.

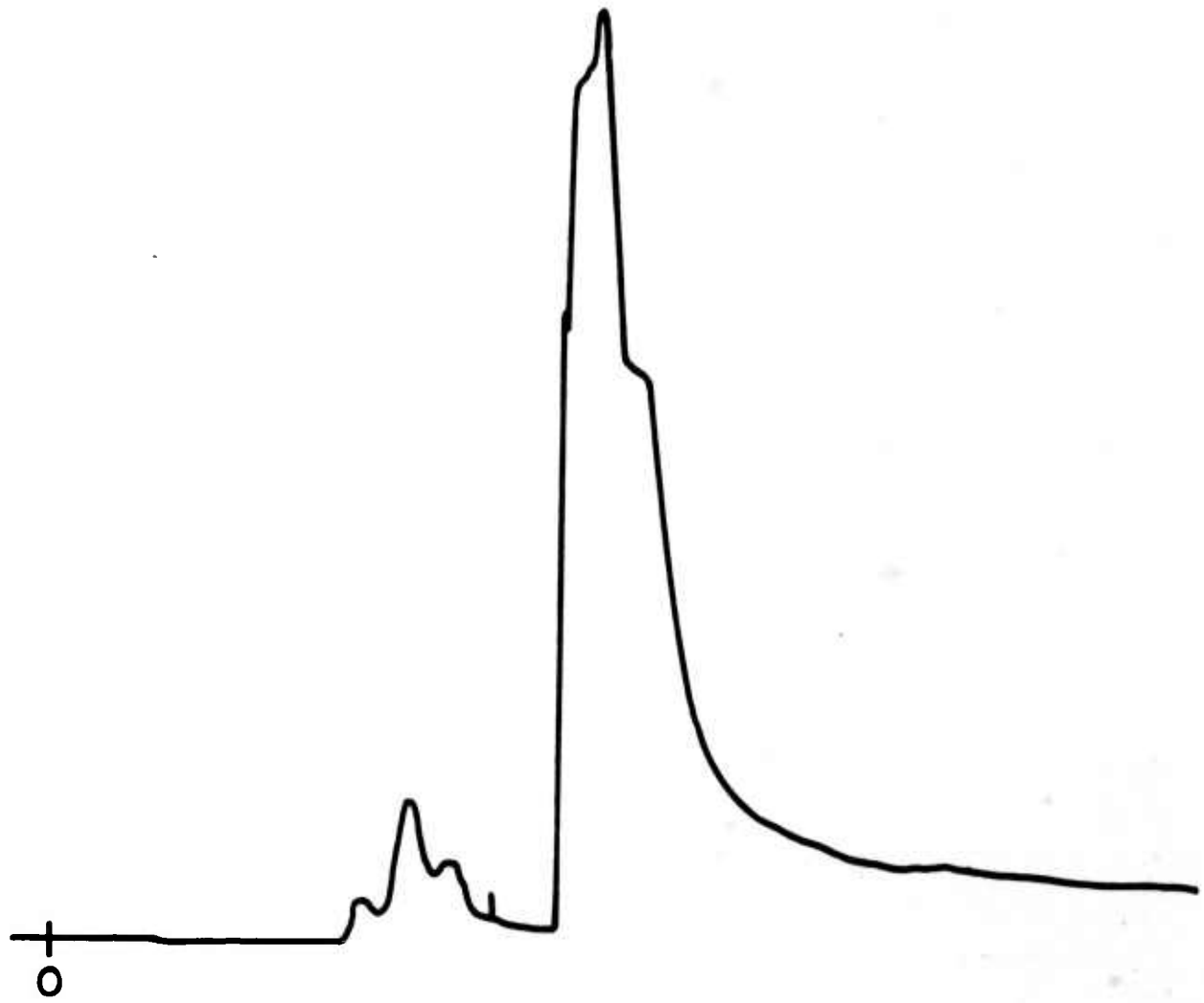


CHROMATOGRAM M TETRAMETHOXYSILANE
ATTENUATION: E = 4
He and H_2 AS IN "N"
DATA AS IN "J"

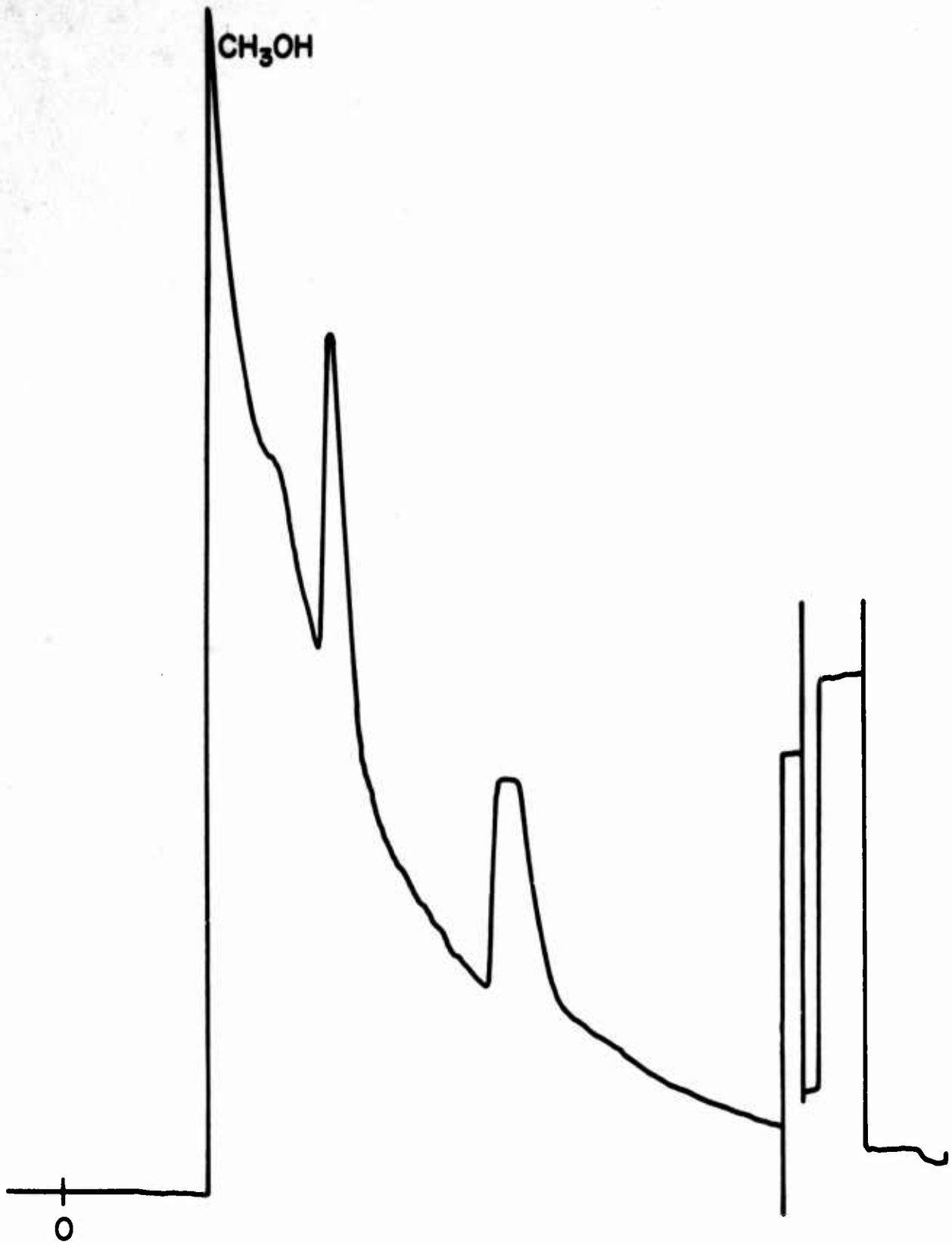


CHROMATOGRAM N COLUMN: 20% SILICONE (FLUORO) FS 1265
QF-1 ON 60-80 MESH P.

ATTENUATION: E = 8
FLOW RATE HELIUM: 75ml./min.
FLOW RATE HYDROGEN: 68ml./min.



CHROMATOGRAM O $(CH_3O)_2$ Si $(CH_3)_2$
ATTENUATION E = 4
REST OF DATA AS IN "N"



<u>CHROMATOGRAM P</u> MIXTURE OF $(CH_3O)_2$ Si $(CH_3)_2$ AND REACTION PRODUCT FROM Au/Si + CH_3OH RATIO 1:2
ATTENUATION: E = 4
REST OF DATA AS IN "N"

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Mallinckrodt Laboratory
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2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE
Synthesis of Silicon Compounds

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Technical Report

5. AUTHOR(S) *(Last name, first name, initial)*
KRAHÉ, Eduard

6. REPORT DATE
June, 1966

7a. TOTAL NO. OF PAGES
72

7b. NO. OF REFS
40

8a. CONTRACT OR GRANT NO.
ARPA SD-88

b. PROJECT NO.

c.

d.

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There is only one binary alloy system of silicon which is liquid below the temperature of decomposition of methyl chloride, alcohol, and ether: the gold-silicon system. The possibility of using a liquid eutectic form of silicon as starting material for the direct synthesis of organosilicon compounds was so inviting, because of the constant exposure of fresh surface to the stream of organic reagent, that experiments were undertaken. It was expected that no gold would be consumed or transported, and so the high price of the gold would represent only capital investment, the cost of which might be overbalanced by operational advantages.

The experiments reported here show that methylchlorosilanes (intermediates for making silicone polymers) are indeed produced from methyl chloride and gold-silicon alloy, but that the gold enters into the reaction in such a way as to be transported as fine dust. The chemical change was studied intensively, along with reactions of methanol and ethers. The report concludes with some work on organobroan chlorides.

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14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
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