THERMAL OXIDATIVE DEGRADATION REACTIONS OF PERFLUOROALKYLETHERS

Prepared by:

K. L. Paciorek, T. I. Ito, and R. H. Kratzer

ULTRASYSTEMS, INCORPORATED
Irvine, California

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William R. Jones, Project Manager

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Project Manager, William R. Jones
NASA Lewis Research Center
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16. Abstract

The objective of this contract was to investigate the mechanisms operative in thermal and thermal oxidative degradation of Fomblin Z and hexafluoropropene oxide derived fluids and the effect of alloys and additives upon these processes.

The nature of arrangements responsible for the inherent thermal oxidative instability of the Fomblin Z fluids has not been established. It was determined that this behavior was not associated with hydrogen end-groups or peroxy linkages. The degradation rate of these fluids at elevated temperatures in oxidizing atmospheres was found to be dependent on the surface/volume ratio. Once a limiting ratio was reached, a steady rate appeared to be attained. Based on elemental analysis and oxygen consumption data, $-CF_2OCF_2CF_2O-$, not $-CF_2CF_2O-$, is one of the major arrangements present. The action of the M-50 and Ti(4 Al, 4 Mn) alloys was found to be much more drastic in the case of Fomblin Z fluids than that observed for the hexafluoropropene oxide derived materials. The effectiveness of antioxidation/anticorrosion additives; P-3 and phospha-s-triazine, in the presence of metal alloys was very limited at 316°C: at 288°C the additives arrested almost completely the fluid degradation. The phospha-s-triazine appeared to be at least twice as effective as the P-3 compound; it also protected the coupon better. The Ti(4 Al, 4 Mn) alloy degraded the fluid mainly by chain scission processes; this took place to a much lesser degree with M-50.

The presence of a certain proportion of hydrogen-terminated chains in Krytox MLO-71-6 fluid was verified by NMR spectroscopy. These were eliminated on exposure of the fluid to oxygen at 343°C. In oxygen at 316°C, aluminum metal did not seem to promote chain scissions; a steady but low rate of degradation was observed for pure titanium metal.

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FOREWORD

This annual report describes the work performed by
Ultrasystems, Inc. during the period 3 September 1980 through
4 September 1981 under Contract NAS3-22517, "Thermal
Oxidative Degradation Reactions of Perfluoroalkylethers". The
investigations were carried out by T. I. Ito, R. H. Kratzer,
and K. L. Paciorek, project manager, at the Chemicals and
Materials Research Department, Irvine, California. The
contract was administered by the NASA Lewis Research Center
with Mr. William R. Jones as the project manager.

We would like to acknowledge the cooperation and
assistance of Mr. C. E. Snyder of the Air Force Wright
Aeronautical Laboratories, Fluids, Lubricants, and Elastomers
Branch. We also would like to express our indebtedness to
Dr. Paul R. Resnick of E. I. DuPont de Nemours and Company
for the determination and interpretation of the NMR spectra of
selected fluids.

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1. SUMMARY

Investigations of the mechanisms operative in thermal and thermal oxidative degradation of Fomblin Z type fluids and the effect of alloys and additives upon these processes are reported. Included are limited studies carried out on hexafluoropropene oxide derived polyethers.

The inherent thermal oxidative instability of the Fomblin Z fluids is not associated with hydrogen termination of the chains. Present investigations point to complete absence of hydrogen in these compositions. After thermal pretreatment, the stability of the fluid to metal alloys in inert atmospheres indicates the absence of peroxide linkages; NMR data support these deductions. The degradation rate at elevated temperatures in oxidizing atmospheres is dependent on the fluid surface to volume ratio. Once a limiting ratio is reached, a steady rate appears to be attained. Based on elemental analysis and oxygen consumption data, $-CF_2OCF_2CF_2O-$, not $-CF_2CF_2O-$, is one major arrangement present. The action of the M-50 and Ti(4 Al, 4 Mn) alloys is much more drastic in the case of Fomblin Z fluids than that observed for the hexafluoropropene oxide derived materials. The effectiveness of anti-oxidation/anticorrosion additives, P-3 and phospha-s-triazine, in the presence of metal alloys is very limited at $316^{\circ}C$; at $288^{\circ}C$ the additives arrest almost completely the fluid degradation. The phospha-s-triazine appears to be at least twice as effective as the P-3 compound; it also protects the coupon better. The Ti(4 Al, 4 Mn) alloy degrades the fluid mainly by chain scission processes; this occurs to a much lesser degree with M-50.

The presence of a certain proportion of hydrogen-terminated chains in Krytox MLO-71-6 fluid was verified by NMR spectroscopy. Prolonged exposure of the fluid to oxygen at $343^{\circ}C$ resulted in degradation of these chains and fluid stabilization. Limited studies of the effect of the pure

metals at elevated temperatures in oxygen upon the hexafluoropropene oxide derived fluid gave results not consistent with the alloy investigations. Aluminum metal did not seem to promote chain scissions at $316^{\circ}C$. A steady but low rate of degradation, under these conditions, was observed for the titanium metal.

2. INTRODUCTION

Perfluorinated polyethers such as those derived from the telomerization of hexafluoropropene oxide exhibit extremely high thermal stabilities with incipient decomposition temperatures in the vicinity of $410^{\circ}C$ [ref. 1,2]. This stability is not diminished in an oxidizing environment as represented by air or pure oxygen, which is in contrast to the behavior of hydrocarbons. The investigations carried out to date on polyperfluoroalkylethers have been fairly extensive [ref. 1-13], however these were concentrated predominantly on the hexafluoropropene oxide derived materials containing pending side chains with only limited work performed on the linear, unbranched materials [ref. 10-13]. Based on these data, the linear polyperfluoroalkylethers exhibit significantly lower thermal and thermal oxidative stabilities than those shown by the hexafluoropropene oxide derived compositions. It has been suggested [ref. 3,4] that the lower-than-expected stability of commercial polyhexafluoropropene oxide fluids is due to the presence of some hydrogen-terminated chains. These apparently can be removed by oxidation at elevated temperatures. The reason for the low thermal stability of the linear ethers is unknown. In view of their low temperature viscosity characteristics and wide fluid ranges, the linear materials are of great potential utility for aircraft applications where extremes of temperature are encountered.

The present investigation was directed at elucidating the mechanisms of the thermal oxidative degradation of the linear materials and the effect of the additives and metals upon this process. The verification of the presence of hydrogen-terminated chains in the "untreated" polyhexafluoropropene oxide derived materials and the determination of the action of pure metals upon these fluids, as opposed to the alloys, constituted other aspects of this program.

3. RESULTS AND DISCUSSION

The present investigation involved two different classes of perfluoro-
alkylethers, namely linear and hexafluoropropene oxide derived materials.
The latter are formed by oligomerization of hexafluoropropene oxide, whereas
the linear perfluoroalkylethers are prepared from tetrafluoroethylene and
oxygen under ultraviolet radiation [ref. 13]. The process as such introduces
peroxide linkages which are then removed by subsequent heat treatment. The
termination reaction used in the preparation of polyhexafluoropropene oxides is
well documented [ref. 1,2] and theoretically should give only perfluoroalkyl end-
groups. No such information is available for the linear materials, although
it is published data [ref. 13] that the grouping is CF_2H. The nature of the
end-groups and the presence of irregularities are the factors which limit
the inherent stability of the perfluoroalkylether systems. Thus, any study
of the thermal and thermal oxidative behavior must incorporate structural
considerations. These, of course, will differ depending on the synthetic
methods involved even when dealing with what should be identical arrange-
ments. Thus, there is no direct comparison between the "tetrafluoroethylene
oxide" and hexafluoropropene oxide derived materials.

To permit clarity of presentation, the investigations of the two fluids
are discussed separately. The implications of these various aspects are
evident by the results discussed in the sections which follow.

3.1   Degradation Studies, Fomblin Z Fluids

Two different batches of Fomblin Z fluid were received from the U.S.
Air Force Wright Aeronautical Laboratories (AFSC). The material found by
the Air Force to be of higher stability, MLO-72-22, was obtained from Monte-
catini Edison in 1972. The less stable sample MLO-79-196 was a later (1979)
received composition. It is noteworthy that both the Air Force and the Bray

Oil Co. concurred [ref. 14] that earlier Fomblin Z samples were thermally more stable; this was ascribed to the possible presence of residual peroxide linkages in more recent batches. The thermal and thermal oxidative investigations carried out on these two materials are summarized in Tables I and II, the tests involving metal coupons and additives are given in Table III, and the compositions of the volatiles are presented in Table IV.
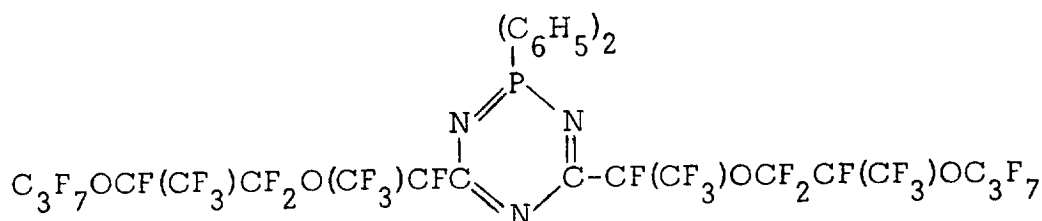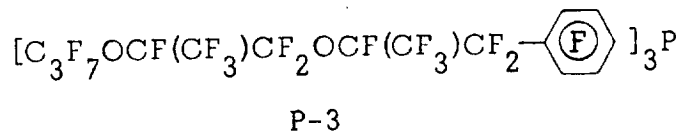
To determine the possible presence of heat "removable" unstable linkages, Test Nos. 1, 2, 3, and 7 were carried out. Based on the quantity of the volatile condensibles formed, it is evident that, at least up to 250°C, the fluid MLO-79-196 degrades more extensively. However, additional heat treatment (see Test No. 3, Table II) does not lead to further degradation showing that exposure of the fluid to 250°C in an inert atmosphere removes some unstable centers.

Concentrating on the MLO-72-22 fluid (see Table I), it is obvious that oxidizing atmospheres at elevated temperatures promote considerable degradation with initial exposure (see Test Nos. 5 and 6) resulting in significantly higher degradation than subsequent exposures to the same temperature. It would appear that the degradation rate at a given temperature, after the initial phase, proceeds at a relatively steady rate (see Test Nos. 6, 9, and 10). An increase in temperature of $\sim 10^{\circ}$C between 332 and 343°C (Test Nos. 12 and 17) increases the rate by a factor of ~ 2 which is in very good agreement with Arrhenius' equation and shows clearly that the change in temperature does not alter the operative mechanism. The change in molecular weight is, however, considerable and there is also some change in the elemental composition (see Table V). Whether this is real is unknown. Ignoring the elemental composition variation, one is tempted to assume that the lowering in the molecular weight took place prior to the attainment of the steady rate, possibly at the stage of Test No. 6 (?).

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On the basis of Test Nos. 17 and 19, it would appear that the degradation rate at 343°C is ~60-65 mg/g per 24 hr. This applies only to small quantities of fluid. When large quantities of fluid are employed, the rate with respect to the quantity of fluid employed drops considerably (see Test Nos. 21, 30, and 39). This drop is not due to oxygen depletion since in Test No. 21 only 5.4% of the available oxygen was consumed and it can be deduced that in Run No. 39 the value would be ~12%. Thus, it must be assumed that the degradation rate is governed by the solubility or diffusion of oxygen into the fluid. The larger the volume of the fluid, the lower the surface area of the fluid in contact with oxygen (all the tests were performed in the same type of a tube). Consequently, in the case of the large samples, the pretreatment in oxidizing atmospheres is not complete as shown by the comparison of Test Nos. 31 and 6. It is believed that the rate observed for the small quantities of fluid (~3 g) is the true rate, since it was unchanged by halving the quantity of the fluid (compare Test Nos. 17 and 19). It should be stressed that, in the case of the hexafluoropropene oxide derived fluids, variations of the ratios of surface area to volume had no effect upon the degradation extent [ref. 3,4].

The thermal oxidative behavior of the MLO-79-196 Fomblin Z fluid paralleled closely that of the MLO-72-22 material as evident by the compilation presented in Table II. The degradation rates at corresponding temperatures are fairly comparable, e.g., 16-17 mg/g for MLO-79-196 versus 19-22 mg/g for MLO-72-22 over a 24 hr period at 316°C. It is noteworthy that no decrease in molecular weight of the residual fluid was found to take place in the case of the MLO-79-196. On the other hand, the final molecular weights were comparable. The nature and relative concentration of the condensible volatiles formed by these two fluids are directly comparable.

The majority of the investigations were carried out on the MLO-72-22 fluid and this fluid only was evaluated in the presence of metal coupons and additives. This series of the tests is compiled in Table III. The metal alloys employed were M-50 and Ti(4 Al, 4 Mn); the additives were P-3 (MLO-80-279) and phospha-s-triazine. The structures of these are given below.

$$[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2 - \langle\!\langle F \rangle\!\rangle \,]_3P$$

P-3

$$C_3F_7OCF(CF_3)CF_2O(CF_3)CFC \overset{(C_6H_5)_2}{\underset{N}{\overset{P}{\underset{\parallel}{\swarrow}}}} C\text{-}CF(CF_3)OCF_2CF(CF_3)OC_3F_7$$

monophospha-s-triazine

The presence of metal coupons was found to accelerate greatly the fluid's degradation. Exposure to oxygen at $316^{\circ}C$ in the presence of M-50 for 24 hr resulted in complete liquid degradation (Test No. 32B, Table III). In 8 hr at $316^{\circ}C$ more than half of the fluid was degraded. The additives (Test Nos. 34 and 35) were effective in arresting this process to a degree at $316^{\circ}C$, although the degradation rate was higher by more than a factor of 10 as compared to the tests carried out in the absence of the M-50 coupon. Based on the quantity of products formed, the phospha-s-triazine additive seems to be twice as effective as the P-3 compound.

The studies performed on hexafluoropropene oxide derived materials [ref. 3,4] showed that the additives arrest the fluid degradation in the absence of metal. The same was found to be the case in Fomblin Z fluids (Test No. 33). However, this action is only partially effective at $316^{\circ}C$ in the presence of

metal (Test Nos. 34 and 35). Whether this is due to the accelerated consumption of the additive is unknown. At $288^{\circ}C$ both of the additives were very effective in arresting degradation (Test Nos. 36 and 37) with the phospha-s-triazine exhibiting a stronger action (factor of 3 as measured by volatiles produced). The Ti(4 Al, 4 Mn) alloy was found to degrade the fluid more extensively at $288^{\circ}C$ than the M-50 coupon as shown by comparison of Test Nos. 38 and 41. The P-3 additive was very effective in arresting this action. No parallel studies were performed with the phospha-s-triazine compound. In the absence of oxygen, both of the alloys failed to promote the fluid's degradation even at $316^{\circ}C$ (Test Nos. 44 and 45).

The coupons recovered from Test Nos. 32A, 32B, 34, 35, and 38 were badly corroded and covered with flaky deposits. Unexpectedly, corrosion was evident on the coupons obtained after Runs 37, 42 , and 45 where the degradation of fluid was very low; the coupons recovered from Test Nos. 36 and 44 were shiny. The surprising aspect is that P-3 additive did not seem to fully prevent the corrosion of M-50, whereas the phospha-s-triazine compound achieved it.

3.2   Mechanistic and Structural Considerations

The ^{19}F and proton NMR spectra of the Fomblin Z fluid recovered after Test No. 19 are given in Figures 1-6. The proton NMR of the "lightly" thermally stressed fluid is given in Figure 7 (Test No. 21). From the ^{19}F NMR the assignment is difficult; the polymer appears to contain CF_3O, $-OCF_2$, $-OCF_2CF_2-$, and $OCF_2CF_2CF_2CF_2-$ groups arranged randomly. Area "A" may be assigned to CF_3O-, $-OCF_2O-CF_2O-$, $-OCF_2OCF_2CF_2$, etc.; areas "B" and "C" may be assigned to $-OCF_2CF_2O-$, $-OCF_2CF_2CF_2CF_2-$ groups depending on what is attached to the oxygen, e.g., $-OCF_2CF_2OCF_2O-$ is different from $-OCF_2CF_2OCF_2CF_2O-$. Area "D" is due to a $-CF_2-$ surrounded by other CF_2 groups, e.g., $-OCF_2CF_2CF_2CF_2O-$. It should be noted that
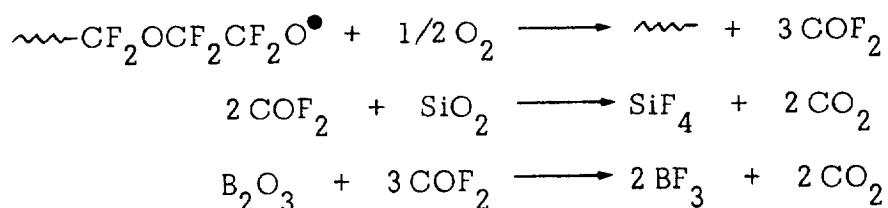
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the integral of "D" is similar to that of "B" suggesting that the $-CF_2O$ absorptions of "B" are related to the CF_2 absorptions of "D". No peaks were found in the 0 to +100 ppm region showing absence of COF groups. The spectra are different from those reported by Sianesi, et al. [ref. 13]. Significantly, there are no doublets with 50-70 HZ splitting characteristic of $-OCF_2H$ or $-OCFH-$ or $-CF_2H$ groups, etc.; in other words, the ^{19}F NMR is consistent with the ^1H NMR in suggesting the absence of protons, Figures 6,7.

The absence of protons is in agreement with the experimental data (discussed in Section 3.1) namely the lack of stabilization after exposure to oxidizing atmospheres for prolonged periods of time. The experimental data would thus indicate that either all the chains are hydrogen-terminated, which should be revealed by proton NMR, or such a termination is insignificantly low and is not responsible for the observed thermal oxidative behavior of the fluids. It is unlikely that residual peroxide linkages are causing the observed thermal oxidative instability since the rate of degradation failed to decrease after prolonged exposure to elevated temperatures. Metals in the absence of oxygen did not cause any fluid degradation supporting further that there are no residual peroxide linkages. Consequently, it must be concluded that the arrangement of the units in the chains or the end-groups are responsible for the observed behavior.

Elemental analyses of the fluid, both "lightly" thermally stressed and after extensive exposure to oxygen at elevated temperature, differ somewhat as evident from the tabulation given in Table V. On the other hand, the variation in carbon content is within acceptable limits and it has been usually found [ref. 15] that in these type of compositions fluorine values are generally low as compared to those actually present. Thus, it is unknown whether the calculated increased oxygen content in the residue of Test No. 19 is real. However, the C:O ratio which is lower for both of the samples than the 2:1 value calculated for $(CF_2CF_2O)_x$

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polymer is definitely real. Consequently, it would appear from these data that the ratio of CF_2O entities to CF_2CF_2O groups is in the vicinity of 1:1. This would further imply that the concentration of $-O(CF_2)_xO-$ units wherein x is higher than 2 is low. All these stipulations do not contradict the NMR spectral findings; unfortunately the latter do not provide information regarding the concentration of specific groups, i.e., $-OCF_2O-$, $-O(CF_2)_2O-$, $-O(CF_2)_4O-$, etc.

From the calculations of the ratios of fluid volatilized to oxygen atoms consumed (given in Table VI) for the different segments, it would appear that the content of $-OCF_2O-$ units is higher than that denoted by $-CF_2OCF_2CF_2O-$ arrangement. Test Nos. 16, 19, 21, and 31 were carried out in the absence of metal coupons. In these runs only traces of materials non-volatile at $-78^{\circ}C$ were formed. Based on the nature of the collected volatiles, it can be deduced that COF_2 was the initial product formed,. SiF_4, CO_2, and BF_3 are the products of COF_2 interactions with constituents of glass at the elevated temperatures:

$$\text{ᴧᴧᴧ-}CF_2OCF_2CF_2O^{\bullet} + 1/2\,O_2 \longrightarrow \text{ᴧᴧᴧ-} + 3\,COF_2$$

$$2\,COF_2 + SiO_2 \longrightarrow SiF_4 + 2\,CO_2$$

$$B_2O_3 + 3\,COF_2 \longrightarrow 2\,BF_3 + 2\,CO_2$$

Inasmuch as at least some COF_2 survived the treatment, one would expect to see CF_3COF or related acid fluorides if there was substantial content of $-O(CF_2)_xO-$ units where x is higher than 2. It should be noted that CF_3COF was found in the volatiles formed by hexafluoropropene oxide derived poly-ethers [ref. 3,4], but none was detected in the Fomblin Z investigations.

Metals definitely promoted scission of the chain bonds as shown by the increased ratio of the volatilized fluid to oxygen consumed and by the type of products formed. This is especially significant in the case of

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Ti(4 Al, 4 Mn) alloy wherein at 288°C almost half of the products were in the form of the relatively involatile -COF terminated chains as determined by infrared spectral analysis. Characterization of these compounds, after transformation to the corresponding methyl esters, by GC-MS analysis, should provide some information with respect to the type of units present in the fluid. This will be performed under the follow-on program.

3.3 Investigation of Polyperfluoroalkylethers Derived from Hexafluoropropene Oxide

The studies conducted under U.S. Air Force sponsorship [ref. 3,4] revealed that hexafluoropropene oxide derived fluids, produced by DuPont de Nemours Co. under the trade name of Krytox, exhibited thermal oxidative instability which could be eliminated by prolonged treatment in oxygen at 343°C (650°F). At that time it was speculated that this phenomenon was due to the presence of a certain proportion of hydrogen-terminated chains which were degraded and volatilized on exposure to oxygen at elevated temperatures leaving behind the stable perfluoroalkyl-terminated materials. NMR spectral analyses verify fully this theory.

The proton NMR of the fluid as received (see Figure 8) shows the presence of CF_3CFHO- as a typical doublet at 5.9 ppm. This doublet is also exhibited by the fully characterized compound $C_3F_7OCF(CF_3)H$ in Figure 9. After the thermal oxidative exposure at 343°C, these peaks disappear entirely as attested by the 812 scans of this region in Figure 10.

The ^{19}F NMR spectra of Krytox MLO-71-6 are given in Figures 11-13. Based on the structure of the hydrogen-free fluid given below,

$$CF_3CF_2CF_2O[\overset{\overset{\displaystyle CF_3}{|}}{CF}CF_2O]_xCF_2CF_3$$
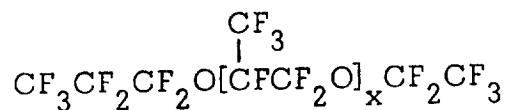
the assignment of the peaks is as follows:

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$$\overset{\displaystyle CF_3}{\underset{\textstyle}{|}}$$

$-OCF-$ and $-CF_2O-$ complex peak at -80.3 ppm

$\underline{CF}_3CF_2CF_2O$ spike at -82.2 ppm

$\underline{CF}_3CF_2O$ spike at -87.7 ppm

$CF_3\underline{CF}_2CF_2O$ spike at -130.0 ppm

$$\underset{\textstyle CF_3}{\overset{\displaystyle O\underline{CF}}{|}}$$ peak at -144.3 ppm

If x is 30 then the integral ratio between the peaks at -130.0 and -144.3 ppm should be $1/15$. It is difficult to measure this ratio accurately, but it seems to be approximately $1/18$. This would make x=36 (see Figure 13) resulting in an average molecular weight of 6280. If one considers the accuracy involved, the agreement with the osmometrically measured value of 5500 [ref. 3,4] is very good.

Past studies have shown that even at $288^{\circ}C$ ($550^{\circ}F$) exposure of the as-received fluid (not pretreated in oxygen at $343^{\circ}C$) to Ti(4 Al, 4 Mn) alloy in oxygen resulted in extensive degradation. The rate of the degradation increased with time. It was postulated at that time that this behavior was due to the aluminum component of the alloy. Based on the results of Test Nos. 22 and 23 (see Table VII), this is not the case since even at $316^{\circ}C$ ($600^{\circ}F$) no increase, but rather a substantial decrease in degradation was noted on successive exposures of the fluid to temperature in the presence of the aluminum metal and oxygen. Fluid which had been pretreated in oxygen at $343^{\circ}C$ was virtually inert to the aluminum coupon at $316^{\circ}F$ (see Test No. 24).

The action of pure titanium metal on the as-received fluid, at least for the first 48 hr (see Test Nos. 25 and 26), was directly comparable to that of the aluminum metal. Yet, the extent of degradation observed with the pretreated fluid, as measured by the volatiles formed, was significantly

larger (compare Test Nos. 24 and 27). Interestingly, this rate of degradation was virtually unaffected whether the coupon was used previously or whether it was freshly polished. Successive exposures and different periods of exposure failed to change the rate from ~ 10 mg/g/24 hr. This finding would indicate that the titanium metal promotes scissions of the bonds within a chain at a steady rate. This action would not seem to be caused by titanium fluoride since if this was the case, an increase in the rate with time would be expected. One would visualize that this type of action is surface area dependent. Thus, the presence of a larger coupon or multiple coupons should increase the rate. Due to funds limitation, this was not established. The results obtained from the investigations of the pure aluminum and titanium metals differ drastically from those found with the Ti(4 Al, 4 Mn) alloy. Whether these differences are due to the alloying process or the presence of manganese will be determined under the follow-on effort.

4. EXPERIMENTAL DETAILS AND PROCEDURES

The perfluoroalkylether fluids employed in this study, namely Krytox, MLO-71-6 fluid (product of E. I. DuPont de Nemours and Co), and the Fomblin Z fluids, MLO-72-22 and MLO-79-129 (products of Montecatini Edison), and P-3 additive were obtained through the courtesy of Mr. C. E. Snyder, Air Force Wright Aeronautical Laboratories.

The degradation apparatus was a modified, scaled-down version of the AFML Micro-O-C-Test arrangement [ref. 6,7]. It was described in detail previously [ref. 3,4]. The schematics given in Figures 14 and 15 show the reaction tube configuration and the rod assembly for holding the metal coupon specimens. The metal coupons were 3/8" OD and 1/8" ID. These were obtained from Metaspec Company, San Antonio, Texas. For heating of sample tubes in a vertical position, a modified Lindberg Heavy-Duty box furnace, Type 51232 (see Figure 16) was utilized. In this arrangement, 180 mm of the 420 mm tube was at temperature; the fluid occupied at the most the lower 75 mm (see Figure 14), the extra gas reservoir was in the ambient environment.

In a typical experiment, the fluid was introduced into the degradation tube (see Figure 14) which was then evacuated and filled to a known pressure at a known temperature with a selected gas (air, N_2, or O_2). Inasmuch as the apparatus was calibrated and the fluid volume measured accurately, the quantity of gas thus introduced was exactly known. The degradation tube was then inserted into the preheated box furnace and kept there for a specified period of time; throughout this exposure the temperature was continuously recorded. After removal from the furnace, the tube was allowed to cool to room temperature, attached to the high vacuum line, and opened. The liquid nitrogen noncondensibles were collected quantitatively, measured, and analyzed by mass spectrometry. The liquid nitrogen con-

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densibles, which were volatile at room temperature, were measured, weighed, and analyzed by infrared spectroscopy and mass spectrometry. The fluid residue itself was weighed and subjected to infrared spectral analysis; in selected instances, molecular weight and NMR determinations were performed.

The metal coupons prior to testing were polished using first Norton No-Fil Durite finishing paper Type 4 220A. This was followed by open coat Silicon Carbide papers grades 400A and 500A, respectively. Subsequently, the coupons were washed with Freon 113, dried, weighed, and suspended in the test apparatus (see Figure 15). After the completion of a given experiment, the metal coupons were washed with Freon 113, dried inside an inert atmosphere chamber, then weighed and visually inspected. The used coupons were subsequently sealed in Mylar envelopes.

5. PRELIMINARY CONCLUSIONS

Summarized below are conclusions reached during the current investigations of thermal oxidative degradation reactions of perfluoroalkylethers.

1. Fomblin Z fluids were found to be inherently unstable when subjected to elevated temperatures, $\sim 316^{\circ}C$ ($600^{\circ}F$), in oxidizing atmospheres. This instability is not due to hydrogen termination or the presence of peroxy linkages, or oxidatively removable impurities.

2. Fomblin Z fluids do not have the structural arrangement derived from tetrafluoroethylene oxide, rather they represent a chain system of difluoroformyl and tetrafluoroethylene oxide units with the former predominating.

3. Fomblin Z fluids in oxidizing atmospheres at $316^{\circ}C$ ($600^{\circ}F$) degrade completely in the presence of M-50 and Ti(4 Al, 4 Mn) alloys. The effectiveness of additives under these conditions is minimal. The additives are effective in arresting the degradation process at $288^{\circ}C$ ($550^{\circ}F$). Metal alloy's action is due to polymer bond scissions. The alloys do not promote the fluids' degradation in inert atmospheres at $316^{\circ}C$ ($600^{\circ}F$).

4. The presence of hydrogen chain termination was established to be the cause of thermal oxidative instability exhibited by "untreated" poly(hexafluoropropene oxide) fluids.

5. Based on pure metal studies, it does not appear that aluminum and titanium metals are responsible for the observed action of Ti(4 Al, 4 Mn) alloy in the poly(hexafluoropropene oxide) fluids.

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TABLE I

THERMAL AND THERMAL OXIDATIVE INVESTIGATIONS OF

FOMBLIN Z FLUID, BATCH MLO-72-22

Test No.[a]	Amt Used, g	Atm	Temp °C	Duration hr	MW	Condensible Products mg	Condensible Products mg/g[b]	Oxygen Consumed mg	Oxygen Consumed mg/g[c]	Oxygen Consumed mg/mg[d]	Oxygen Consumed %[e]	CO Produced mg	CO Produced mg/mg[f]
1	26.33	N_2	150	3				—	—	—	—	—	—
			200	2				—	—	—	—	—	—
			250	2	15500[g]			—	—	—	—	—	—
4[h]	3.46	Air	150	3		0.2	0.01	—	—	—	—	—	—
			200	3		1.0	0.29	—	—	—	—	—	—
			250	3		1.3	0.38	—	—	—	—	—	—
			288	3		1.1	0.32	—	—	—	—	—	—
			316	3		1.2	0.35	—	—	—	—	—	—
			316	3		2.6	0.75	n.d.[i]	n.d.	n.d.	n.d.	n.d.	n.d.
5[h]	3.44	Air	316	24		165.0	47.97	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6[h]	3.26	O_2	316	24		72.7	22.30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
9[h]	3.16	O_2	316	24		90.3	28.58	1.59	0.50	0.02	0.5	2.7	0.03
10[h]	3.07	O_2	316	48		118.9	38.73	4.27	1.39	0.04	1.4	4.7	0.04
12[h]	3.02	O_2	332	24		81.4	26.95	1.69	0.53	0.02	0.5	2.7	0.03
17[h]	2.95	O_2	343	100		792.2	268.54	23.81	8.07	0.03	7.8	6.2	0.01
19[h]	1.76	O_2	343	48	8600	216.1	122.78	7.46	4.23	0.03	2.4	4.7	0.01
21[j]	19.51	O_2	343	24	15100	422.5	21.65	15.86	0.81	0.03	5.4	6.9	0.02
30	24.15	O_2	343	24	14100	435.3	18.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
31[k]	4.27	O_2	316	24		278.5	65.22	11.21	2.62	0.04	3.7	2.7	0.01
39	54.54	O_2	343	24		942.0	17.27	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
40[k]	3.74	O_2	288	24		92.0	24.60	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

a) Test Nos. 1 and 4 were conducted on a vacuum line; the remainder of the tests were carried out in a 428 ml straight tube apparatus (ref. 3).
b) Products in mg per g of fluid employed.
c) Oxygen consumed in mg per g of fluid employed.
d) Oxygen consumed in mg per mg of products formed.
e) Percent of oxygen available.
f) Mg of carbon monoxide formed per mg of products liberated.
g) Molecular weight of as received MLO-72-22 was found to be 13100.
h) Fluid used for this test was the involatile residue of the preceding test.
i) Not determined.
j) Fluid used for this test was the residue of Test No. 1.
k) Fluid used was the combined residues of Test Nos. 21 and 30.

TABLE II

THERMAL AND THERMAL OXIDATIVE INVESTIGATIONS OF

FOMBLIN Z FLUID, BATCH MLO-79-196

Test No. [a]	Amt Used, g	Atm	Temp °C	Duration hr	MW	Condensible Products		Oxygen Consumed				CO Produced	
						mg	mg/g [b]	mg	mg/g [c]	mg/mg [d]	% [e]	mg	mg/mg [f]
2	35.29	N_2	150	3									
			200	2									
			250	2	7100[g]	16.9	0.48						
3[h]	32.71	N_2	250	6.6		0.8	0.02	-	-	-	-		
7[h]	5.03	N_2	288	6		0.5	0.10					n.d.[i]	n.d.
			316	6		0.8	0.16						
8[h]	5.03	Air	288	3	6500	0.2	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
11[h]	3.90	Air	316	24		62.7	16.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
13[h]	3.82	O_2	316	24		60.6	15.86	5.42	1.42	0.09	1.8	2.7	0.04
14[h]	3.77	O_2	316	24		63.6	16.87	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15[h]	3.71	O_2	332	48		245.9	66.55	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
16[h]	3.46	O_2	332	48	6000	271.5	78.46	8.48	2.45	0.03	2.9	4.2	0.02

a) Test Nos. 2, 3, and 7 were conducted on a vacuum line; the remainder of the tests were carried out in a 428 ml straight tube apparatus (ref. 3).
b) Products in mg per g of fluid employed.
c) Oxygen consumed in mg per g of fluid employed.
d) Oxygen consumed in mg per mg of products formed.
e) Percent of oxygen available.
f) Mg of carbon monoxide formed per mg of products liberated.
g) Molecular weight of as received MLO-79-196 was found to be 6400.
h) Fluid used for this test was the involatile residue of the preceding test.
i) Not determined.

TABLE III

EFFECTS OF METAL COUPONS AND ADDITIVES ON THERMAL AND

THERMAL OXIDATIVE BEHAVIOR OF FOMBLIN Z FLUID, BATCH MLO-72-22

Test No. [a]	Amt Used, g	Atm	Temp °C	Duration hr	Coupon	Additive	Condensible Products		Oxygen Consumed				CO Produced	
							mg	mg/g [b]	mg	mg/g [c]	mg/g [d]	% [e]	mg	mg/g [f]
31	4.27	O_2	316	24	None	None	278.5	65.22	11.21	2.62	0.04	3.7	2.7	0.01
32A	4.24	O_2	316	24	M-50	None	?	?	n.d. [g]	n.d.	n.d.	n.d.	n.d.	n.d.
32B	4.17	O_2	316	8	M-50	None	2666.0	639.33	104.69	25.10	0.04	35.0	2.5	0.00
33	3.84	O_2	316	24	None	1% P-3 [h]	11.3	2.94	n.d.	n.d.	n.d.	n.d.	11.7	0.01
34	4.08	O_2	316	24	M-50	1% P-3	1176.2	286.28	27.51	6.74	0.02	9.2	11.7	0.01
35	3.39	O_2	316	24	M-50	1% C_2PN_3 [i]	535.1	157.85	n.d.	n.d.	–	n.d.	–	–
36	3.34	O_2	288	24	M-50	1% C_2PN_3	1.1	0.33	–	–	–	–	–	–
37	3.57	O_2	288	24	M-50	P-3	3.4	0.95	–	–	–	–	–	–
38	3.34	O_2	288	15	M-50	None	1117.1	421.55	40.42	12.10	0.04	13.57	1.3	0.00
40	3.74	O_2	288	24	None	None	92.0	24.60	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
41	3.84	O_2	288	8	Ti (4 Al, 4 Mn)	None	2235.0	582.03	51.14	13.31	0.02	17.24	4.2	0.00
42	3.67	O_2	288	24	Ti (4 Al, 4 Mn)	1% P-3	4.1	1.12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
43	3.65	N_2	316	24	None	None	8.1	2.22	–	–	–	–	–	–
44	3.96	N_2	316	24	M-50	None	9.0	2.27	–	–	–	–	–	–
45	3.87	N_2	316	24	Ti (4 Al, 4 Mn)	None	9.2	2.38	–	–	–	–	–	–

a) All the fluids used were pretreated at 343°C for 24 hr.
b) Products in mg per g of fluid employed.
c) Oxygen consumed in mg per g of fluid employed.
d) Oxygen consumed in mg per mg of products formed.
e) Percent of oxygen available.
f) Mg of carbon monoxide formed per mg of products liberated.
g) Not determined.
h) MLO-80-279.
i) $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2[(C_6H_5)_2PN]$, monophospha-s-triazine.

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TABLE IV

PRODUCT DISTRIBUTION, THERMOOXIDATIVE DEGRADATION

OF FOMBLIN Z FLUIDS[a]

Test No.	O_2 consmd. mmol	Volatile Products			CO_2	Type %		
		mmol	MW found	MW calcd.		COF_2	SiF_4	BF_3
5	n.d.[b]	2.576	64	60	65	3.1	22	9.5
6	0.387	1.137	64	62	60	3.7	26	9.8
9	0.050	1.353	67	63	63	2.2	26	9.8
10	0.134	1.887	63	64	60	2.0	28	9.9
12	0.050	1.294	63	60	66	2.2	22	10.3
13	0.169	0.943	64	57	68	5.2	16	10.6
14	n.d.	0.977	65	54	73	4.0	11	12.0
15	0.499	3.796	65	70	53	0.9	41	5.0
16	0.265	4.406	62	74	46	1.3	46	6.8
17	0.729	10.888	73	69	52	0.4	36	11.7
19	0.233	3.056	71	67	55	1.5	34	9.0
21	0.496	6.727	63	62	66	0.4	27	6.6
31	0.351	4.149	64	62	61	6.6	25	7.0
32B	3.272	31.299	78	62	54	19.7	21	5.2
33	0.025	0.152	74	76	47	0.9	52	0.5
34	0.860	15.358	70	66	49	13.6	30	6.9
38	1.263	13.905	63	56	67	13.9	13	5.8
40	0.246	1.116	66	54	70	14.9	9	6.4
41	2.169	17.574	67	56	64	23.3	11	2.0

a) The quantities of CO_2, COF_2, and BF_3 were determined by infrared spectral analysis; the proportion of SiF_4 was obtained by difference.
b) Not determined.

TABLE V

ELEMENTAL ANALYSIS CONSIDERATIONS

Material	C %	F %	C : F : O
MLO-72-22 (Test 21)	20.03	61.21	2.85 : 5.50 : 2
MLO-72-2 (Test 19)	19.63	60.09	2.57 : 4.99 : 2 3.86 : 7.48 : 3
$(CF_2CF_2O)_x$	20.69	65.52	2 : 4 : 1
$(CF_2OCF_2OCF_2CF_2O)_x$	19.37	61.29	4 : 8 : 3
$(CF_2OCF_2CF_2O)_x$	19.80	62.64	3 : 6 : 2

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TABLE VI

INFLUENCE OF METAL COUPONS UPON RATIOS OF

VOLATILIZED FLUID TO OXYGEN CONSUMED

Test No.	Atm	Temp $^\circ$C	Coupon	Products mg	Ratio mmol fluid lost to O atoms consmd Segm,116[a]	Segm,182[b]
16	O_2	332	None	272	2.1 : 1	1.3 : 1
19	O_2	343	None	216	2.6 : 1	1.5 : 1
21	O_2	343	None	426	2.1 : 1	1.3 : 1
31	O_2	316	None	279 (4)[c]	2.0 : 1	1.2 : 1
32B	O_2	316	M-50	2666 (10)	2.6 : 1	1.7 : 1
38	O_2	288	M-50	1117 (22)	3.7 : 1	2.3 : 1
41	O_2	288	Ti (4 Al, 4 Mn)	2235 (47)	4.6 : 1	2.9 : 1

a) Segment $-CF_2CF_2O-$.

b) Segment $-CF_2OCF_2CF_2O-$.

c) Values in brackets correspond to the percentage of products which were involatile at -78°C.

TABLE VII

EFFECT OF METAL COUPONS ON THERMAL OXIDATIVE BEHAVIOR

OF POLYHEXAFLUOROPROPENE OXIDE FLUIDS

Test No.[b]	Metal	Amt Used	Temp $^\circ C$	Duration hr	Total Products[c] mg	mg/g[d]
18/20	–	28.22	343	194	1950	69.1
22	Al	4.52	316	24	201.1	44.5
23[e]	Al	4.32	316	24	52.6	12.2
24[f]	Al	4.52	316	24	1.8	0.4
25	Ti	4.34	316	24	224.1	51.6
26[g]	Ti	4.12	316	24	51.6	12.5
27[f]	Ti	4.38	316	24	24.9	8.0
28[h]	Ti	3.48	316	24	39.9	11.5
29[i]	Ti	3.44	316	64	97.1	28.2

a) In all tests, Krytox MLO-71-6 was employed in an oxygen atmosphere.

b) All tests were carried out in a 418 ml sealed ampoule.

c) These are room temperature volatiles condensible at $-196^\circ C$.

d) Products formed in mg/g of material employed.

e) The residue of Test No. 22 was utilized in this experiment.

f) A portion of the involatile residue of Test No. 20 was used in this experiment.

g) The residue of Test No. 25 was used in this experiment.

h) The residue of Test No. 27 was used in this experiment with a fresh Ti metal coupon.

i) The residue of Test No. 28 was used in this experiment, the coupon was not changed.
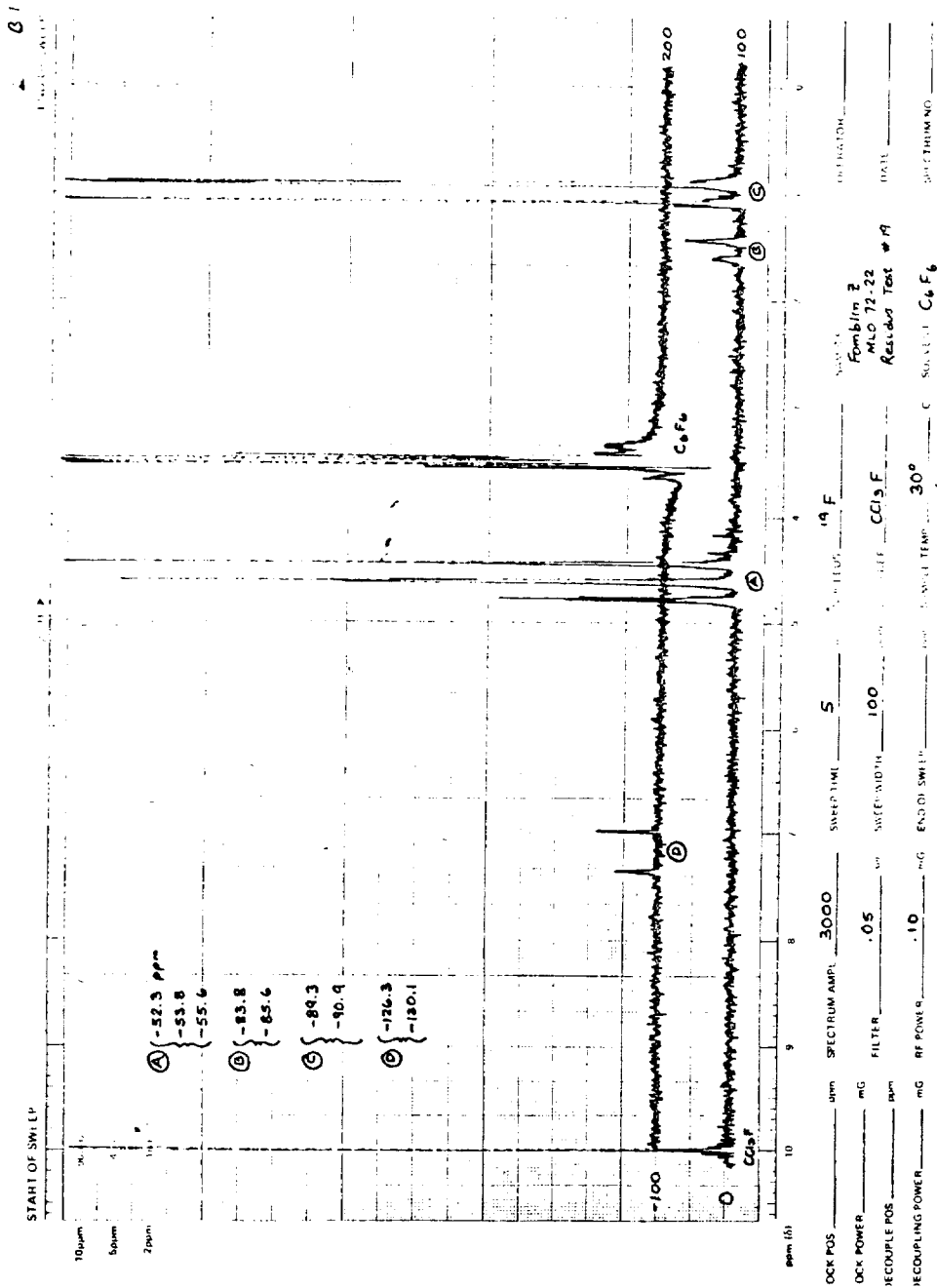
Figure 1: ^{19}F NMR spectrum of Fomblin Z fluid MLO-72-22
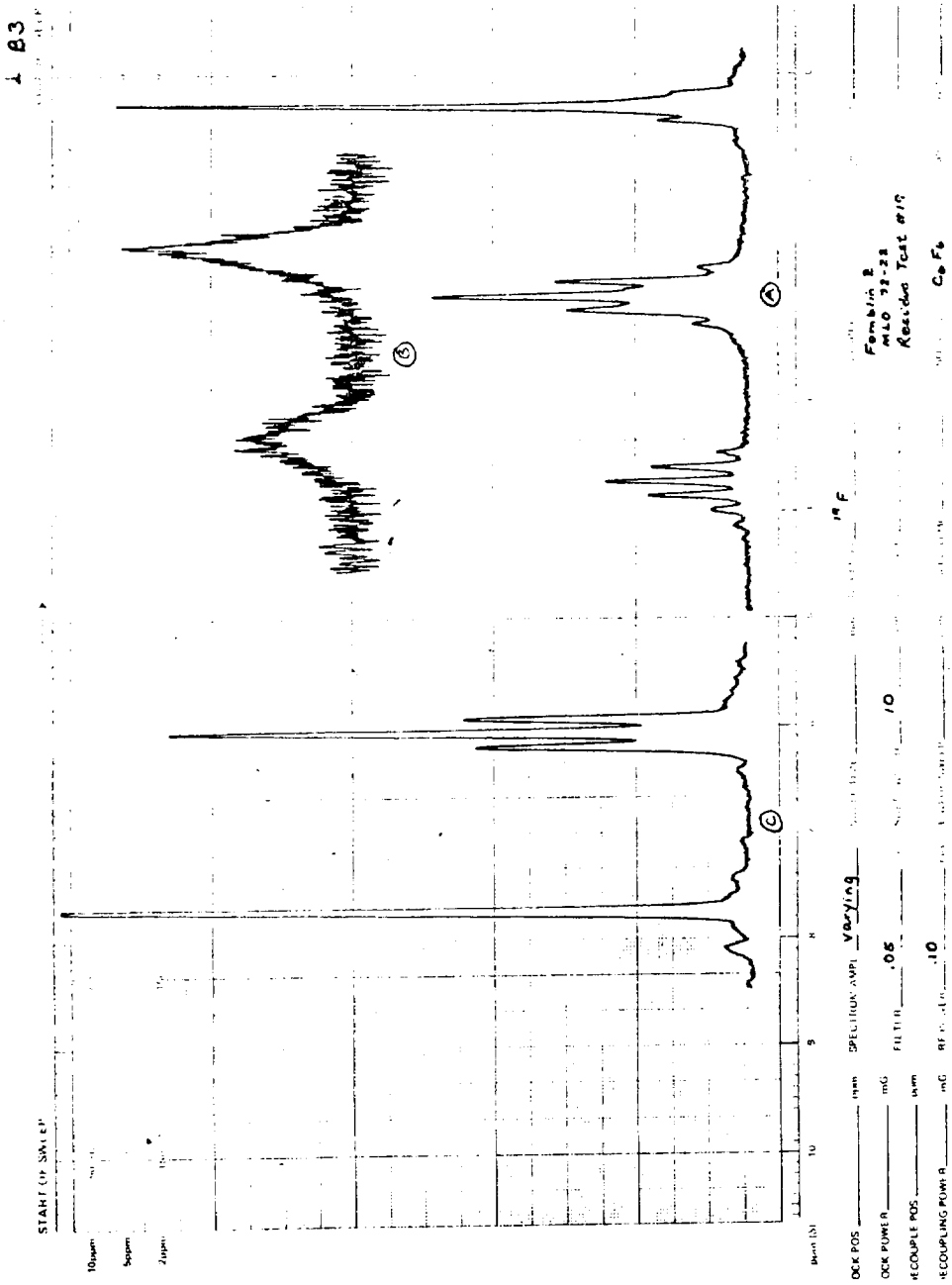
Figure 2: ^{19}F NMR spectrum of Fomblin Z fluid MLO-72-22, expanded sections A, B, and C

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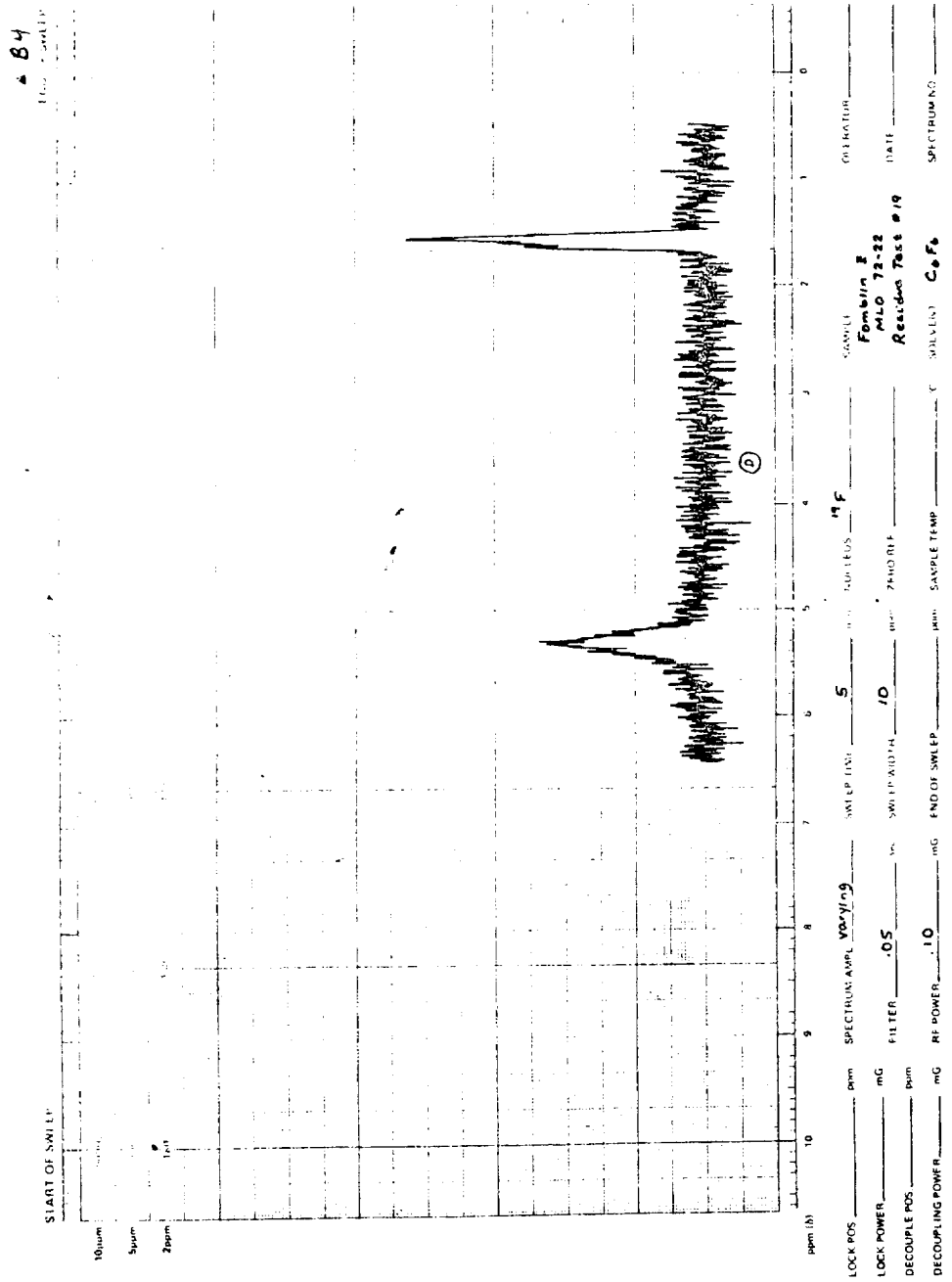
Figure 3: ^{19}F NMR spectrum of Fomblin Z fluid MLO-72-22, expanded section B
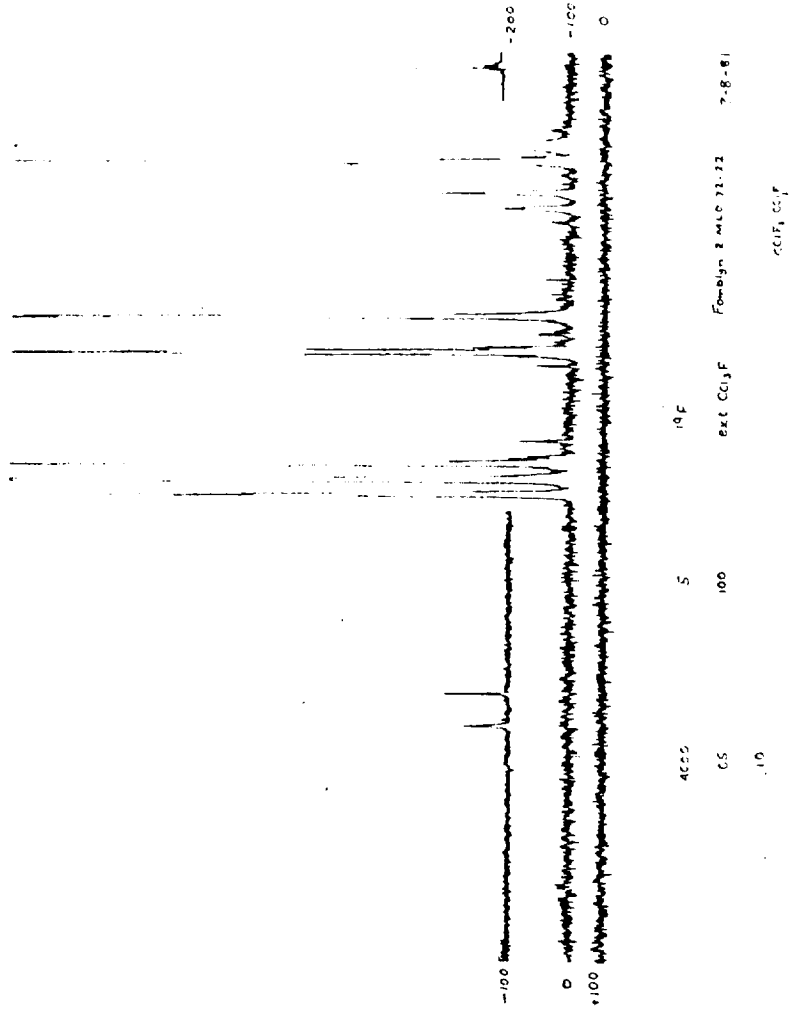
Figure 4: ^{19}F NMR spectrum of Fomblin Z fluid MLO-72-22, from -200 to $+100$ ppm
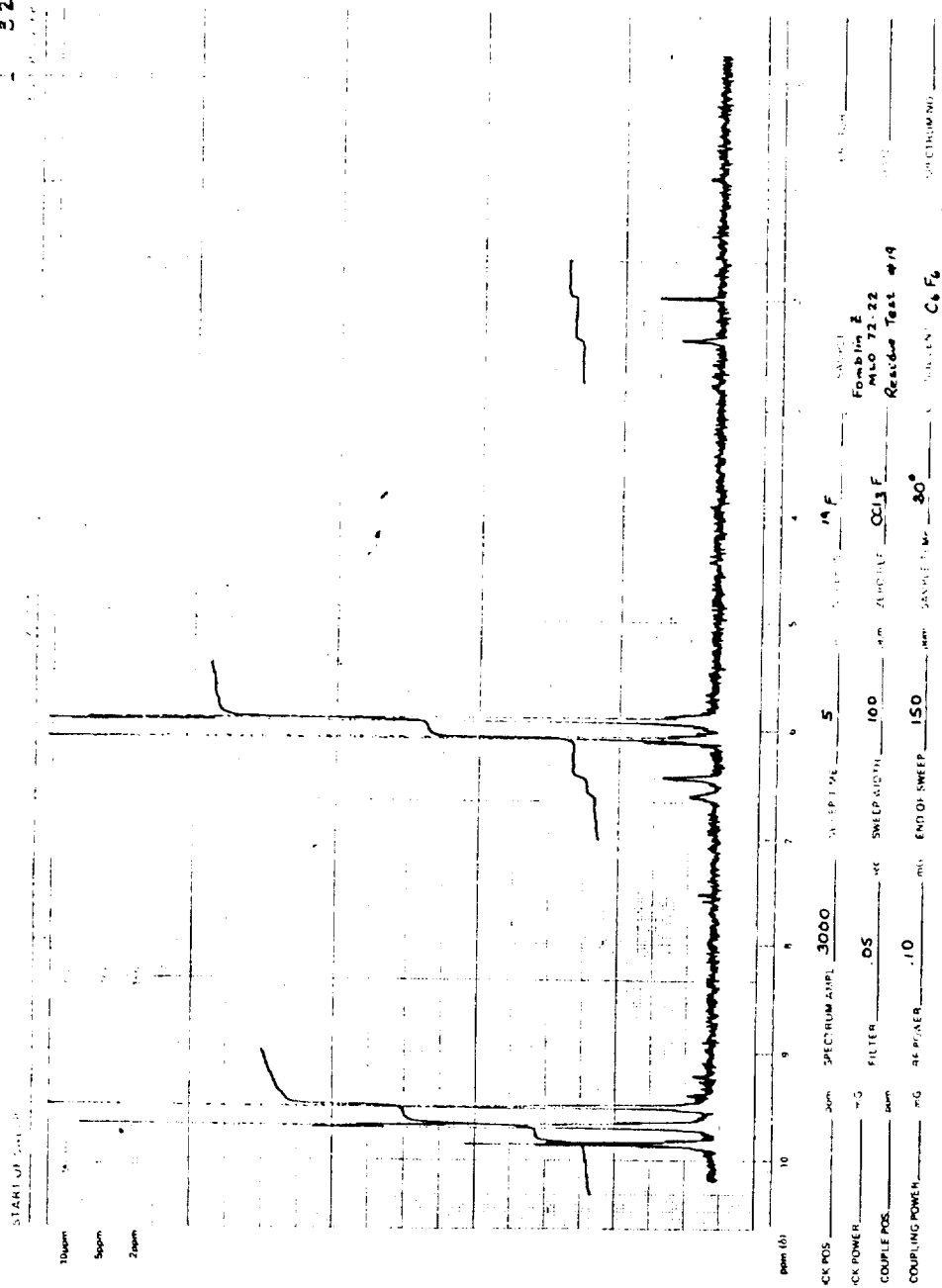
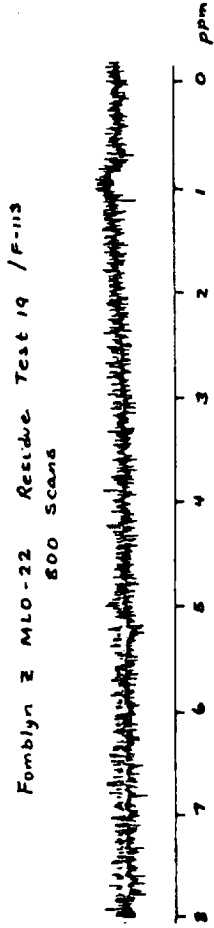Figure 5: ^{19}F NMR spectrum of Fomblin Z fluid MLO-72-22, integrated data

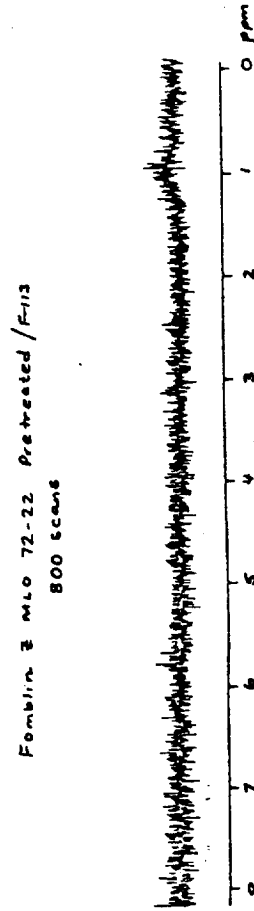30

Figure 6: Proton NMR spectrum of Fomblin Z fluid
(Residue Test No. 19)

Figure 7: Proton NMR spectrum of Fomblin Z fluid
(Residue Test No. 21)
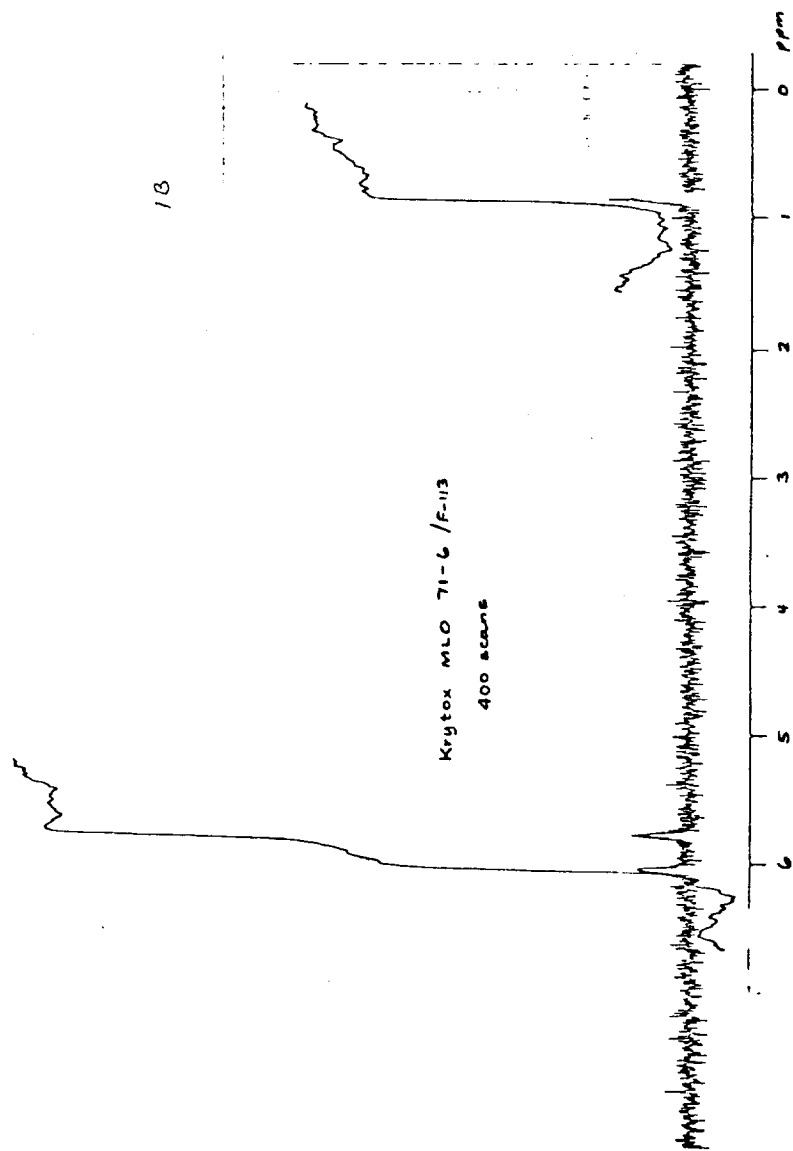
Figure 8: Proton NMR spectrum of Krytox MLO-71-6 fluid (as received)
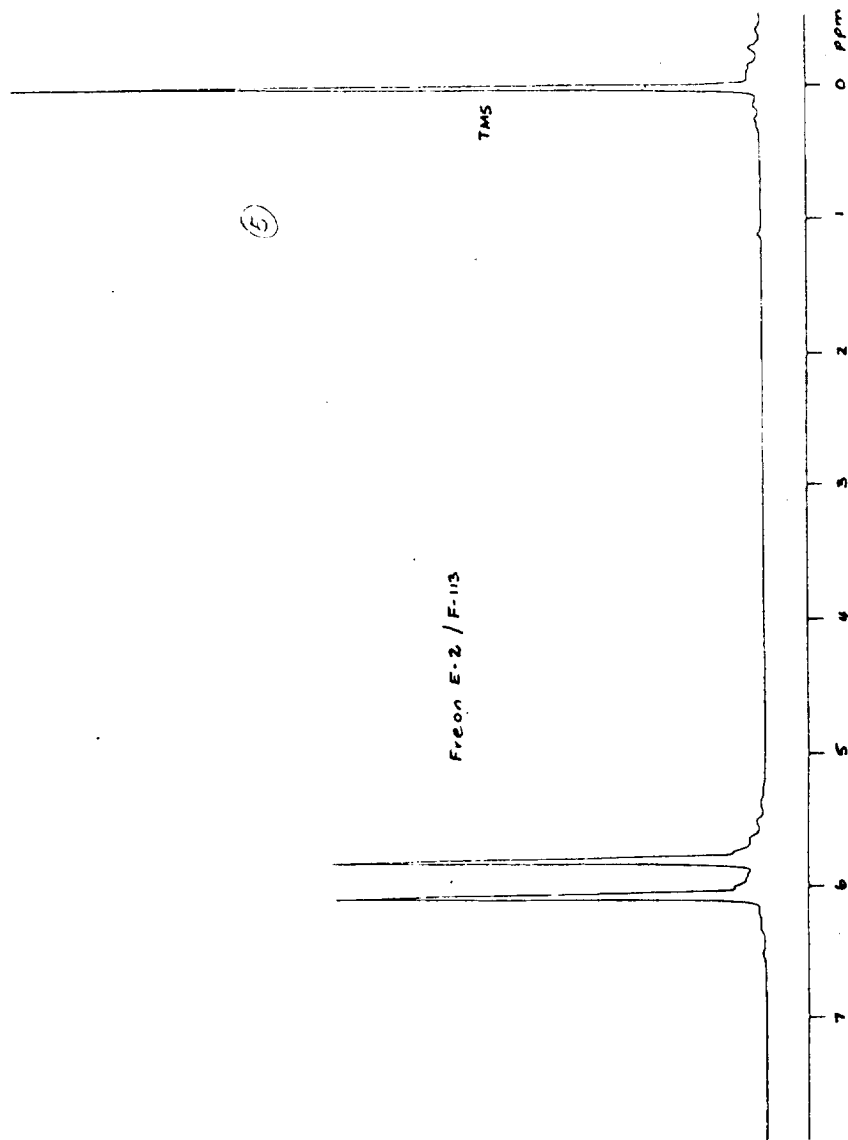
Figure 9: Proton NMR spectrum of Freon E-2, $C_3F_7OCF(CF_3)H$
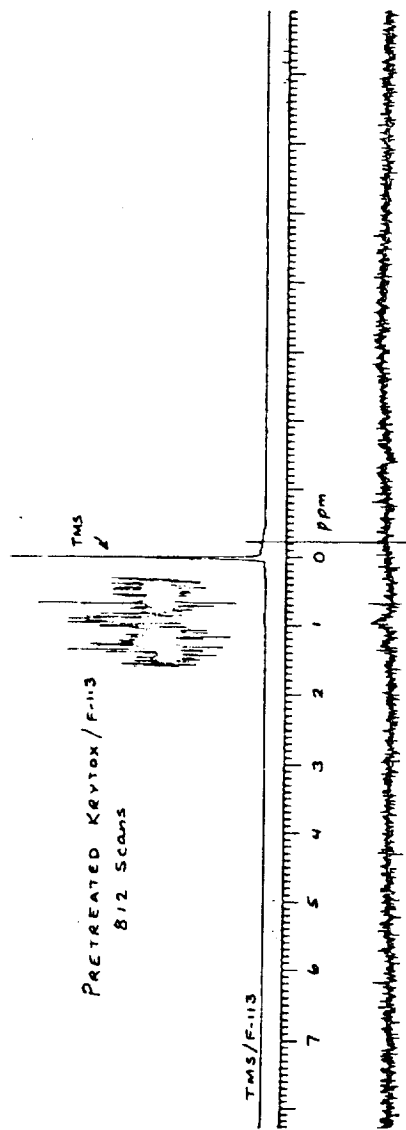
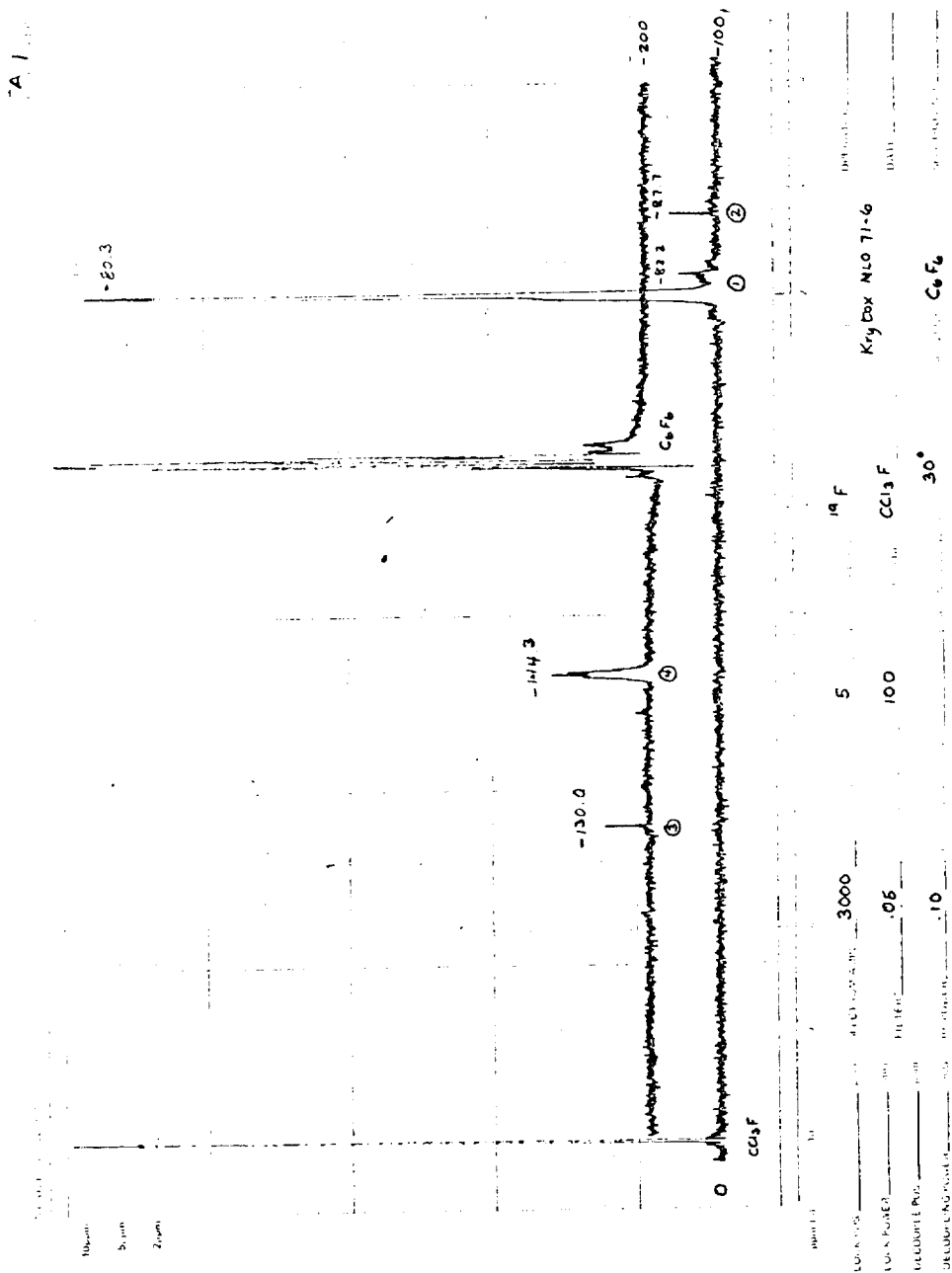Figure 10: Proton NMR spectrum of Krytox MLO-71-6 fluid (recovered
after Test 18/20)

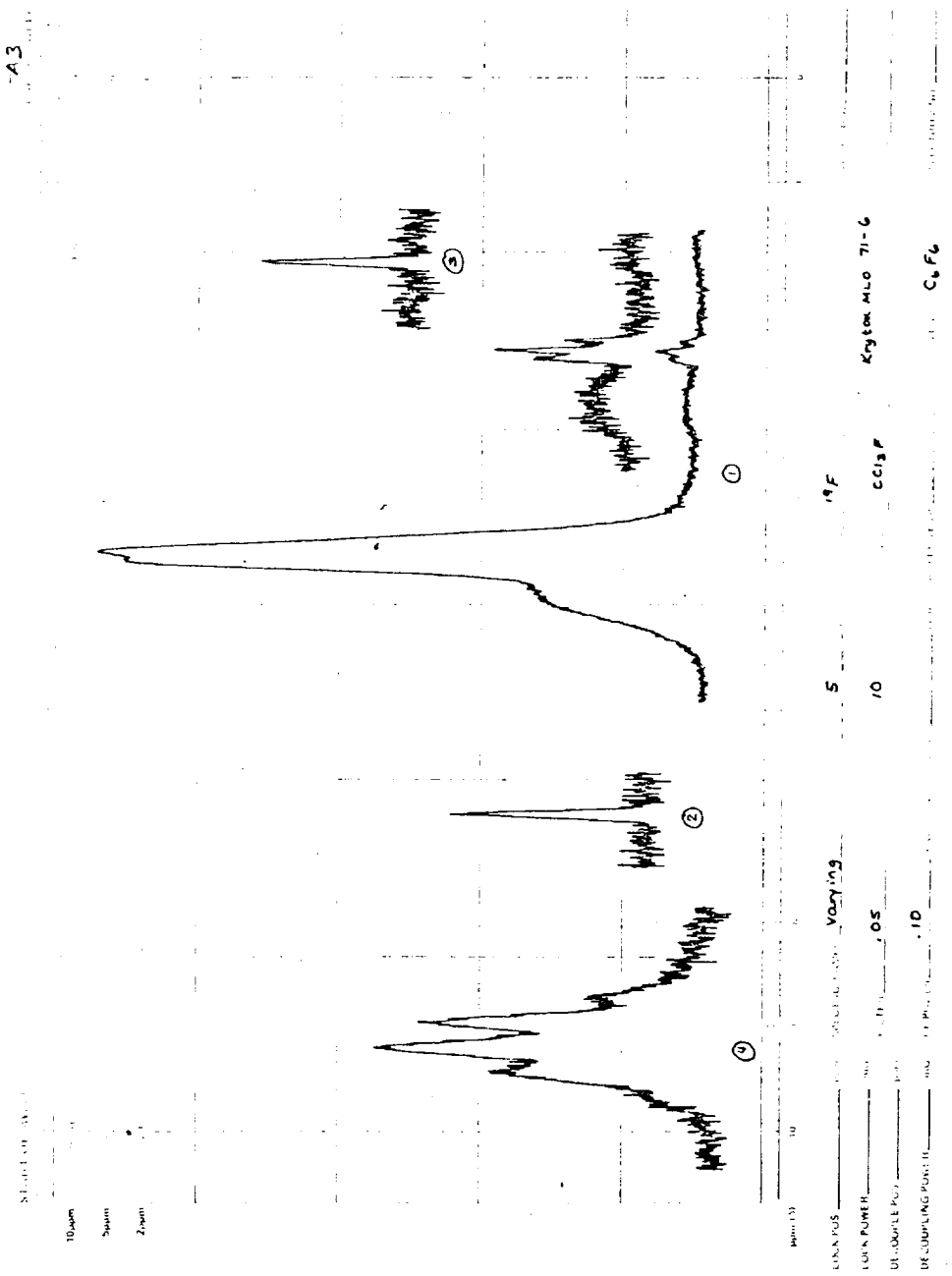Figure 11: ^{19}F NMR spectrum of Krytox MLO-71-6 fluid (as received)

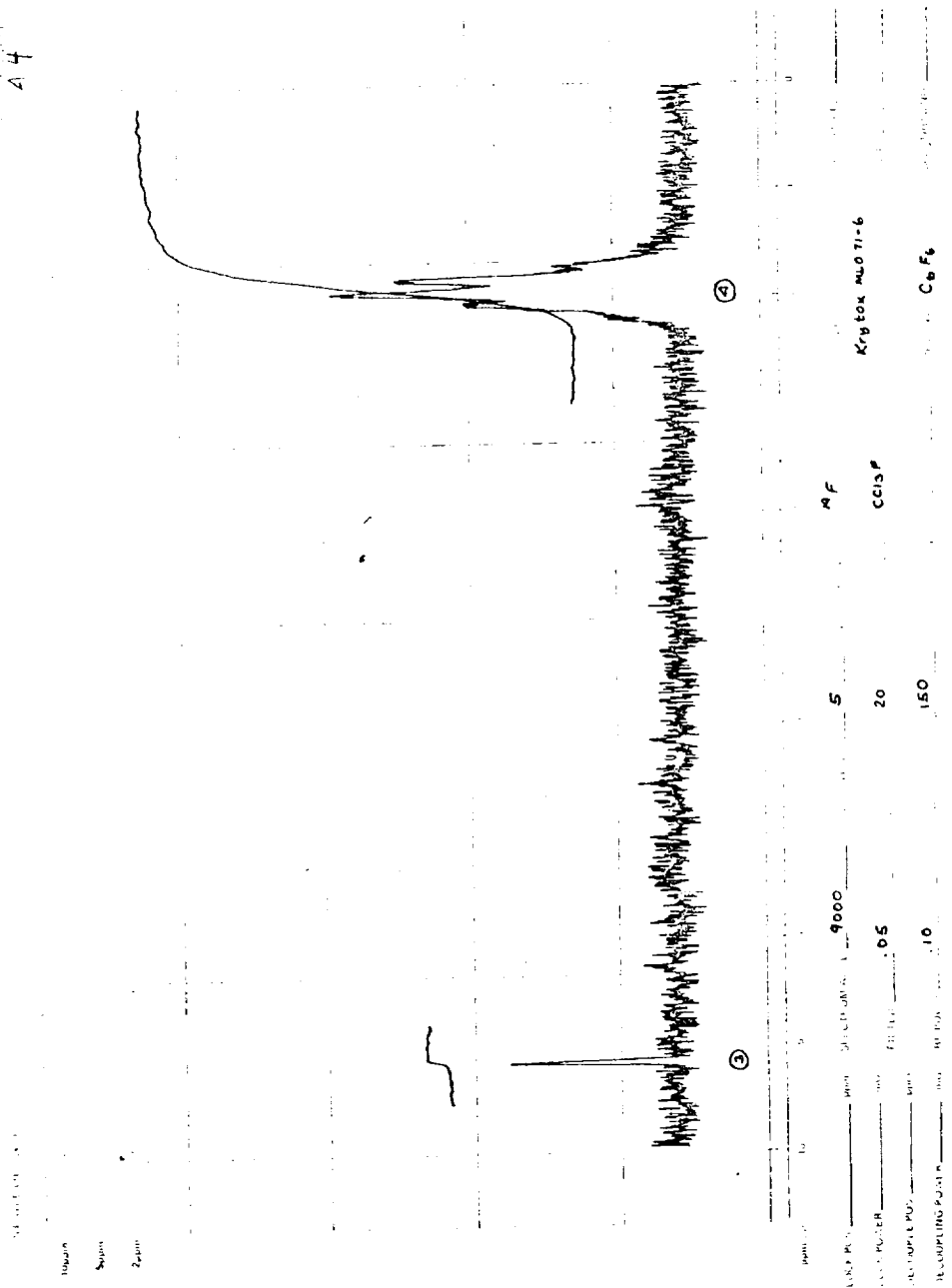Figure 12: ^{19}F NMR spectrum of Krytox MLO-71-6 fluid, expanded to 10 ppm sweep

Figure 13: Portion of ^{19}F NMR spectrum of Krytox MLO-71-6 fluid, expanded to 20 ppm
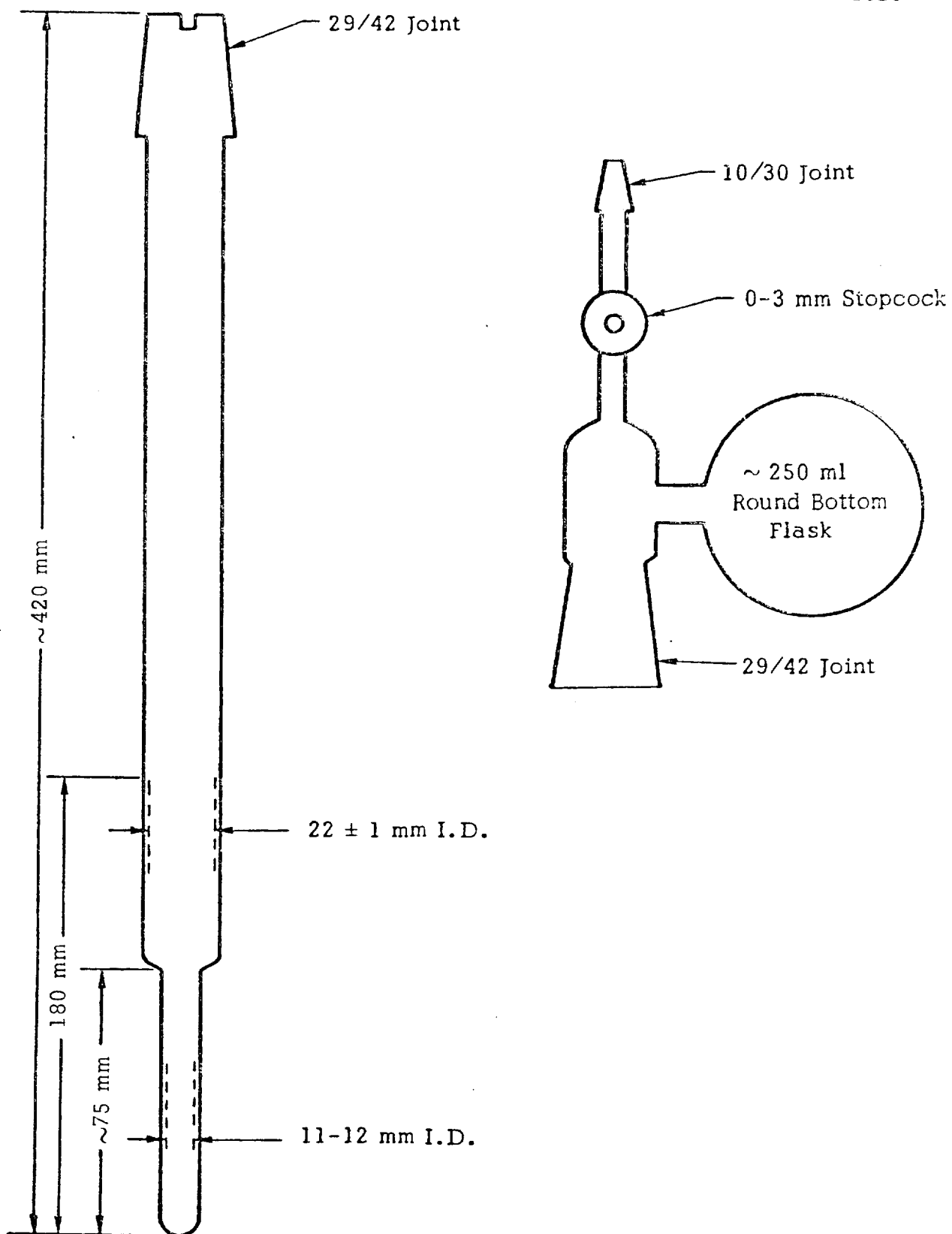
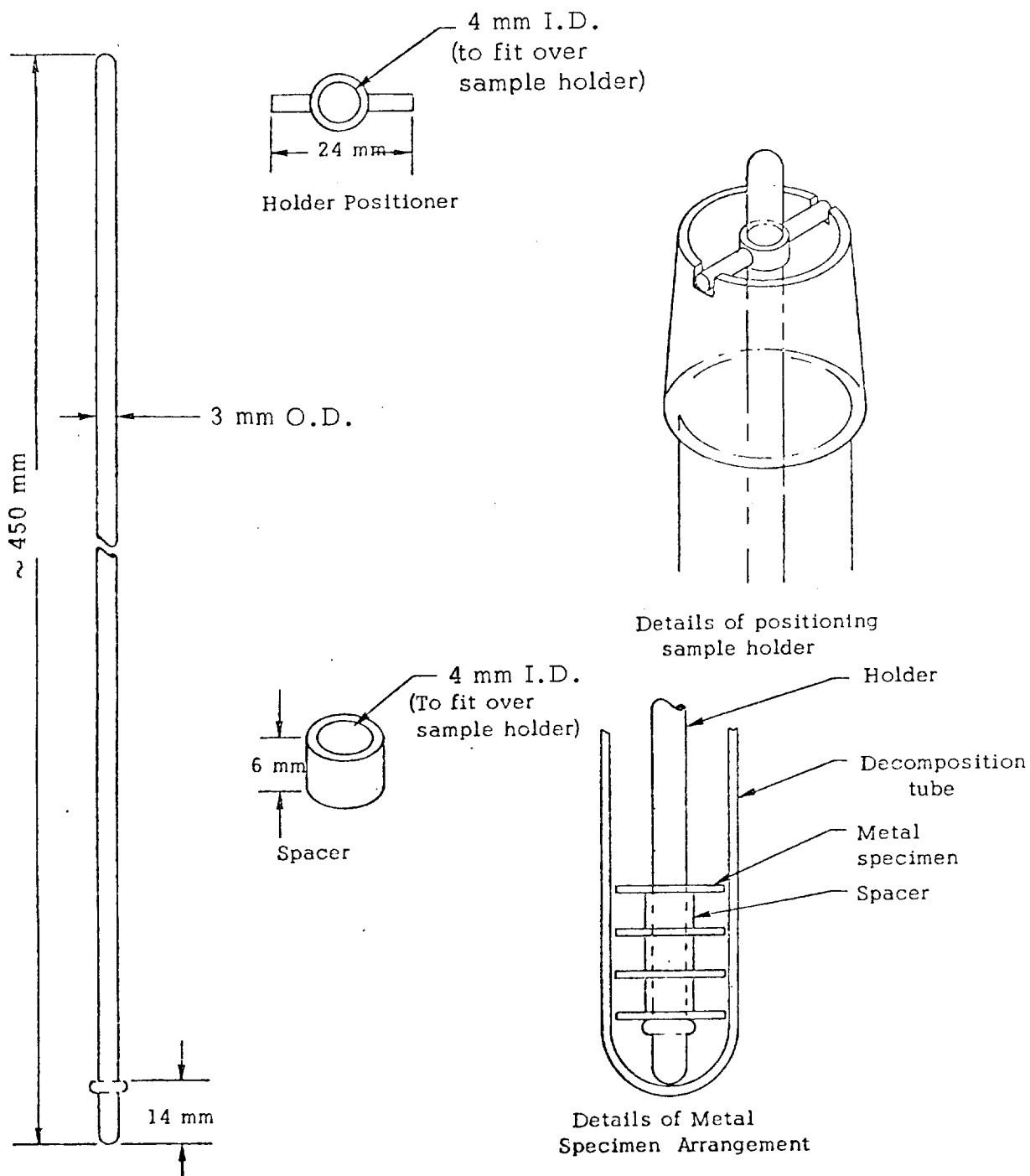Figure 14: Decomposition tube and adapter

4 mm I.D.
(to fit over
sample holder)

← 24 mm →

Holder Positioner

← 3 mm O.D.

~ 450 mm

Details of positioning
sample holder

4 mm I.D.
(To fit over
sample holder)

6 mm

Spacer

Holder

Decomposition
tube

Metal
specimen

Spacer
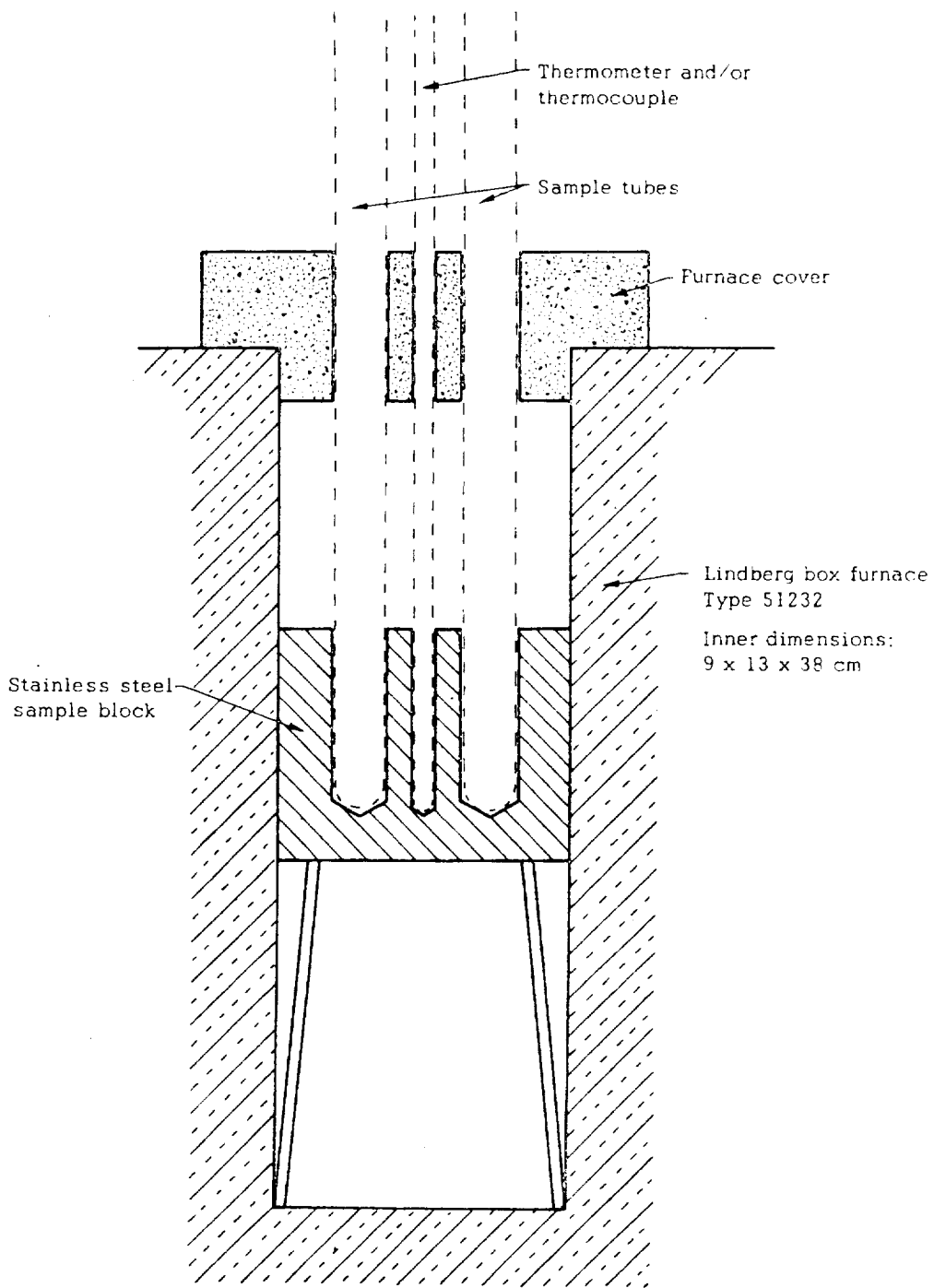
14 mm

Details of Metal
Specimen Arrangement

Figure 15: Metal specimen holder arrangement

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Figure 16: Box furnace arrangement

The figure labels include:

- Thermometer and/or thermocouple
- Sample tubes
- Furnace cover
- Lindberg box furnace Type 51232

  Inner dimensions: 9 x 13 x 38 cm
- Stainless steel sample block