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Final Report

MASTER

Synthesis of Volatile Uranium Compounds

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The research programs of our laboratory are extremely diverse. The synthesis of volatile uranium compounds and specifically $U(CF_3)_6$ is of such significance that we are devoting more effort to this project than to any other synthetic project.

Initial efforts in the uranium program were concentrated on tungsten, an element whose chemistry is recognized as similar to that of uranium. The reasons for this substitution were several: (1) compounds which might be desirable as starting materials were more readily available, for example WBr_6 and $W(CO)_6$, the uranium analogues of which could not be obtained; (2) the ^{19}F NMR spectra used to identify products in the postreaction mixture would be easier to interpret since tungsten does not possess a pseudocontact shift as does uranium. (There was also a possibility that ^{183}W-C-F coupling would occur and the satellites so produced in the NMR would identify the peak of interest.); and (3) $W(CH_3)_6$ had just been prepared and indications were that $W(CF_3)_6$ would be stable at or near room temperature.

Reactions of the C_2F_6 plasma with freshly sublimed WCl_6 and WBr_6 (see Figure 1), or with a tungsten mirror formed inside the reactor by thermal decomposition of $W(CO)_6$, each produced similar products. These products consisted of fluorocarbons from C to approximately C_{14}, a small amount of WF_6, the free halogen where appropriate, and a white volatile solid which stopped at -78°C in the plasma line. This solid was only slightly stable thermally, decomposing within hours at room temperature and turning blue immediately upon exposure to air. When allowed to decompose under vacuum, the white solid produced a gas which mass spectrometry indicated was fluorocarbons and WF_6. The characterization of this relatively unstable compound, believed to be $W(CF_3)_6$, is nearly complete.

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DISCLAIMER

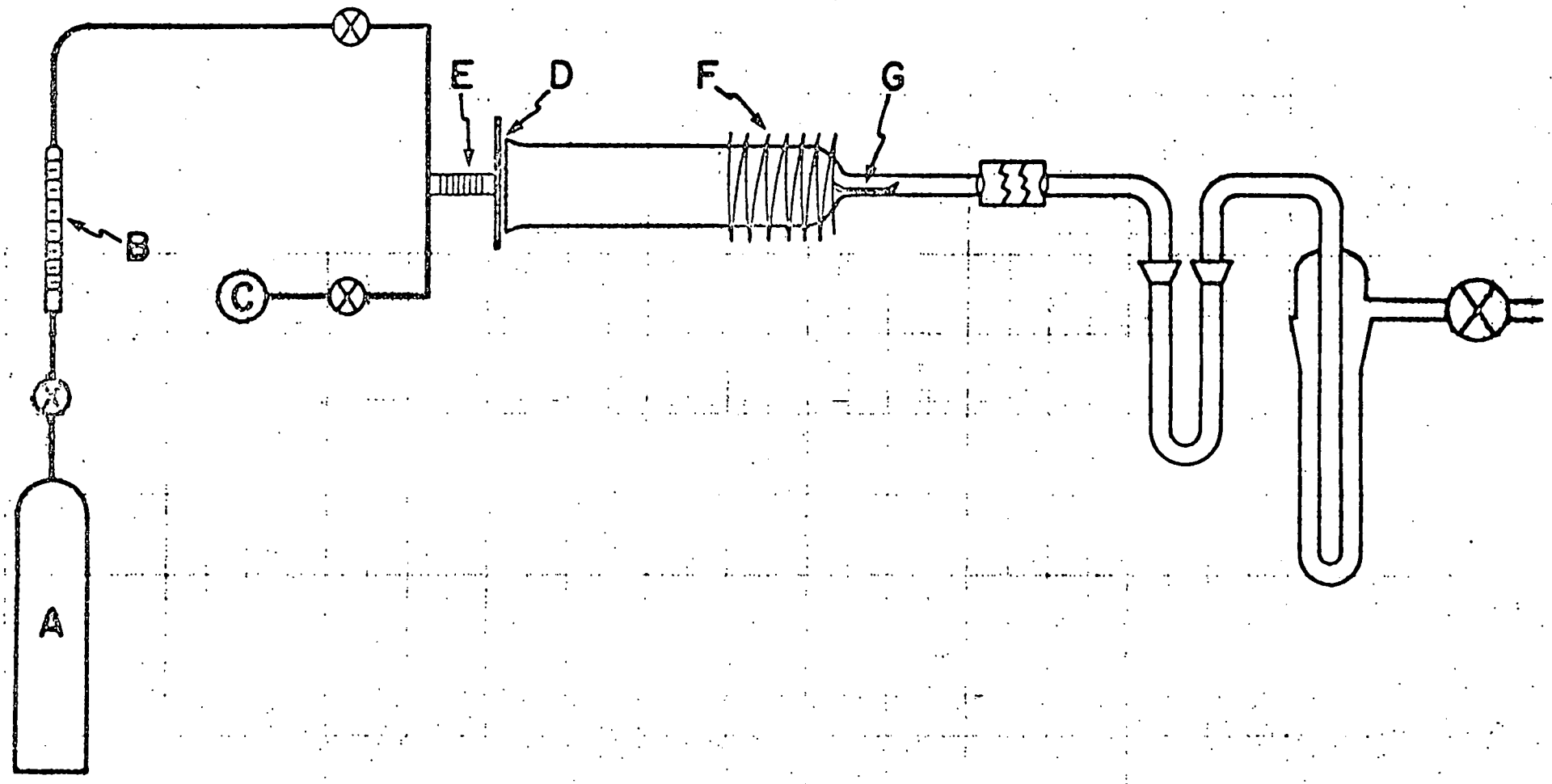


Figure 1. Diagram of plasma apparatus

Concurrent with the above investigations were several experiments using uranium halides as starting materials. Uranium tetraiodide and UBr_4 obtained from Atomergic Chemetals Co., Carle Place, Long Island, when reacted in the plasma produced only fluorocarbons and free halogen as volatile products. After combining the products from 25 forty-eight hour runs and cryogenically separating them into three fractions, no uranium containing compounds could be identified. This was not surprising, however, since $U(CF_3)_n X_{4-n}$ compounds were predicted to be thermally unstable. Due to its large pseudocontact shift, UF_6 would probably not be detected in our routine ^{19}F spectra which covered ±250 ppm from trifluoroacetic acid.

Uranium in the hexavalent state, particularly $U(CF_3)_6$, was calculated to be more stable than the analogous tetravalent compound. Halogenated starting materials such as UCl_6, UBr_6 or UI_6, however, are not commercially available; and, indeed, the latter two compounds have not yet been prepared. In order to synthesize UCl_6 for our work, stoichiometric quantities of UF_6 and BCl_3 were condensed in an evacuated bulb held at -196°C [Ref. Inorg. Chem. 5 #8 (1966) 1438]. The temperature of the bulb was raised slowly to room temperature. The metathetical reaction, $UF_6 + 2BCl_3 \rightarrow UCl_6 + 2BF_3$, occurred causing the bulb to be filled with a green-black solid. After remaining at room temperature for 30 minutes, all volatiles were pumped off. The bulb which contained the UCl_6 was opened and maintained in an inert atmosphere. One gram of the solid was placed in a boat and reacted in the C_2F_6 plasma.

Prior to the reaction of UCl_6, an attempt was made to optimize plasma and instrument conditions using HgI_2 as the reactant. The maximum rate of production of $Hg(CF_3)_2$ was taken as an indication of optimum instrumental parameters. For the reaction of UCl_6, therefore, the following conditions were used.

C_2F_6 reactor pressure - 3 to 5 torr

Tank capacitor setting - $18^{\frac{26}{}}$

Plate voltage	-	400 volts
Plate current	-	40 ma
Grid current	-	25 ma

The reaction was allowed to proceed for approximately 48 hours, at which time the traps on the plasma line were emptied by condensing the contents into previously evacuated take-off tubes. The products from each 48-hour run were cryogenically separated in vacuo (10^{-4} torr) into two fractions. That material which passed a trap held at -126°C was discarded. The material which stopped at -126°C was saved and combined with the same fraction from other 48-hour runs. When a considerable amount of material was collected at -126°C, this fraction was further separated into four fractions: that which stopped at -10°C; that which passed -10°C but stopped at -78°C; that which passed -78°C but stopped at -95°C; and that which passed -95°C. Material from each of these fractions was condensed into a separate evacuated bulb and gamma-counted for 20 minutes each using a NaI crystal and a multichannel analyzer. A ^{19}F NMR spectrum was also taken of each fraction. Interpretation of these spectra suggested the possibility of U-CF_3 bonds, as did the volatility of the fractions (-78°C and -95°C) having higher than background counts. In all, 40 forty-eight hour reaction runs were made.

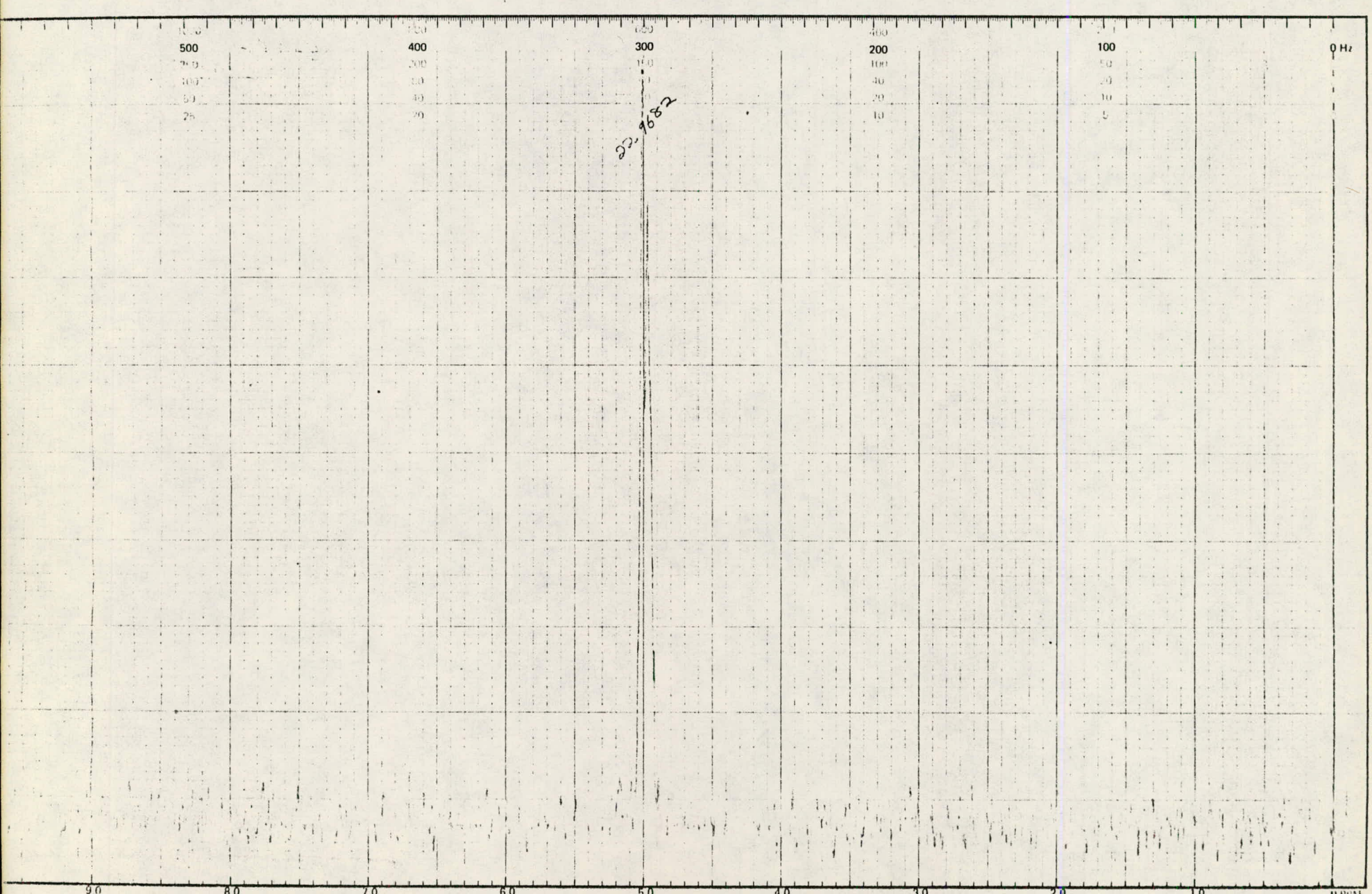
Current Project Status

Further isolation and identification of all uranium-containing products which resulted from UCl_6 in the plasma reactor will be pursued. Instead of a NaI detector, a Ge(Li) drifted detector will be employed to screen fractions for uranium; and samples are being counted in their liquid, rather than gaseous, state. This arrangement will increase sensitivity to any uranium present and shorten necessary reaction times. Further careful cryogenic separation using a low-temperature still will be carried out on those fractions having uranium in them. Various temperature cuts are being checked for uranium and discarded if none is found. By continually concentrating the

uranium-containing fractions in this manner, it should be possible to obtain a pure compound and to obtain further physical data.

Experience has shown that optimal plasma conditions (pressure, Rf generator parameters) for one metal halide reactant are not necessarily the same for each metal halide. Investigations should therefore be carried out with UCl_6 in which the parameters listed earlier are systematically varied. Once a convenient and sensitive assay for uranium in the products has been established, only a short time will be required for this optimization procedure.

The design and construction of a new reactor which allows greater exposure (increased surface area) of UCl_6 to the plasma is also underway. We believe that a tiered arrangement using Teflon s lves will serve the purpose.



SPECTRUM NO. H-17

NUC. & FREQ.

MHz

SAMPLE

TEMP.

SOLVENT

CONC.

REFERENCE

SWEEP WIDTH

SWEEP TIME

TIME CONST.

SHIFT

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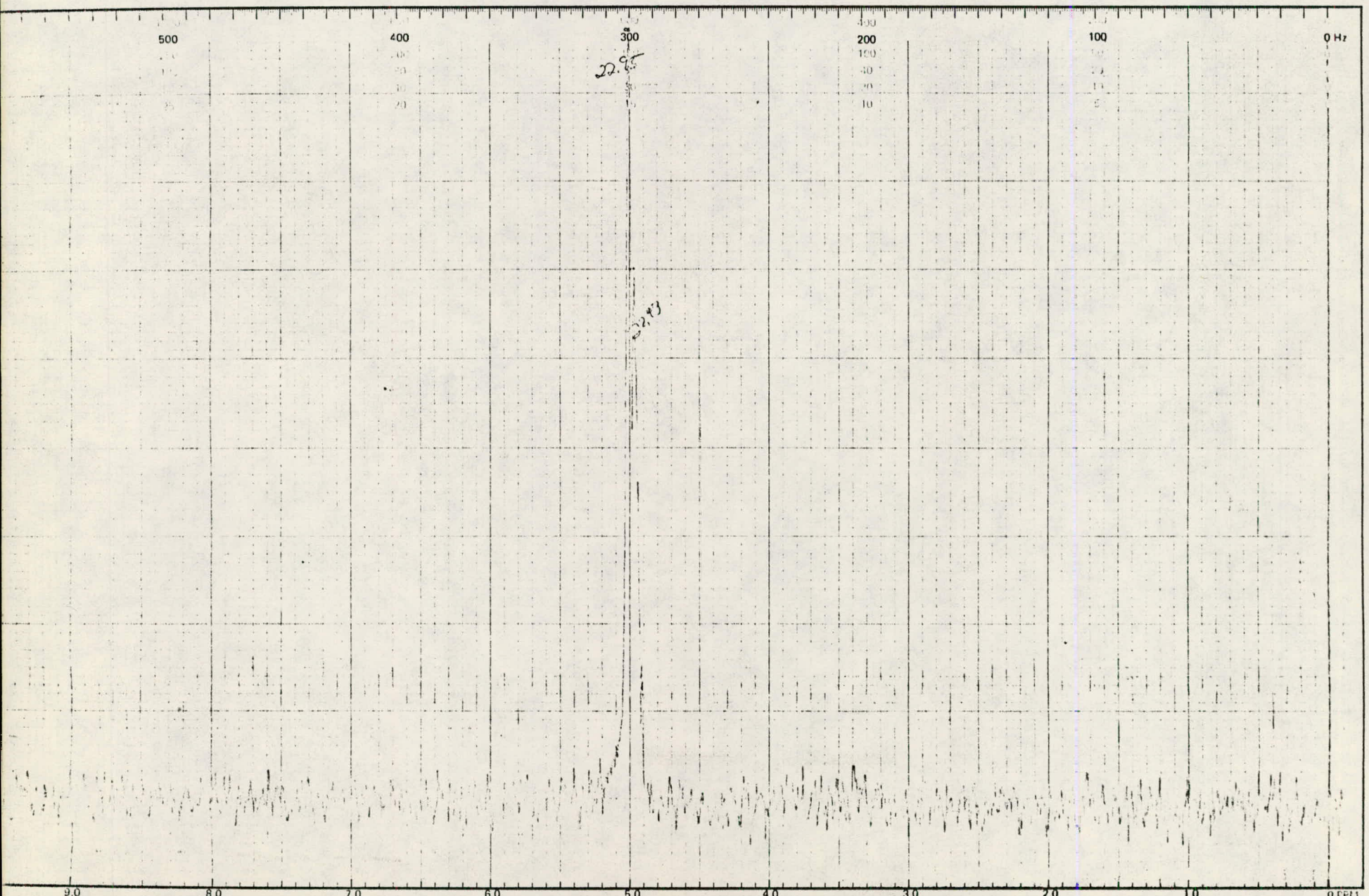
SENSITIVITY
NOR
INT

DATE

OPERATOR

REMARKS

TPE-60 (WSPE-60


500
400
300
200
100
0 Hz
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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0 PPM
SPECTRUM NO.
NUC & FREQ
MHz
SAMPLE:
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REMARKS
TPE-60 (WCPE 60)
THOMPSON PACKARD

SPECTRUM NO.

DATE 1/2/73

SAMPLE

[illegible] 75

[illegible] - aptam

SOURCE [illegible]

STRUCTURE [illegible]

[illegible]

Run 301 (50) VI4

PATH mm

SOLVENT

CONCENTRATION

PHASE

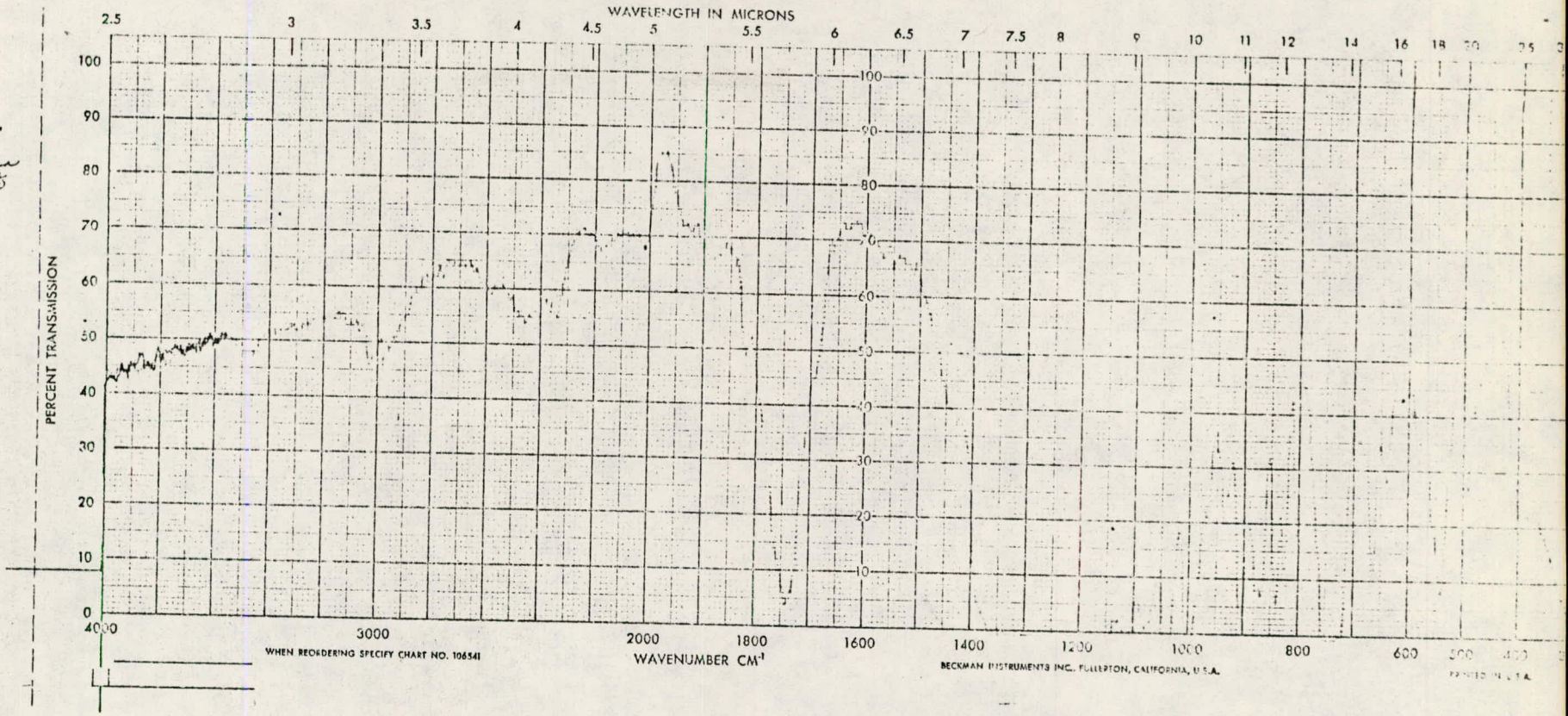
COMMENTS

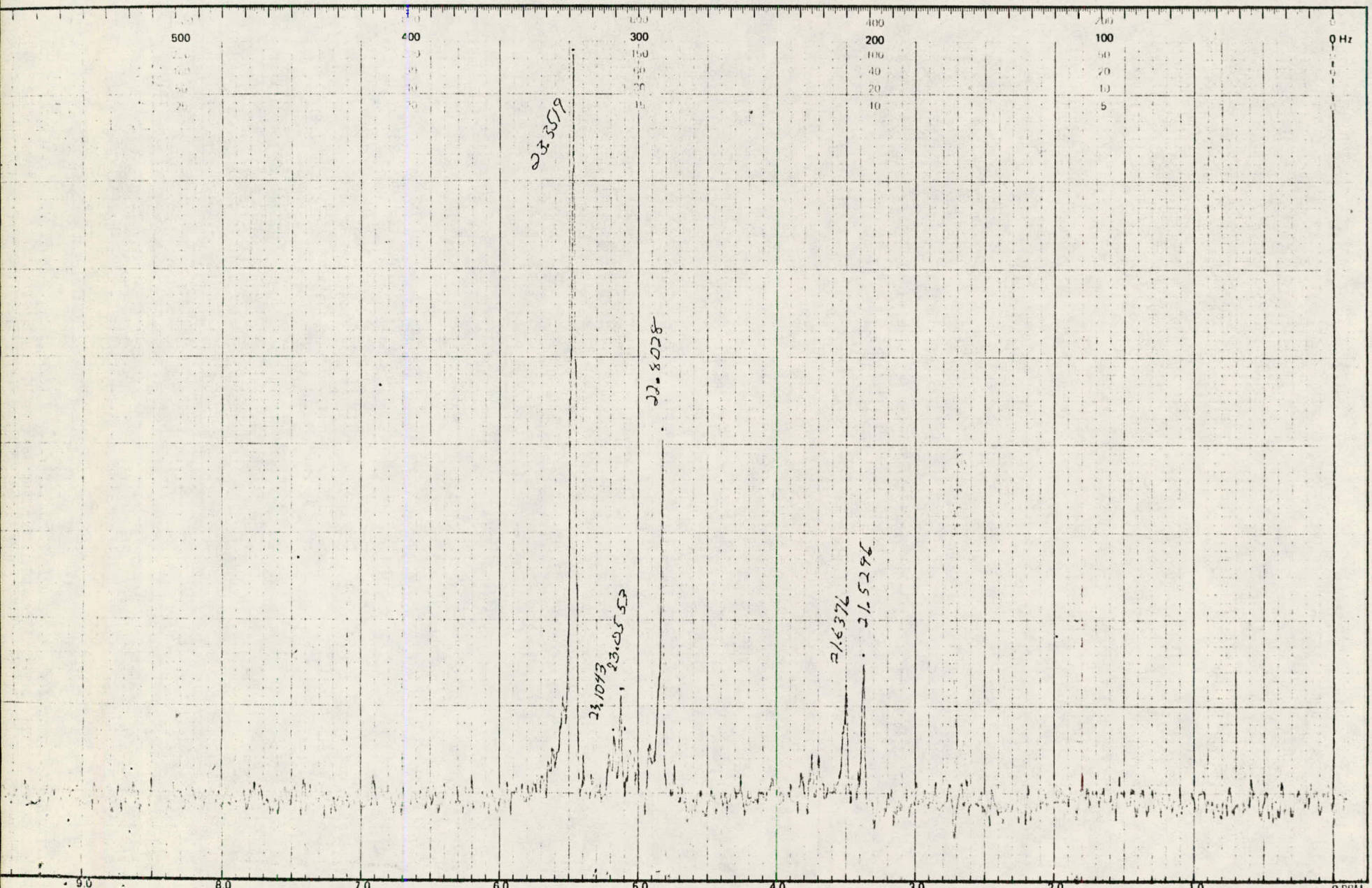
ANALYST

Beckman®

INFRARED

SPECTROPHOTOMETER





SPECTRUM NO 434

NUC & FREQ FLUORINE MHz

SAMPLE UI_4 soln. Paramagnetic Stopped - Run 3 UI_4

TEMP 35°C

SOLVENT

CONC

REFERENCE FI_3

SWEEP WIDTH

SWEEP TIME 200 SEC

TIME CONST .1 SEC

SHIFT

HI LEVEL

SENSITIVITY NOR INT 63

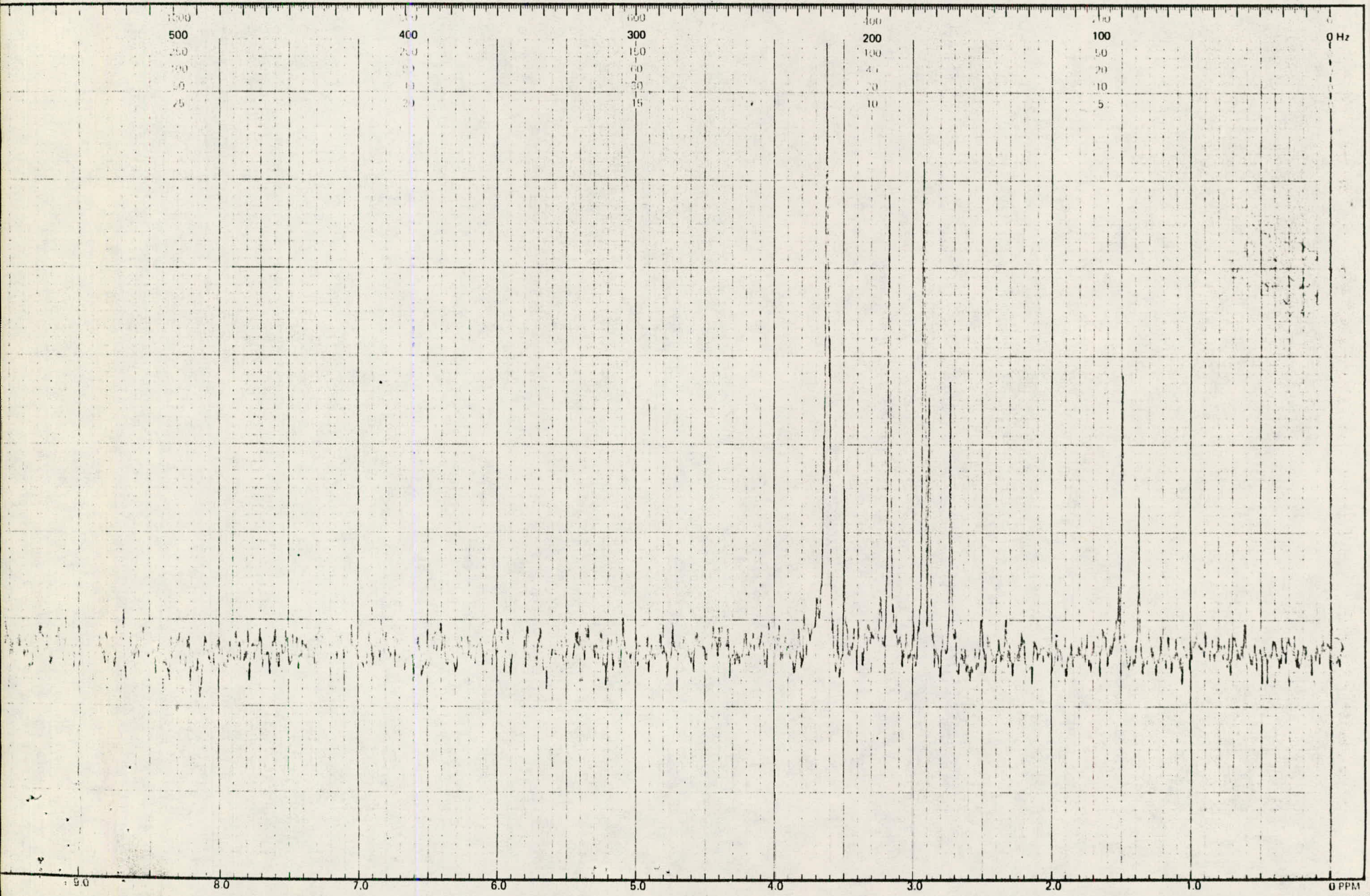
DATE 1/2/75

OPERATOR CH

REMARKS

TPE-60 (WCPE-60)

60 NOTCH ROAD, LITTLE FALLS, NEW JERSEY 07424
(201) 777-3115
THOMPSON PACKARD



SPECTRUM NO. #37

NUC & FREQ: FLOURINE MHz

SAMPLE: Run 301-5 UI_4 fances -45 stopper -78

TEMP

SOLVENT

CONC

REFERENCE

SWEEP WIDTH: 5K PPM

SWEEP TIME: 200 SEC

TIME CONST: .1 SEC

SHIFT: 1531

HI LEVEL

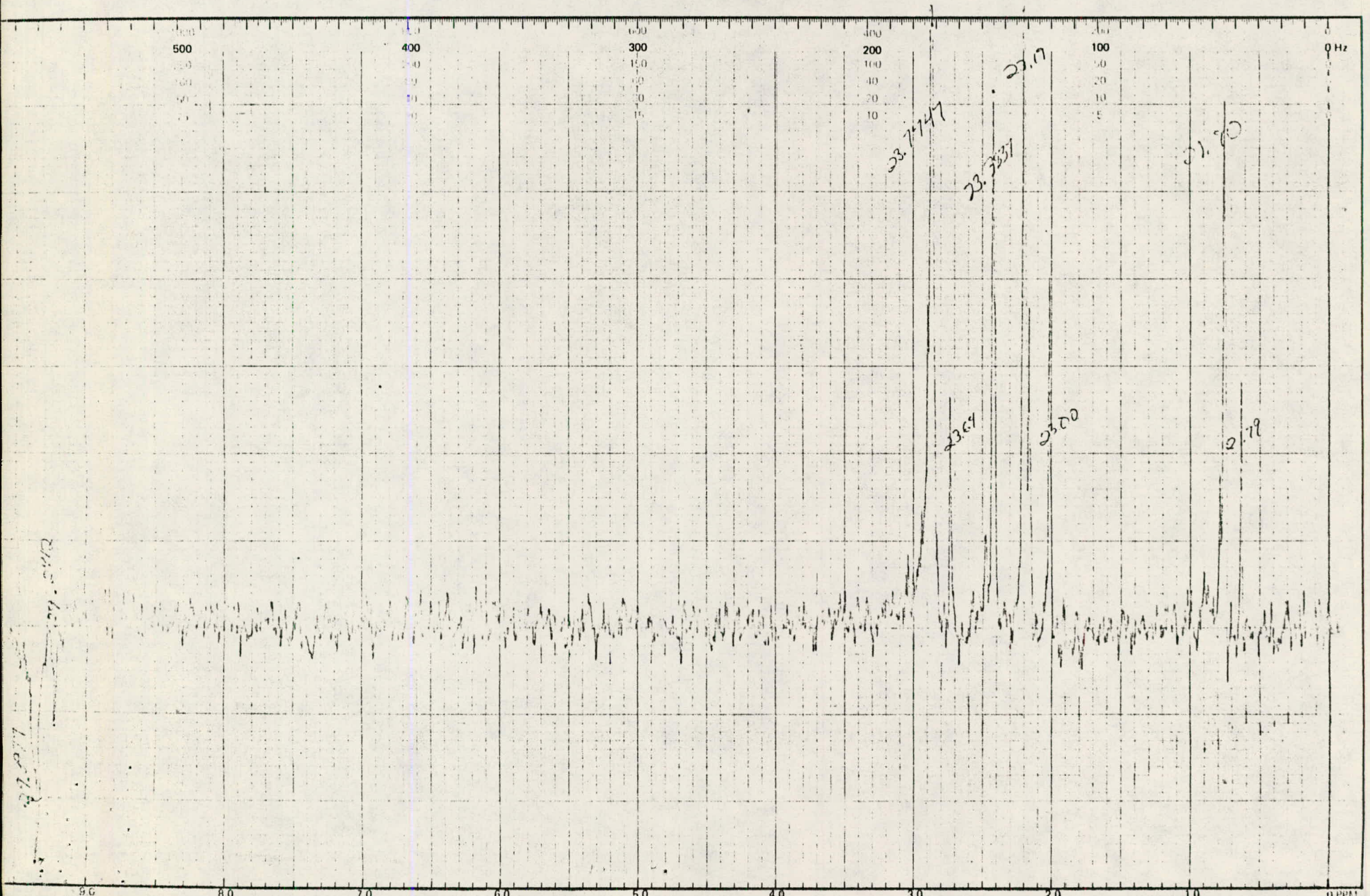
SENSITIVITY NOR INT 500

DATE: 7/8/75

OPERATOR: LM

REMARKS: not worked on

TPE 60 (WCPE 60)



SPECTRUM NO

NUC & FREQ

MHz

SAMPLE

TEMP

SOLVENT

CONC

REFERENCE

SWEEP WIDTH

SWEEP TIME

SEC

TIME CONST

.1 SEC

SHIFT

HI LEVEL

SENSITIVITY

NOR

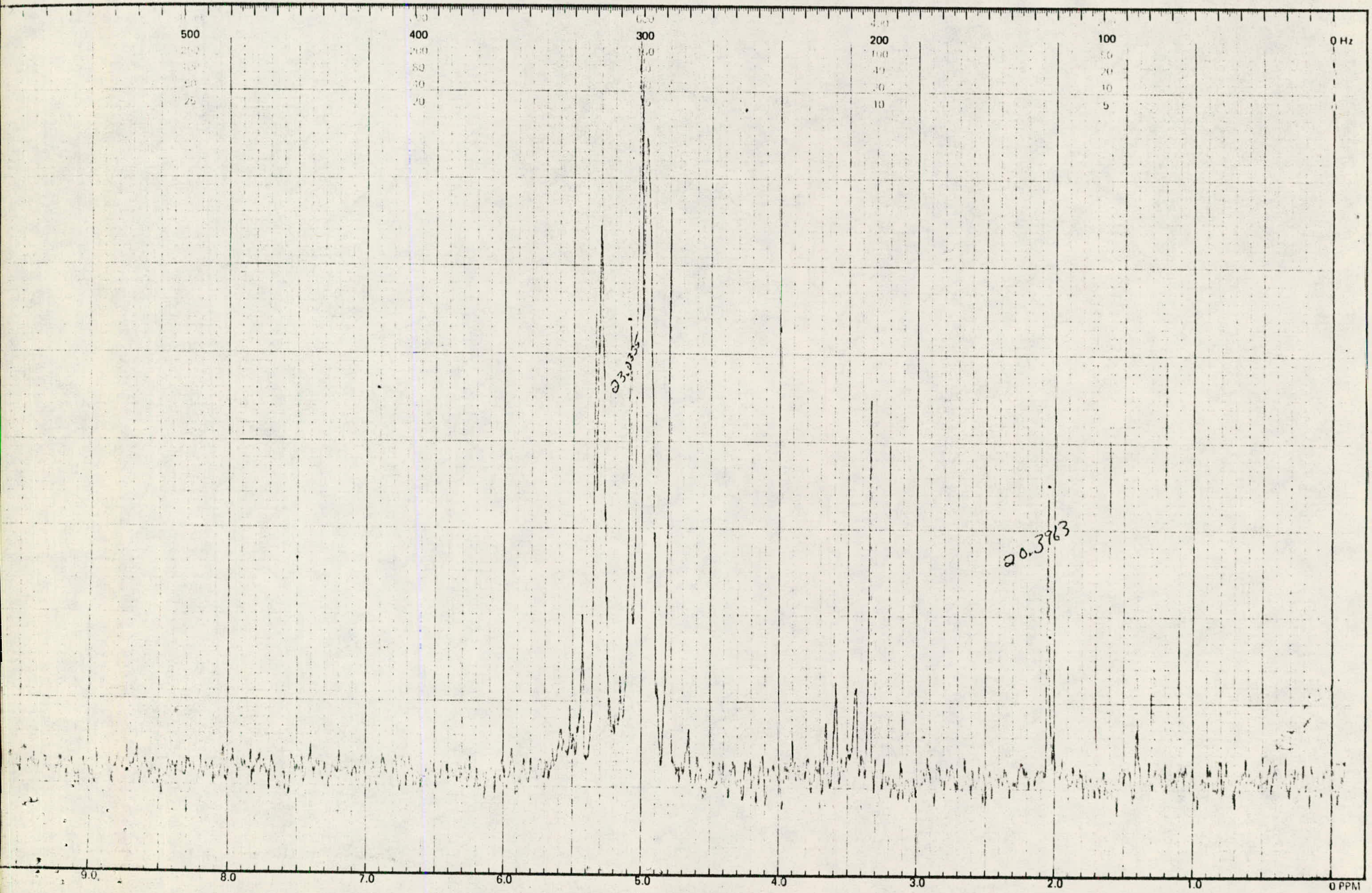
INT. 400

DATE

OPERATOR

REMARKS

TPE-60 (WCPE-60)



SPECTRUM
No. 1

NUC. & FREQ.
Fluorine
MHz

SAMPLE
UF_4

TEMP

SOLVENT

CONC

REFERENCE

SWEEP WIDTH

SWEEP TIME

TIME CONST.

SHIFT

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SENSITIVITY
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DATE

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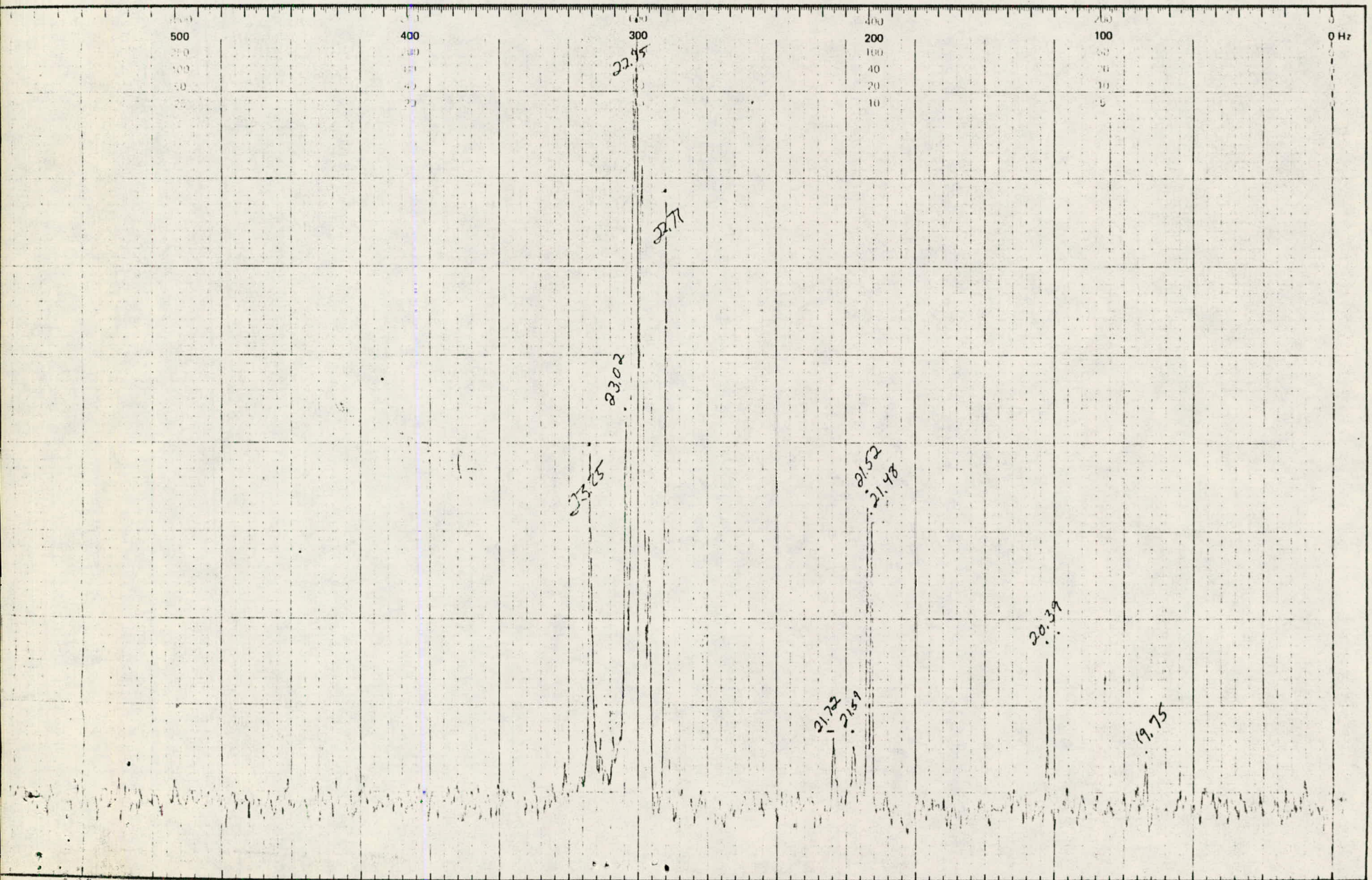
REMARKS

TPE-60 (W. PE 60



SPECTRUM NO

NUC & FREQ. MHz

SAMPLE

TEMP

SOLVENT

CONC

REFERENCE

SWEEP WIDTH

SWEEP TIME SEC

TIME CONST SEC

SHIFT

HI LEVEL

SENSITIVITY
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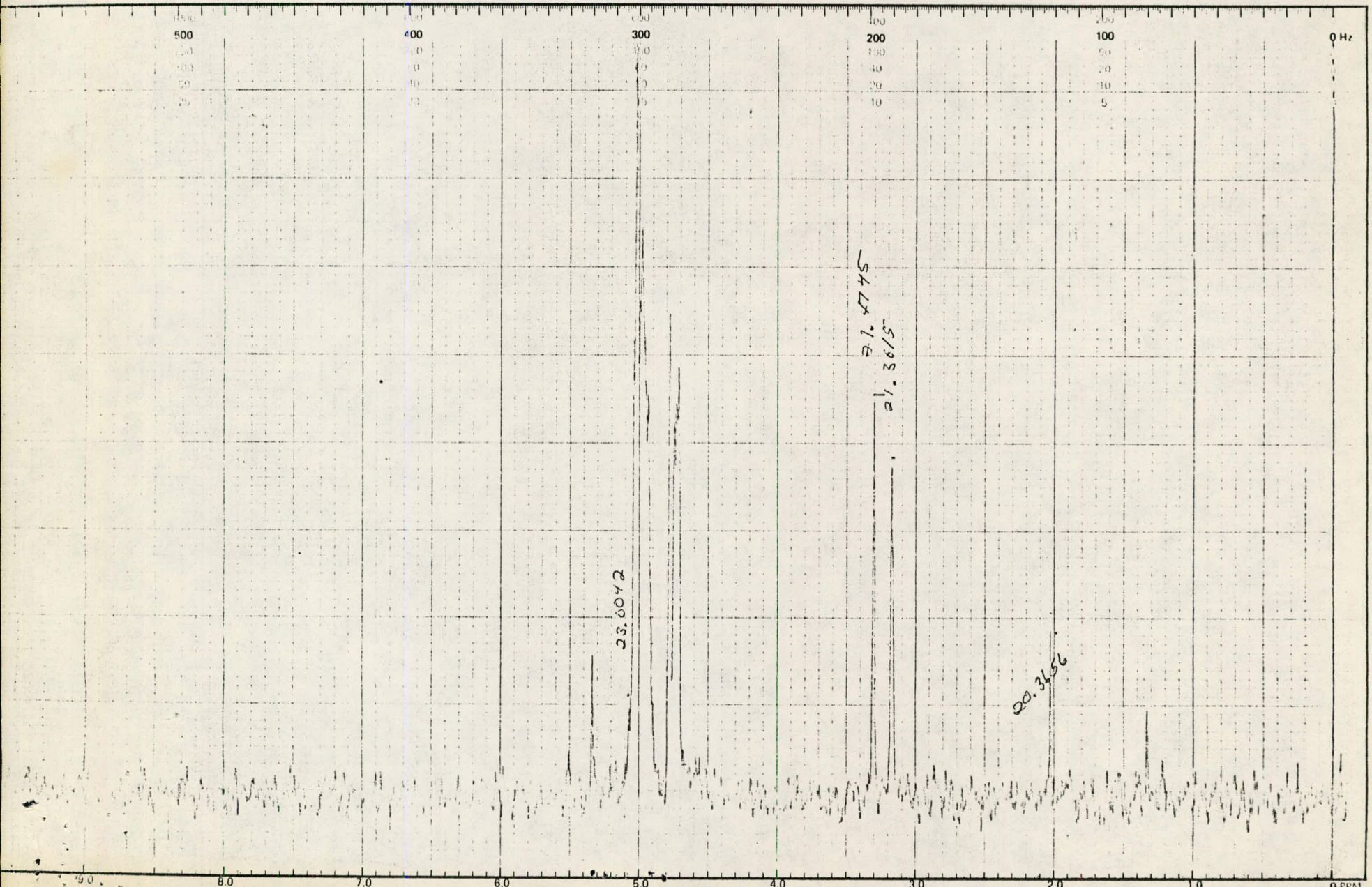
INT

DATE

OPERATOR

REMARKS

TPE-60 (WCPE-60)



SPECTRUM NO #44

NUC & FREQ
FLOURINE
MHz

SAMPLE
N/B UF_4
STDS-IDI
PASSES-75

TEMP
35 C

SOLVENT

CONC

REFERENCE
TMS

SWEEP WIDTH

SWEEP TIME
SEC

TIME CONST.
SEC

SHIFT

HI LEVEL

SENSITIVITY
NOR
INT

DATE
7/19/75

OPERATOR

REMARKS

TPE-60 (WCPE-60)

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