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INFRARED SPECTROSCOPIC OBSERVATIONS ON THE FATE OF ORGANOPHOSPHORUS COMPOUNDS EXPOSED TO ATMOSPHERIC MOISTURE

PART I. G-AGENTS AND RELATED COMPOUNDS

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RESEARCH AND TECHNOLOGY DIRECTORATE

JULY 2003

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13. ABSTRACT *(Maximum 200 words)*

This report is part one of a three part series dedicated to observing the degradation of organophosphorus compound exposure to atmospheric moisture as a function of time. The investigation begins with G-type agents, precursors and related impurities from the synthetic process. Experimental observation of chemical degradation is interpreted from the measured infrared over the 4000 to 400 wavenumber region. Infrared band assignments are reported and newly formed compounds are identified. The final fate of the compound from starting material is reported. Infrared stack plots are provided illustrating the chemical changes as a function of time.

14. SUBJECT TERMS

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PREFACE

The work described in this report was authorized under Project No. 3RDC11, Treaty Verification. This work is based on infrared spectroscopic data obtained from 1979 through 1992.

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Special thanks are due James Bouck for his expertise in handling very toxic materials and for his many years of experience in the infrared spectroscopic identification of such materials.

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INFRARED SPECTROSCOPIC OBSERVATIONS ON THE FATE OF ORGANOPHOSPHORUS COMPOUNDS EXPOSED TO ATMOSPHERIC MOISTURE
PART I. G-AGENTS AND RELATED COMPOUNDS

1. INTRODUCTION

Many infrared spectra have been collected over the years pertaining to chemical agents and related compounds (precursors and impurities). After initial spectra were obtained for many of these compounds the original pure material was allowed to remain between salt windows and repeated scans made with time as the material sar (in a fume hood) exposed to the atmospheric moisture. This report will present and discuss the spectra obtained for many organophosphorus compounds as they sat exposed to atmospheric moisture. These spectra should be of interest to the Chemical Weapons (CW) treaty verification program as many of the studied compounds comprise Schedules 1, 2, and 3 materials of the Chemical Weapons Convention. This data should be of value as part of the verification regime that includes on-site inspection of declared chemical warfare related facilities. Infrared analysis of bulk (near) hazardous material is rapid and efficient and offers minimal sample preparation.

2. EXPERIMENTATION

2.1 Instrumentation

All the spectra included in this report were determined on either a Nicolet Model 10 DX (Nicolet Analytical Instruments, Madison, WI) or on a Perkin-Elmer Model 1750 (Perkin-Elmer Corporation, Norwalk, CT) Fourier Transform spectrometer. The spectra were saved on individual magnetic floppy disks that were resident to the particular instrument used. The spectra were also transferred to a Zenith PC via a Sprouse Scientific Micro-Trace program (Sprouse Scientific Systems, Incorporated, Paoli, PA) for inclusion into a central search system. Hard copies of the spectra were plotted on a Hewlett-Packard Model 7475A plotter (Hewlett-Packard, Palo, Alto, CA). Some Spectra were also plotted utilizing Nicolet Omnic® FT-IR software and Epson *Stylus*® color printer (Epson America, Inc.). The instruments were purged with the boil off from a liquid nitrogen cryogenic container. The sample compartments of the instruments were placed inside fume hoods as a safety precaution.

2.2 Sample Handling

Liquid samples were determined as capillary films (neat) between 25 mm diameter X 4 mm thick KBr or CsI discs at a resolution of 2 cm^{-1}. After an initial spectrum was obtained, the sample film/salt window sandwich was allowed to sit in the hood air for a period of time, then returned to the sample compartment of the instrument and a spectrum determined. The sample film was returned to the hood air and allowed to sit until the sample was completely hydrolyzed as evidence by no further changes occurring in the infrared spectrum.

Solid samples were run as either KBr pellets or directly as solids between KBr or CsI windows (disc). Potassium bromide pellets were prepared using infrared grade KBr (Harshaw Chemical Company, Cleveland, OH). The sample KBr matrix was ground in a stainless steal vial with a Wig-L-Bug amalgamator (Crescent Dental Manufacturing Company, Chicago, IL). Some of the solid samples were determined directly (no KBr matrix) by placing a small amount of solid (1 mg or less) between two polished salt discs. The solid was ground by moving the salt discs across one another with a back and forth motion, alternating with a figure-eight motion. This grinding lasted about 20 seconds. An IR spectrum was then determined to see if the grinding was sufficient to produce an acceptable spectrum, one essentially free of distorted band shapes. The spectra thus produced by this second method were smoothed, flattened and ordinate expanded as needed.

Vapor phase spectra were determined at a resolution of 1 cm^{-1}, in a 10 cm glass body gas cell having two stopcocks, one of which was fitted with a rubber sleeve septum, for injection of liquid samples. The cell was equipped with demountable KBr windows. A Teflon body gas cell equipped with CdTe windows was also used to determine vapor phase spectra. Initial vapor phase spectra were determined in an evacuated cell first, then air was admitted by momentarily opening one stopcock. Scans were then repeated, over a period of time, for the vapor samples now containing air. The procedure followed for vapor sample was similar to that used for liquid samples as discussed above.

2.3 List of Compounds (The CAS number is given in the [ ])

All the following compounds were used as received, with no further purification.

GA Tabun, ethyl N,N-dimethylphosphoramidocyanidate	[77-81-6]	**Figs. 21, 22**
GA PYRO, bis(ethyl N,N-dimethylphosphoramidic) anhydride, *sym*-Bis(dimethylamido)-diethyl pyrophosphate		**Figs. 23, 24**
GB, Sarin, isopropyl methylphosphonofluoridate	[107-44-8]	**Figs. 1, 2**
GD, Soman, pinacolyl methylphosphonofluoridate [96-64-0], stabilized with DICDI (1,3-diisopropylcarbodiimide)	[693-13-0]	**Figs. 3, 4**
GF, cyclohexyl methylphosphonofluoridate	[329-99-7]	**Figs. 5, 6-9**
EA 1356, 2-methylcyclohexyl methylphosphonofluoridate	[85473-32-1]	**Figs. 10, 11**
EA 1232, methyl methylphosphonofluoridate	[353-88-8]	**Figs. 12, 13**
n-Butyl isopropylphosphonofluoridate		**Figs. 14, 15**
Ethyl vinylphosphonofluoridate		**Figs. 16, 17A-B**
Trimethylsilyl N,N-dimethylphosphoramidofluoridate		**Fig. 25A-B**
Trimethylsilyl methylphosphonocyanidate		**Figs. 18, 19**
Ethyl dichlorophosphate (ethyl phosphorodichloridate)	[1498-51-7]	**Figs. 72, 73**
Fluoro Acid, methylphosphonofluoridic acid	[1511-67-7]	**Figs. 53, 55**
Sodium salt of GA acid; ethyl N,N-dimethylamidophosphoric acid, sodium salt		**Fig. 79**
IMPA, GB Acid, isopropyl methylphosphonic acid	[5514-35-2]	**Fig. 46**
PMPA, GD Acid, pinacolyl methylphosphonic acid	[616-52-4]	**Fig. 60**
CMPA, GF Acid, cyclohexyl methylphosphonic acid	[1932-60-1]	**Fig. 59**
EA 1356 Acid, 2-methylcyclohexyl methylphosphonic avid		**Fig. 63**
MPA, methylphosphonic acid	[993-13-5]	**Figs. 20 & 54 (wet); 47, 48**
Methylphosphonic anhydride		**Figs. 49, 50**

NAIMP, sodium isopropyl methylphosphonate (isopropyl methylphosphonic acid, sodium salt)		**Fig. 66**
NA$_2$MP, disodium methylphosphonate (methylphosphonic acid, disodium salt)		**Fig. 65**
NAMPA, methylphosphonic acid monosodium salt		**Fig. 64**
NA$_2$PYRO, disodium dimethylpyrophosphonate		**Fig. 67**
DMMP, dimethyl methylphosphonate	[756-79-6]	**Figs. 43, 44**
DIMP, diisopropyl methylphosphonate	[1445-75-6]	**Figs. 56, 57**
DPMP, dipinacolyl methylphosphonate	[7040-58-6]	**Fig 61**
N,N-dimethylphosphoramidic dichloride	[1899-02-1]	**Figs. 70, 71**
TH, Phosphorus trichloride	[7719-12-2]	**Figs. 32, 33**
Pinacolyl alcohol (3-dimethyl-2-butanol; 1,2,2-trimethyl-l-propanol)	[464-07-3]	**Fig. 62**
Pinacolone, (*tert*-butyl methyl ketone; 3,3-dimethyl-2-butanone)	[75-97-8]	**Fig. 45**
SW, methylphosphonous dichloride	[676-83-5]	**Figs. 26, 27**
DC, Dichlor, methylphosphonic dichloride	[676-97-1]	**Fig. 29**
Methylphosphonic chlorofluoride		**Figs. 30, 31**
DF, Difluor, methylphosphonic difluoride	[676-99-3]	**Figs. 51, 52A-E**
Dimethyl phosphite	[868-85-9]	**Figs. 34, 35**
TMP, trimethyl phosphite	[121-45-9]	**Figs. 36, 37**
Diisopropyl phosphite	[1809-20-7]	**Figs. 38, 39**
Triisopropyl phosphite	[116-17-6]	**Figs. 40, 41; 42A-F**
THO, phosphorus oxychloride (phospheryl chloride)	[10025-87-3]	**Fig. 69**
TEPO, triethyl phosphate	[78-40-0]	**Figs. 74, 75**
Dimethylamine hydrochloride	[506-59-2]	**Fig. 68**
Hydroxylamine hydrochloride	[5470-11-1]	**Fig. 76**
Phosphoric acid	[7664-38-2]	**Fig. 77**

2-Propanol (isopropyl alcohol)	[67-63-0]	**Fig. 58**
Ethyl alcohol	[64-17-5]	**Fig. 78**
Methylphosphonocyanidic fluoride		**Figs. 80A-B, 81**
Phenyl methylphosphonofluoridate		**Figs. 82, 83, 84**
Diethyl cyanophosphonate	[2537-48-6]	**Figs. 85, 86**
t-Butylphosphonic difluoride		**Fig. 87**
t-Butylphosphonic acid		**Fig. 88**
Isopropyl *t*-butylphosphonofluoridate		**Fig. 89**
Isobutyl *t*-butylphosphonofluoridate		**Fig. 90**
Isobutyl hydrogenmethylphosphinate		**Figs. 91, 92A-D**

2.4 List of Abbreviations

Band Intensities

w	weak
m	medium
s	strong
v	very
sh	shoulder

Vibrations

ν	sretching	ω	wagging
as	asymmetric	τ	twisting
sy	symmetric	β	in-plane deformation
δ	deformation	γ	out-of-plane deformation

3. RESULTS AND DISCUSSION

3.1 G-Type Agents

3.1.1 Isopropyl Methylphosphonofluoridate (GB, Sarin) $CH_3P{=}O(F)[O\text{-}CH(CH_3)_2]$

The infrared spectrum of **GB (Sarin)** is qiven in ***Figure 1***. The infrared bands may be assigned as follows: 2986 cm^{-1} m and 2935 cm^{-1} w (aliphatic CH stretching), 1469 and 1458 cm^{-1} vw (δ CH_3), 1420 cm^{-1} vw (δ_{as} P-CH_3), 1389 and 1379 cm^{-1} m [δ_{sy} CH_3 (isopropyl)], 1321 cm^{-1} ms (δ_{sy} P-CH_3), 1278 cm^{-1} s (ν P=O), 1180,1145 and 1106 cm^{-1} all weak (characteristic of P-O-isopropyl), 1015 cm^{-1} s (ν P-O-C), 924 and 907 cm^{-1} m (CH_3 rock of P-CH_3 and isopropyl), 838 cm^{-1} ms (ν P-F), 778 cm^{-1} w (POC), 723 cm^{-1} w (ν P-C).

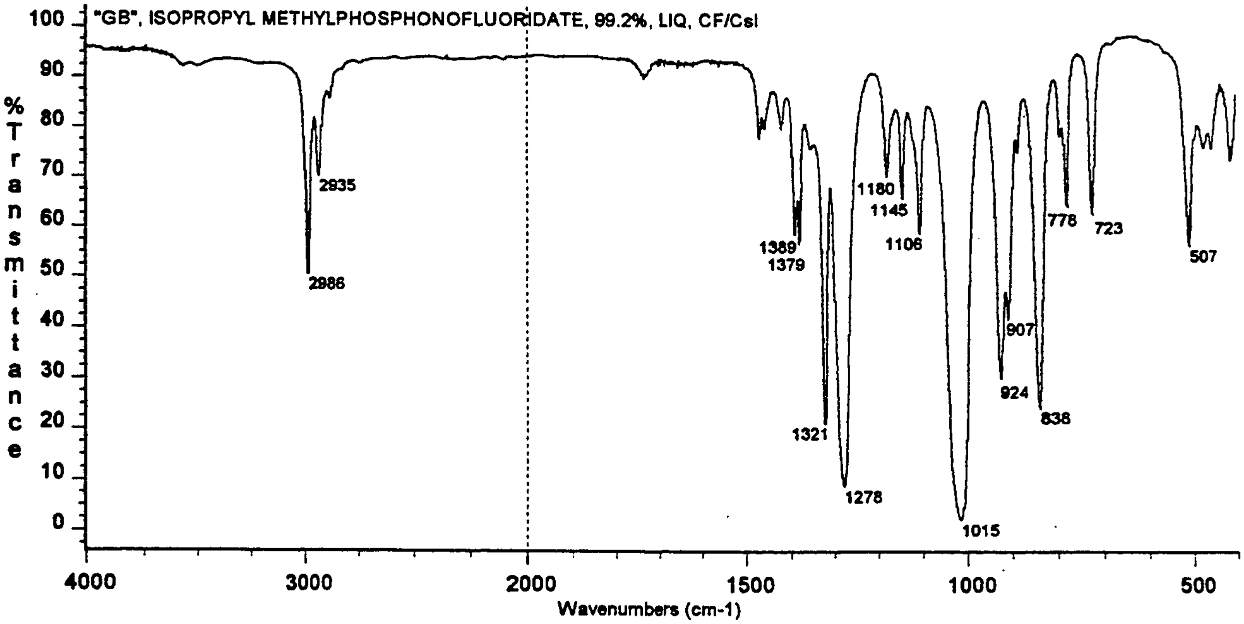

Figure 1 GB, SARIN, ISOPROPYL METHYLPHOSPHONOFLUORIDATE, 99.2%, LIQUID, CF/CsI

The effect of atmospheric moisture on a liquid sample of **GB** while between KBr windows is represented by ***Figure 2***. The top spectrum in the figure shows **GB** (stabilized with **CDI**, a carbodiimide) at time zero. Succeeding spectra show the effect of moisture, with time, on the **GB** sample. After some 4 days the resulting spectrum is that of **GB ACID**, isopropyl methylphosphonic acid (isopropyl hydrogen methylphosphonate), $CH_3P{=}O(OH)[O\text{-}CH(CH_3)_2]$.

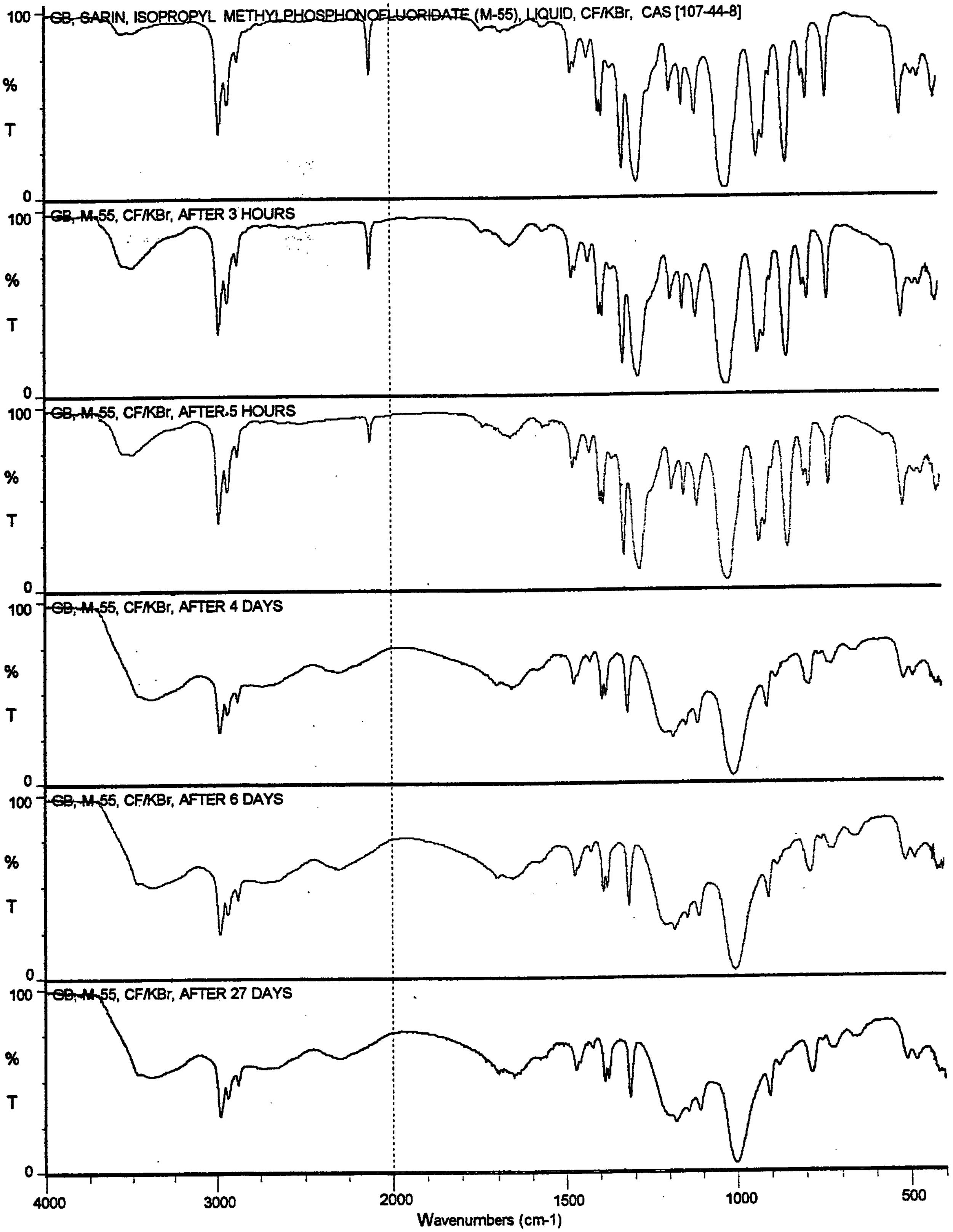

Figure 2 MUNITION ROUND GB (WITH A CARBODIIMIDE), LIQUID, CF/KBr, EXPOSED TO ATMOSPHERIC MOISTURE

3.1.2 Pinacolyl Methylphosphonofluoridate (GD, Soman) $CH_3P{=}O(F)[O\text{-}CH(CH_3)C(CH_3)_3]$

The infrared spectrum of **GD** (**Soman**) is given in ***Figure 3***. The infrared bands may be assigned as follows: 2971 cm^{-1} ms and 2876 cm^{-1} m (aliphatic CH stretaching), 1483 cm^{-1} m and 1464 cm^{-1} w (δ CH_3), 1418 cm^{-1} vw (δ_{as} P-CH_3), 1399 cm^{-1} w, 1383 cm^{-1} m and 1367 cm^{-1} m (δ_{sy} C-CH_3), 1320 cm^{-1} ms (δ_{sy} P-CH_3), 1283 cm^{-1} s (ν P=O), 1226 cm^{-1} vw, 1211 cm^{-1} w , 1117 cm^{-1} w and 1078 cm^{-1} m (pinacolyl moiety, 1018 cm^{-1} s (ν P-O-C), 987 cm^{-1} m (ν C-C of pinacolyl moiety), 935 cm^{-1} w, 919 cm^{-1} m and 871 cm^{-1} w (CH_3 rock of P-CH_3 and C-CH_3), 838 cm^{-1} ms (ν P-F), 750 cm^{-1} m (ν P-C), 504 cm^{-1} m (δ P=O ?).

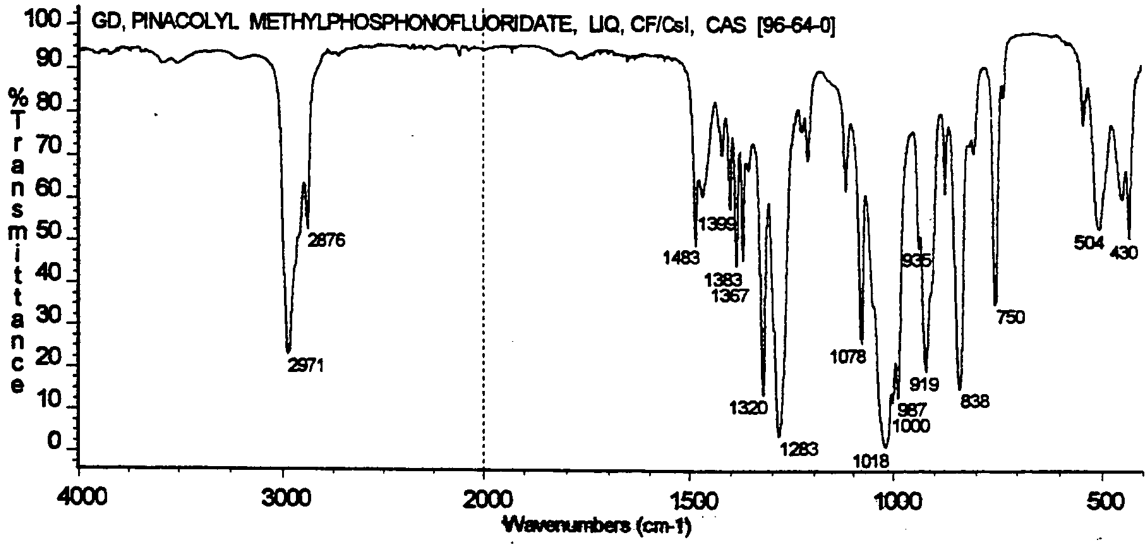

Figure 3 **GD, PINACOLYL METHYLPHOSPHONOFLUORIDATE, 99%, LIQUID, CF/CsI**

The effect of atmospheric moisture on a thin film of **GD** liquid between KBr windows is given in ***Figure 4***. The top spectrum is that for a sample of **GD** stabilized with **DICDI** (diisopropyl carbodiimide). After 2.5 hours the band due to **DICDI** at 2115 cm^{-1} is decreasing in intensity as the coumpound begins to pick up moisture. After 72 hours the spectrum resembles that of a phosphonic acid, namely, pinacolyl methylphosphonic acid (pinacolyl hydrogen methylphosphonate). Acid bands are evident in the spectrum at ca. 2700, 2298, 1670 and 1208 cm^{-1}. The P-O-C band (pinacolyl moiety) occcurs at ca. 1016 cm^{-1} .

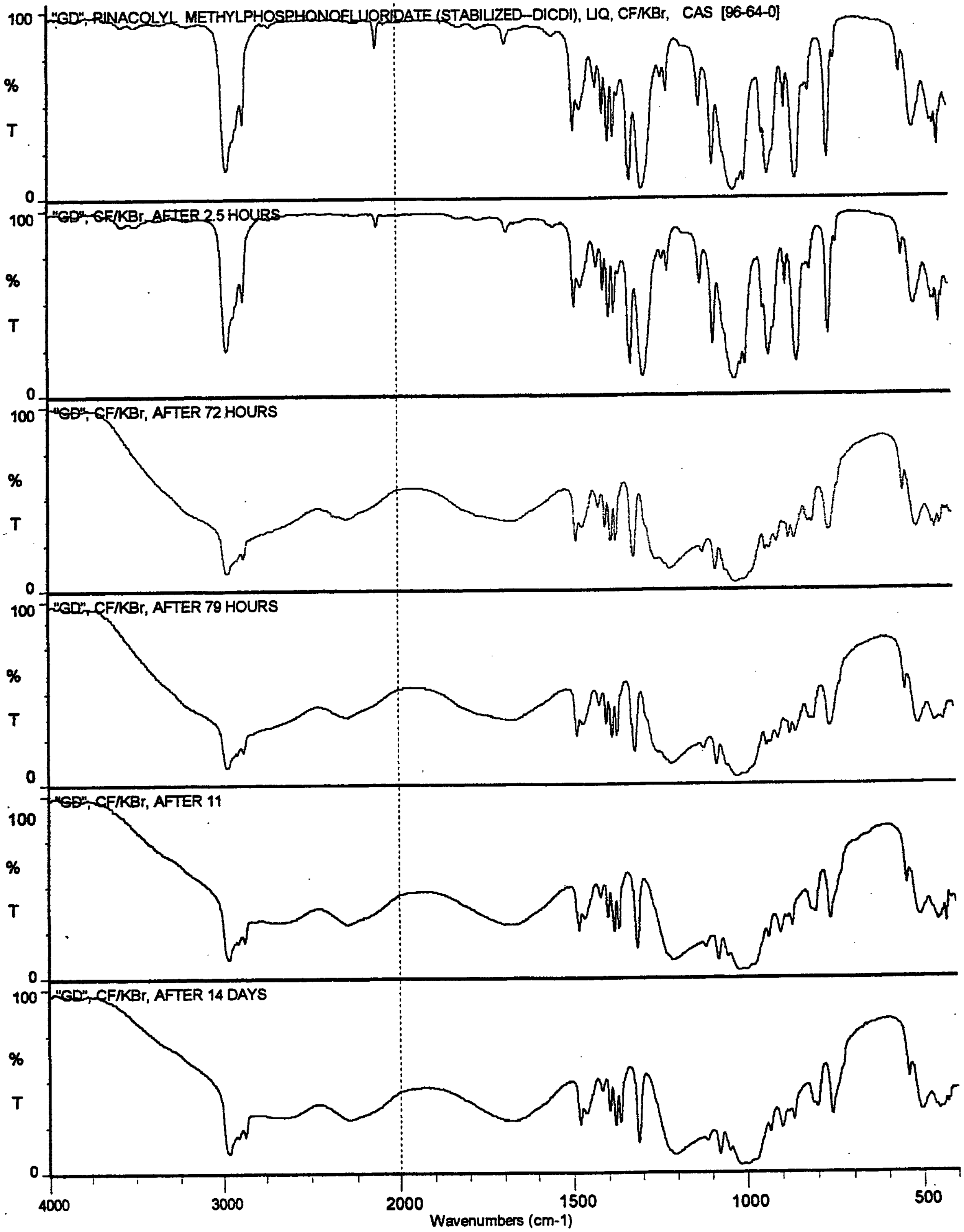

Figure 4 GD, LIQUID, CF/KBr, EXPOSED TO ATMOSPHERIC MOISTURE

3.1.3 Cyclohexyl Methylphosphonofluoridate (GF) $CH_3P=O(F)(O\text{-}C_6H_{11})$

The infrared spectrum for **GF** is given in ***Figure 5***. The infrared bands may be assigned as follows: 2999 cm^{-1} vw, 2940 cm^{-1} ms, 2862 cm^{-1} m (aliphatic ν CH), 1453 cm^{-1} w (δ CH ring), 1418 cm^{-1} vw (δ_{as} P-CH_3), 1321 cm^{-1} ms (δ_{sy} P-CH_3), 1281 cm^{-1} s (ν P=O), 1039 cm^{-1} sh and 1017 cm^{-1} s (ν P-O-C), 907 cm^{-1} m (P-CH_3 rock), 753 cm^{-1} m (ν P-C), 503 cm^{-1} w (δ P=O ?).

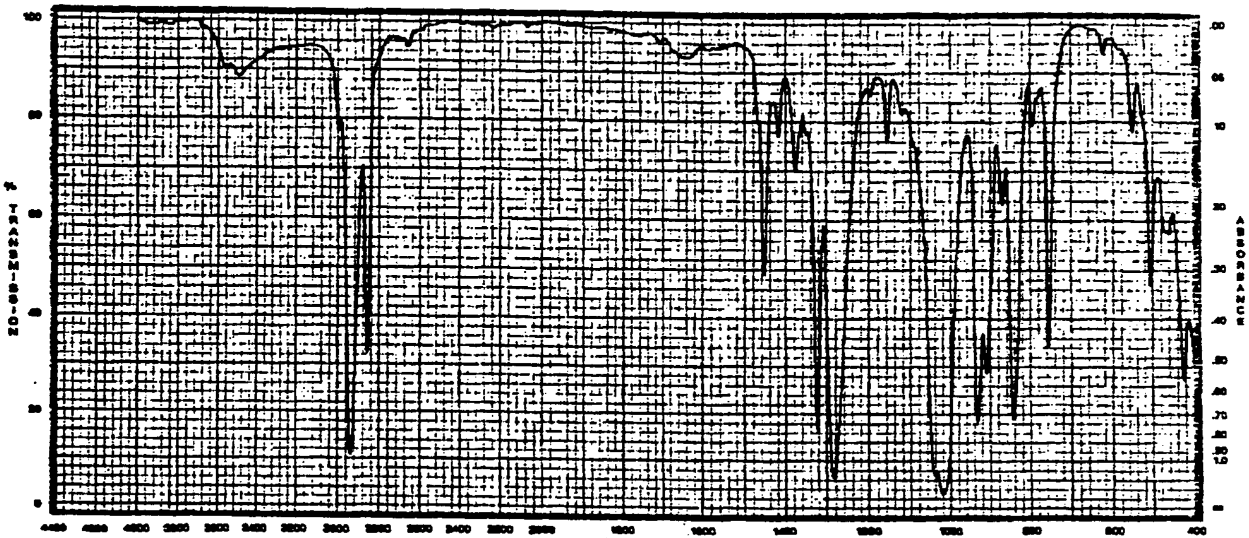

Figure 5 GF, CYCLOHEXYL METHYLPHOSPHONOFLUORIDATE, LIQUID, CF/KBr

The effect of atmospheric moisture of the infrared spectrum of **GF** is given in ***Figures 6*** through ***9***. After 22 hours, the infrared spectrum (***Figure 7***) shows the presence of bands indicative of a P-acid, namely ca 2800, ca 2300 and ca 1700 cm^{-1} (POH), ca 1200 cm^{-1} (ν P=O), ca 1020 cm^{-1} (ν P-OH). A band is also present near 1250 cm^{-1} which may be due to the P=O stretch of a pryo compound namely, dicyclohexyl dimethylpyrophosphonate, $(C_6H_{11}O)CH_3P(=O)\text{-}O\text{-}P(=O)CH_3(OC_6H_{11})$. By 26 hours, ***Figure 8***, the 1250 cm^{-1} band is almost gone, appearing as but a shoulder on the side of the P-acid ν P=O band near 1200 cm^{-1} . The sample, after some 30 hours of exposure to moist air was dried for 3 days and the resultant infrared spectrum (***Figure 9***) showed the presence of **GF ACID**, cyclohexyl methylphosphonic acid (cyclohexyl hydrogen methylphosphonate), $CH_3P=O(OH)(O\text{-}C_6H_{11})$.

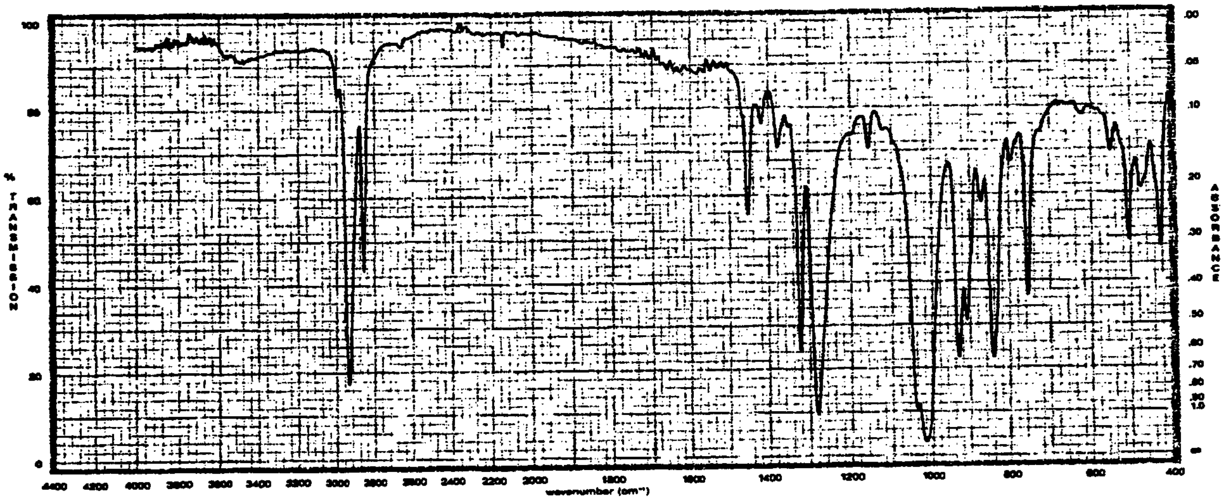

Figure 6 GF, LIQUID, CF/CsI, AFTER 2 HOURS

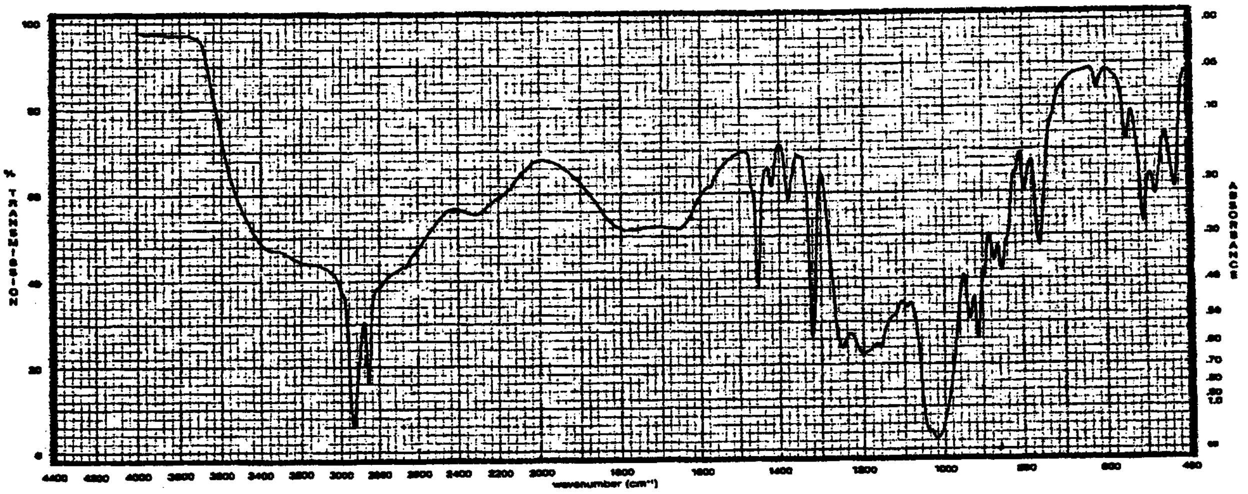

Figure 7 GF, LIQUID, CF/CsI, AFTER 22 HOURS

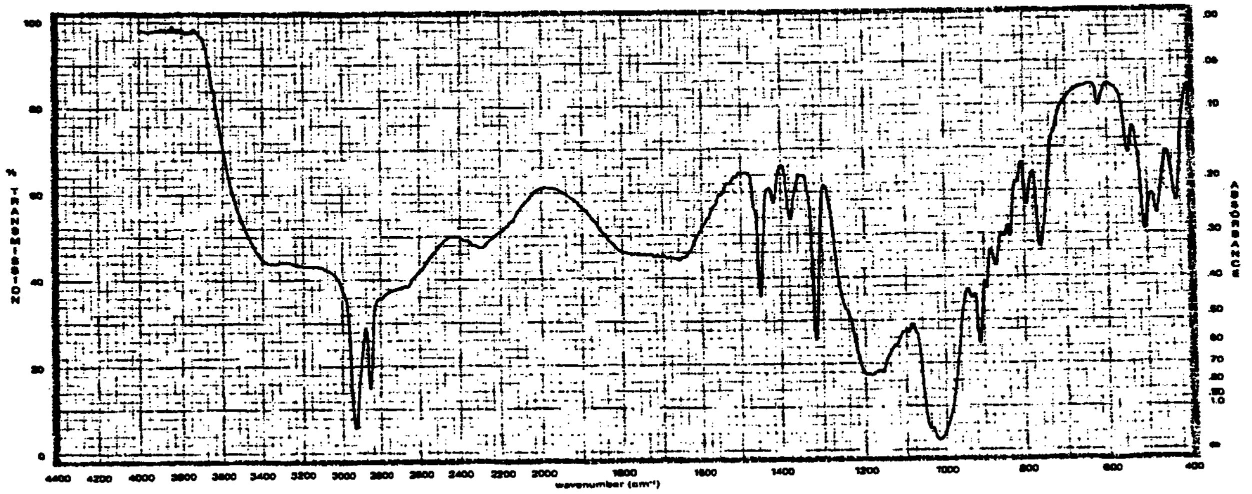

Figure 8 GF, LIQUID, CF/CsI, AFTER 26 HOURS

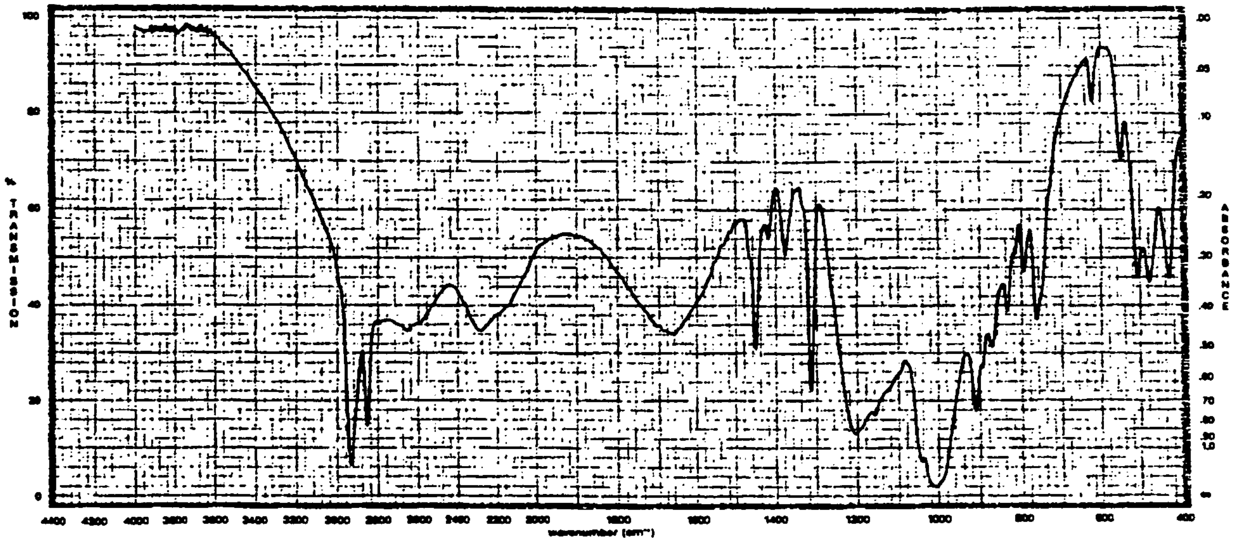

Figure 9 GF, LIQUID, CF/CsI, DRIED FOR 3 DAYS AFTER 30 HOURS IN LAB AIR

3.1.4 2-Methylcyclohexyl Methylphosphonofluoridate (EA 1356) $CH_3P{=}O(F)[O\text{-}(2\text{-}CH_3\text{-}C_6H_{10})]$

The infrared spectrum for 2-methylcyclohexyl methylphosphonofluoridate is given in ***Figure 10***. The infrared bands may be assigned as follows: 2934 cm^{-1} ms and 2861 cm^{-1} m aliphatic ν CH, 1452 cm^{-1} m (δ CH), 1418 cm^{-1} w (δas P-CH_3), 1319 cm^{-1} m (δ_{sy} P-CH_3), 1281 cm^{-1} ms (ν P=O), 1018 cm^{-1} s (ν P-O-C), 909 cm^{-1} m (P-CH_3 rock), 837 cm^{-1} m (ν P-F), and 752 cm^{-1} m (ν P-C).

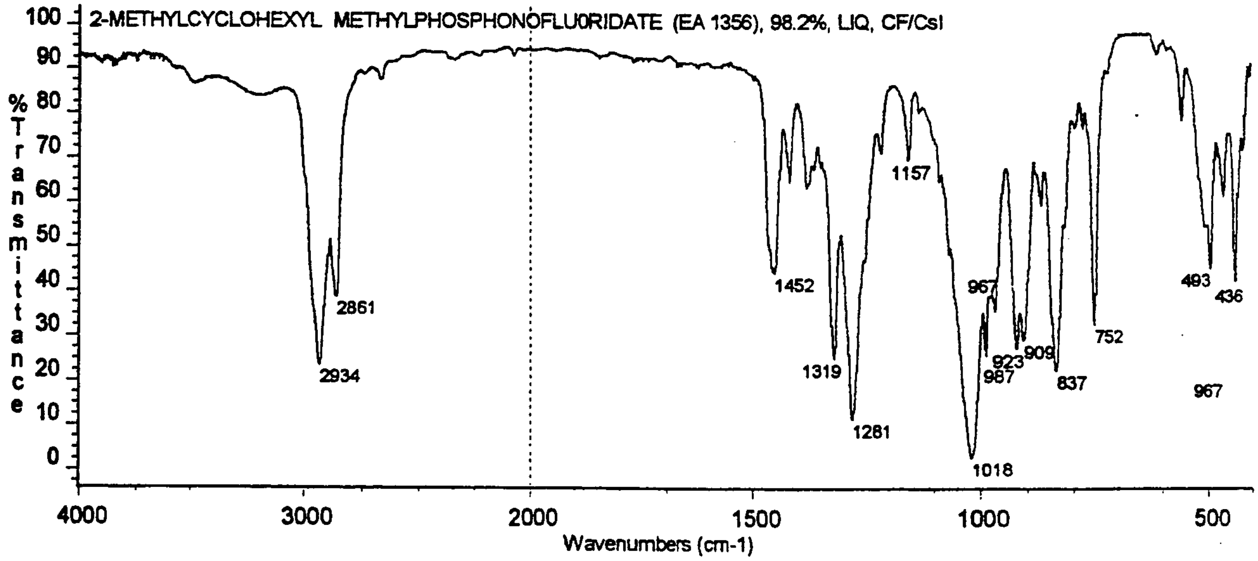

Figure 10 2-METHYLCYCLOHEXYL METHYLPHOSPHONOFLUORIDATE, 98.2 %, LIQUID, CF/CsI

The effect of atmospheric moisture on the infrared spectrum of 2-methylcyclohexyl methylphosphonofluoridate is given in ***Figures 11*** and ***11A***. After 4 days the spectrum shows the presence of a P-acid moiety with POH bands at ca 2600, 2259, 1670, and 1000 cm^{-1}. A band at ca 1200 cm^{-1} can be assigned to an acid ν P =O. This trend continues through the 22 days of observation. Now the predominant species is 2-methylcyclohexyl methylphosphonic acid (2-methylcyclohexyl hydrogen methylphosphonate). By the 39th day, bands at ca 1097 and 610 cm^{-1} are quite strong in the spectrum, and can be assigned to what is believed to be cesium sulfate, Cs_2SO_4.

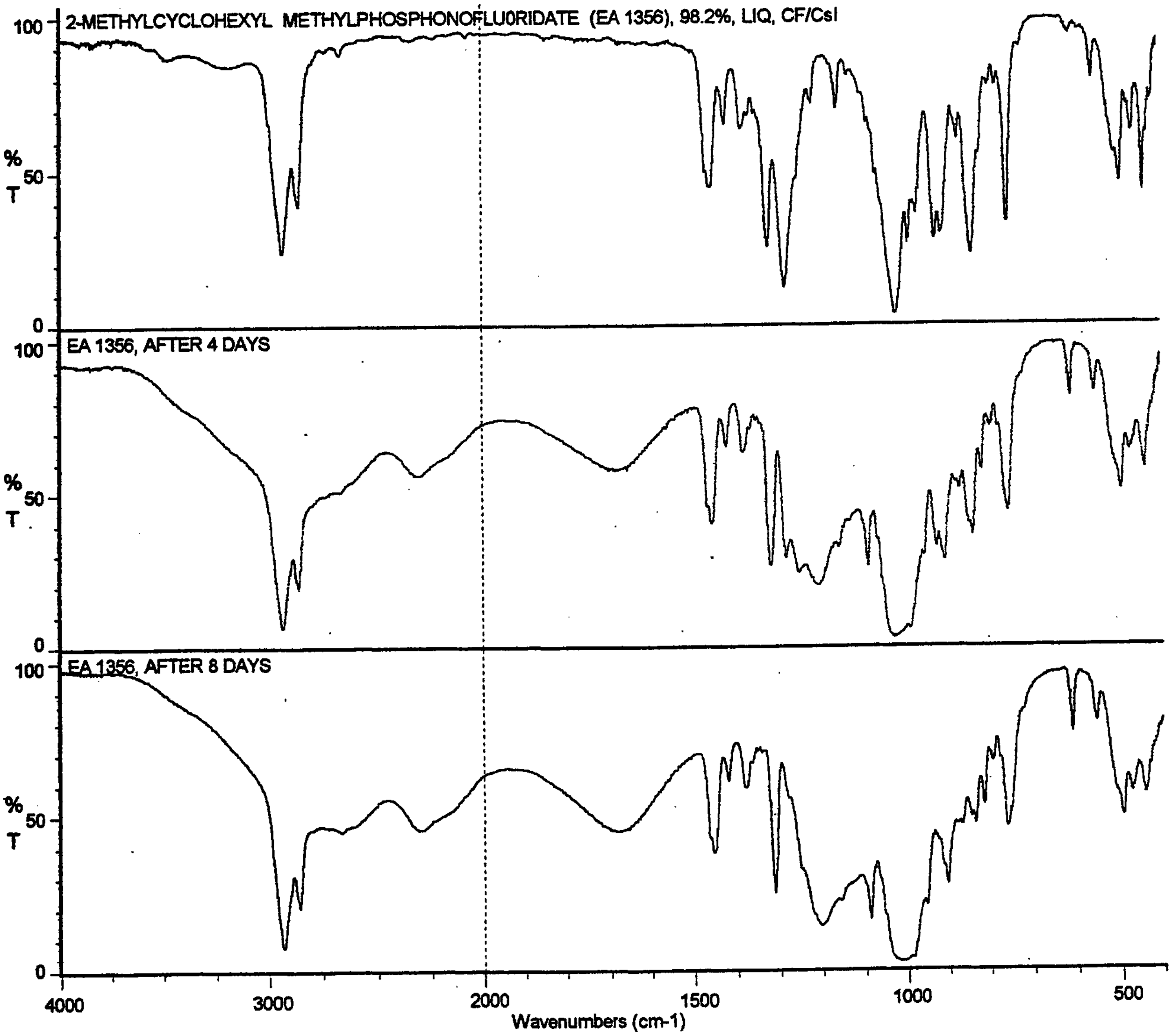

Figure 11 2-METHYLCYCLOHEXYL METHYLPHOSPHONOFLUORIDATE (EA 1356), LIQUID, CF/CsI, EXPOSED TO ATMOSPHERIC MOISTURE

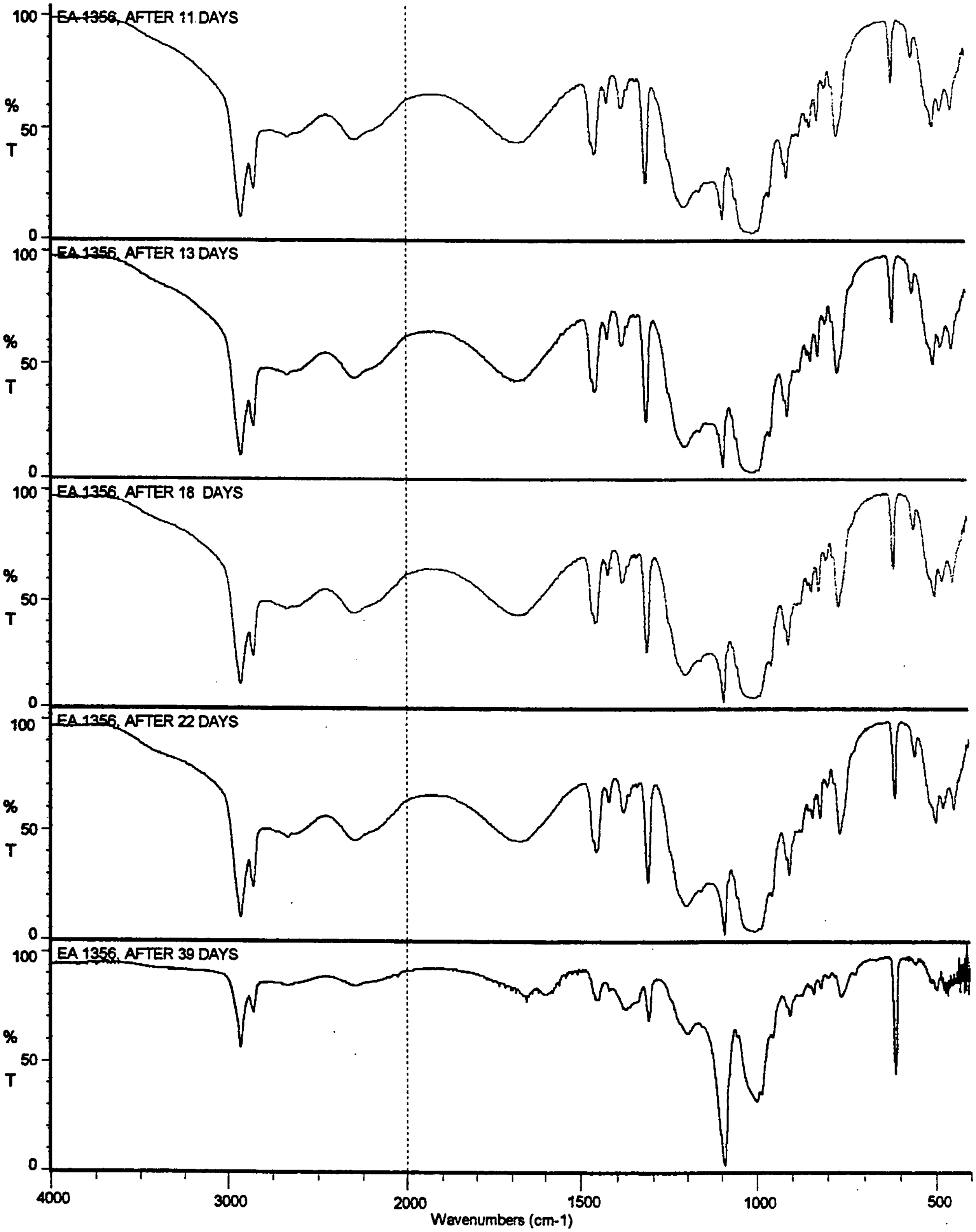

Figure 11 **2-METHYLCYCLOHEXYL METHYLPHOSPHONOFLUORIDATE (EA 1356), LIQUID, CF/CsI, EXPOSED TO ATMOSPHERIC MOISTURE** (CONTINUED)

3.1.5 Methyl Methylphosphonofluoridate (EA 1232) $CH_3P{=}O(F)(OCH_3)$

The infrared spectrum for methyl methylphosphonofluoridate is given in ***Figure 12***. The band assignments are as follows: 3003 cm^{-1} w, 2965 cm^{-1} w, 2932 cm^{-1} w and 2860 cm^{-1} vw (ν CH_3), 1465 cm^{-1} w (δ CH_3), 1420 cm^{-1} w (δ_{as} P-CH_3), 1324 cm^{-1} ms (δ_{sy} P-CH_3), 1282 cm^{-1} s (ν P=O), 1187 cm^{-1} w (OCH_3, CH_3 rock), 1052 cm^{-1} s (ν P-O-C), 925 cm^{-1} ms (P-CH_3 rock), 844 cm^{-1} ms (ν P-F), 815 cm^{-1} m (POC), 733 cm^{-1} m (ν P-C), 502 cm^{-1} m (δ P=O ?).

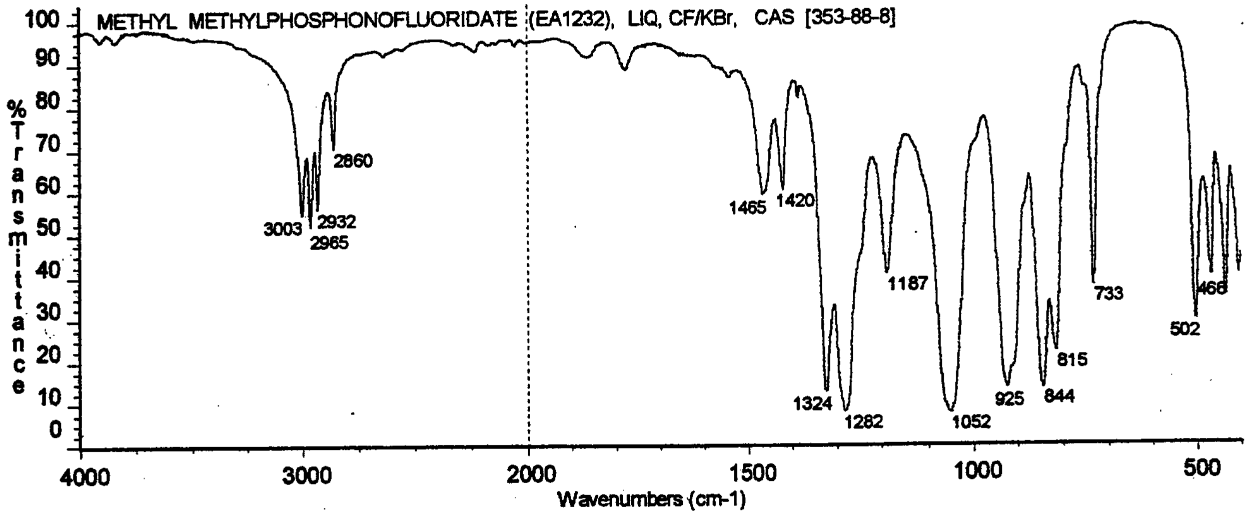

Figure 12 METHYL METHYLPHOSPHONOFLUORIDATE (EA 1232), LIQUID, CF/KBr

Figure 13 **shows the effect of atmospheric moisture on the thin liquid film of EA 1232** while between KBr windows for a period of 43 days. The broadening of the CH stretching band in the vicinity of 3000 cm^{-1} after only 1 hour is indicative of the formation of the P-OH moiety. As time progresses bands indicative of the POH moiety (ca 3000, 2250, 1680 and 1000 cm^{-1}) become more predominant in the infrared spectrum. The band due to the P=O (1282 cm^{-1}) decreases to the 1200 cm^{-1} region and the P-F band (844 cm^{-1}) disappears from the spectrum. The resultant spectrum gradually takes on the appearance of the P-acid, $CH_3\text{-}P{=}O(OH)(OCH_3)$, methyl hydrogen methylphosphonate (methyl methylphosphonic acid). Perhaps finally going to methylphosphonic acid as follows:

$CH_3P{=}O(F)(OCH_3) \xrightarrow{HOH} CH_3P{=}O(OH)(OCH_3) + HF\uparrow \xrightarrow{HOH} CH_3P{=}O(OH)_2$.

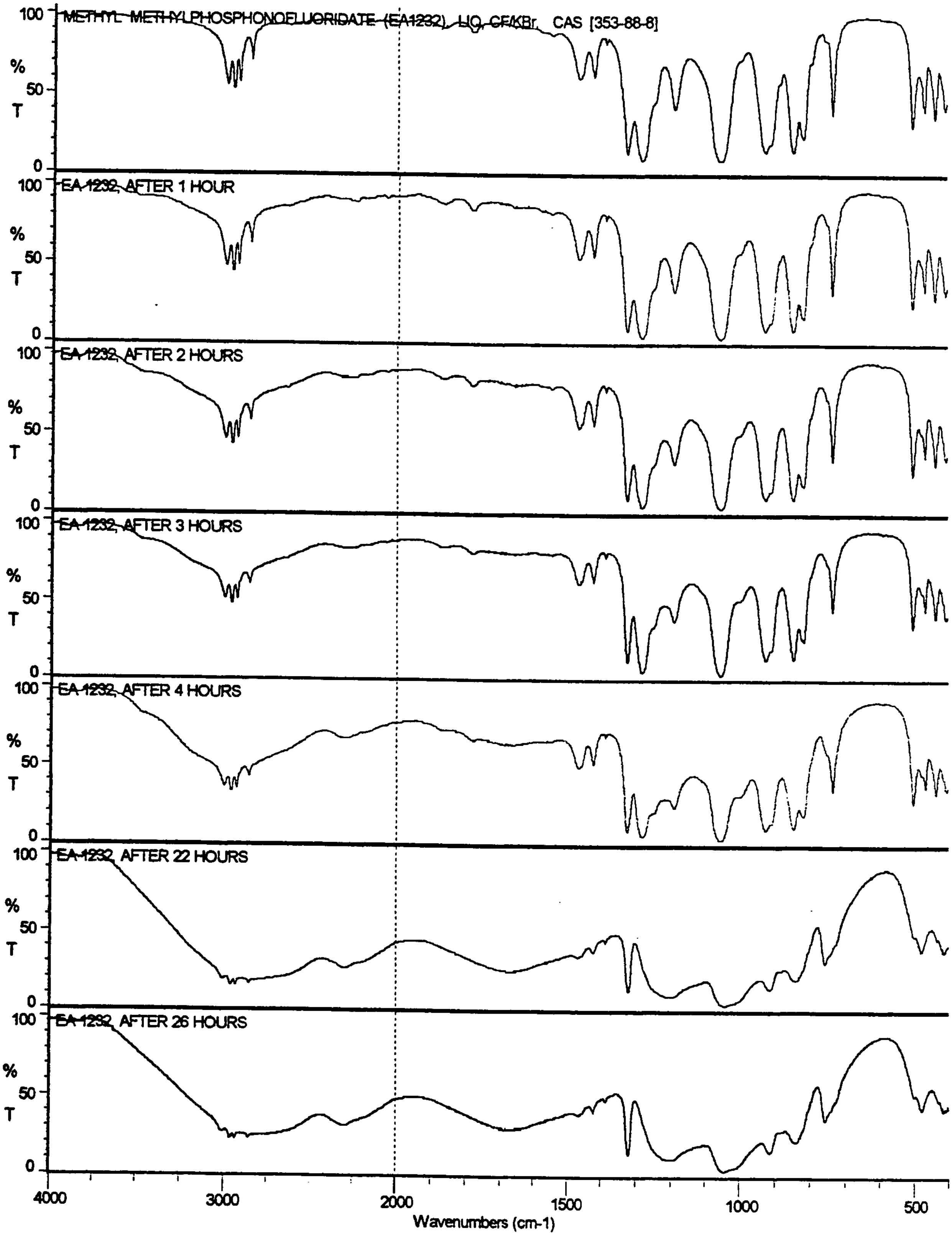

Figure 13 METHYL METHYLPHOSPHONOFLUORIDATE (EA 1232), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

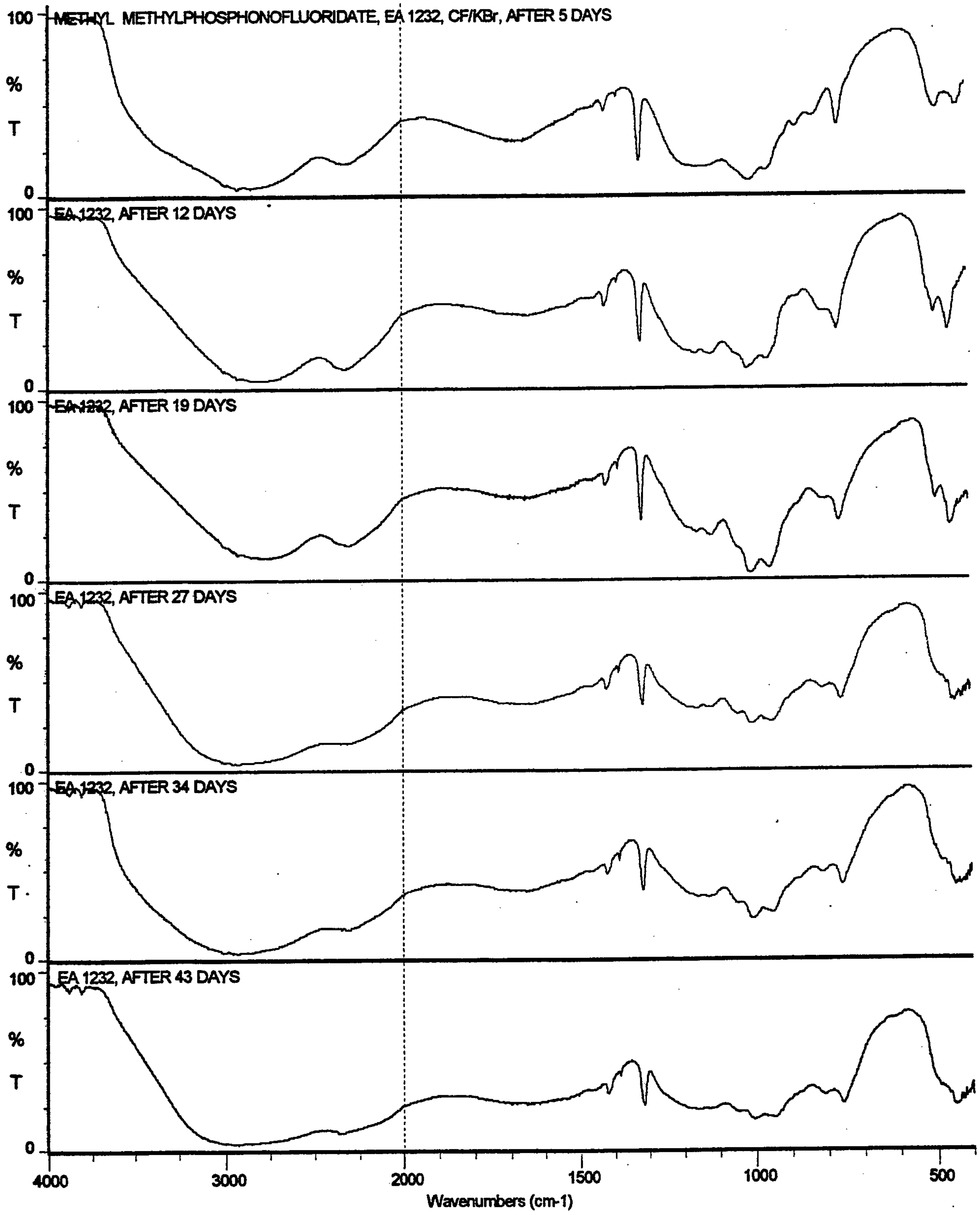

Figure 13 METHYL METHYLPHOSPHONOFLUORIDATE (EA 1232), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

3.1.6 *n*-Butyl Isopropylphosphonofluoridate $(CH_3)_2CH\text{-}P{=}O(F)(O\text{-}n\text{-}C_4H_9)$

The infrared spectrum of *n*-butyl isopropylphosphonofluoridate is given in ***Figure 14***. The band assignments are as follows: ca 3500 cm^{-1} w and ca 1650 cm^{-1} vw (water), 2966 cm^{-1} s, 2939 cm^{-1} sh and 2878 cm^{-1} ms (ν CH_3 and CH_2), 1469 cm^{-1} ms and 1436 cm^{-1} sh (δ CH_3 and CH_2), 1392 cm^{-1} m and 1372 cm^{-1} vw (δ_{sy} CH_3), 1358 cm^{-1} vw (δ CH, isopropyl moiety), 1303 cm^{-1} ms (P-isopropyl ?), 1283 and 1259 cm^{-1} ms (the average of these two frequencies is 1271 cm^{-1}, the ν P=O has a calculated value of 1272 cm^{-1}), 1169 cm^{-1} w, 1150 cm^{-1} w and 1119 cm^{-1} w (may be characteristic of the P-O-butyl moiety), 1062 cm^{-1} sh and 1030 cm^{-1} s (ν P-O-C), 993 cm^{-1} ms (ν C-C of P-O-butyl), 891 cm^{-1} ms (CH_3 rock of the isopropyl moiety), 845 cm^{-1} ms (ν P-F), 792 cm^{-1} m (POC ?), 688 cm^{-1} m (ν P-C ?).

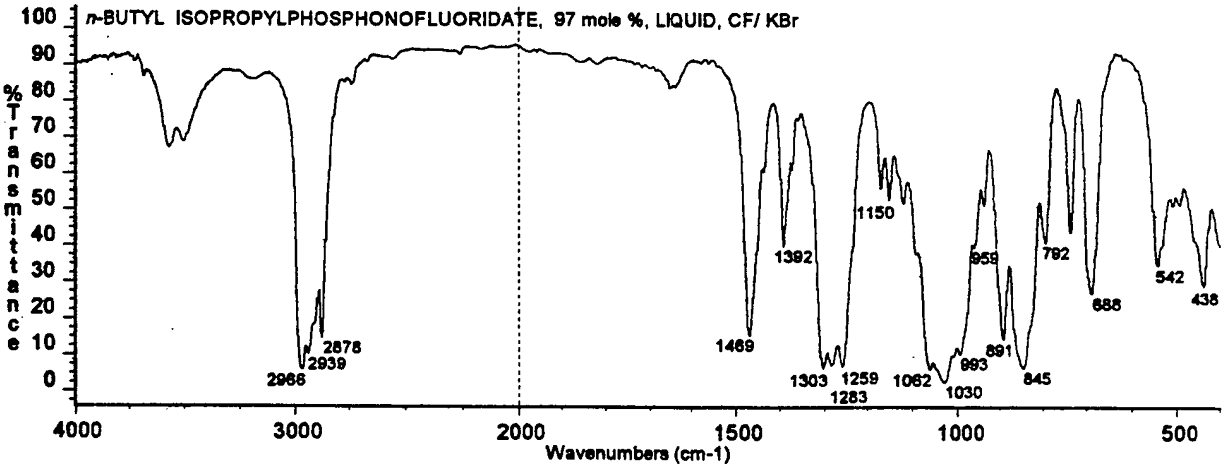

Figure 14 ***n*-BUTYL ISOPROPYLPHOSPHONOFLUORIDATE, 97 MOLE % ,LIQUID, CF/KBr**

The effect of atmospheric moisture on a thin film of *n*-butyl isopropylphosphonofluoridate while between KBr windows is given in ***Figure 15***. The effect of moisture on the compound can be seen after 22 hours when bands indicative of a POH moiety become evident near 2750, 2250 and 1680 cm^{-1}. By 5 days the POH bands are even more pronounced and the P-F band is almost completely gone. The hydrolysis study continued for 13 days and the film between the KBr windows was dried for 24 hours in the dry air purge of the instrument. This was repeated until the resultant film had been dried for some 16 days. The hydrolysis product may be represented by the structure $(CH_3)_2CH\text{-}P{=}O(OH)(O\text{-}n\text{-}Butyl)$,

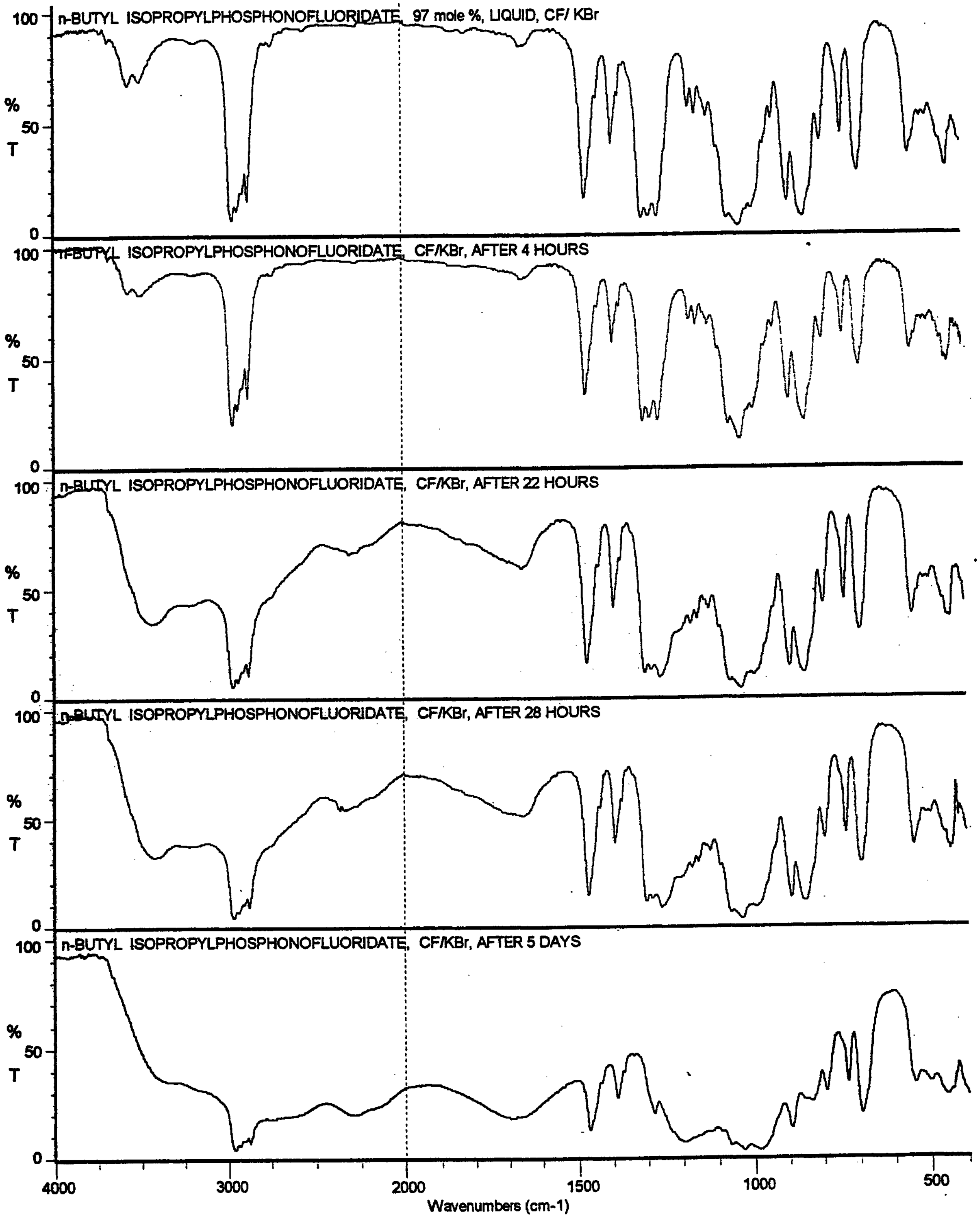

Figure 15 ***n*-BUTYL ISOPROPYLPHOSPHONOFLUORIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE**

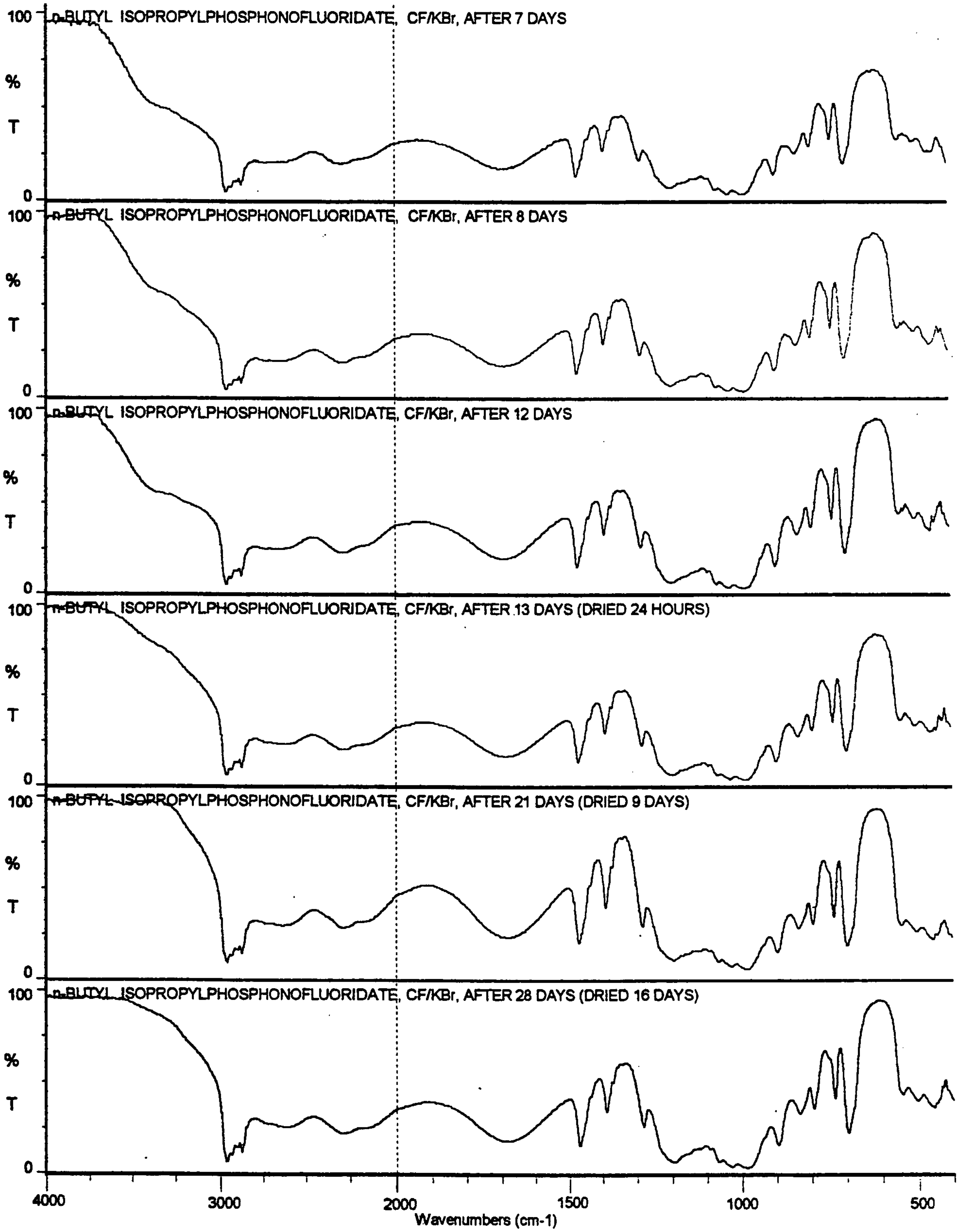

Figure 15 *n*-BUTYL ISOPROPYLPHOSPHONOFLUORIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

n-butyl hydrogen isopropylphosphonate (*n*-butyl isopropylphosphonic acid).

3.1.7 Ethyl Vinylphosphonofluoridate $H_2C{=}CH\text{-}P{=}O(F)(OCH_2CH_3)$

The infrared spectrum of ethyl vinylphosphonofluoridate is given in ***Figure 16***. The band assignments are as follows: 3096 cm^{-1} vw (ν_{as} =CH_2), 3049 cm^{-1} vw (ν_{sy} =CH_2), 2989 cm^{-1} w, 2938 cm^{-1} vw and 2916 cm^{-1} vw (ν CH of POEt), 1616 cm^{-1} vw (ν C=C), 1481 cm^{-1} vw (δ O-CH_2), 1447 cm^{-1} vw (δ_{as} CH_3), 1403 cm^{-1} w (ω CH_2), 1372 cm^{-1} vw (δ_{sy} CH_3), 1293 cm^{-1} ms (ν P=O), 1166 cm^{-1} w and 1098 cm^{-1} w (CH_3 rock, characteristic of POEt), 1043 cm^{-1} s (ν P-O-C), 983 cm^{-1} m (ν C-C of POEt, a shoulder near 965 cm^{-1} on the side of the 983 cm^{-1} band may be due to the *trans* CH wag), 858 cm^{-1} ms (ν P-F), 796 cm^{-1} m (POC).

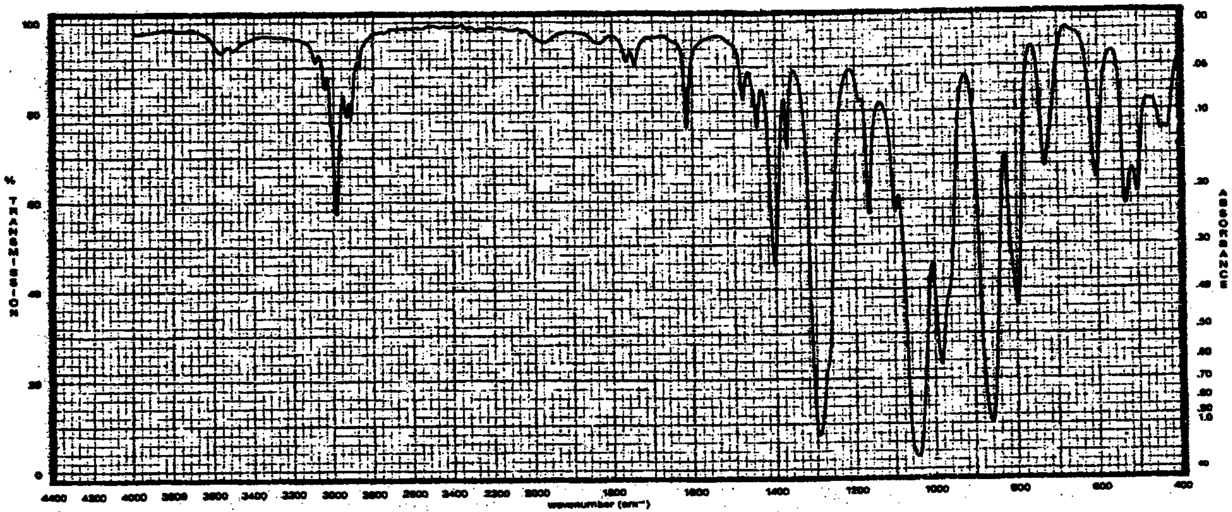

Figure 16 ETHYL VINYLPHOSPHONOFLUORIDATE, 99.5 MOLE %, LIQUID ,CF/CsI

The effect of atmospheric moisture on the thin film of ethyl vinylphosphonofluoridate is given in ***Figures 17A*** and ***17B***. After seven days the infrared spectrum is that of mainly a P-acid with perhaps a trace of residual P=F at 863 cm^{-1} . The spectrum after 20 days is essentially that of ethyl hydrogen vinylphosphonate (ethyl vinylphosphonic acid), $CH_2{=}CH\text{-}P{=}O(OH)(OC_2H_5)$, which has bands at 2987 cm^{-1} vw and 2910 cm^{-1} vw (ν CH), ca 2700 cm^{-1} m broad, 2290 cm^{-1} m broad and 1660 cm^{-1} m broad (indicative of a POH moiety), 1616 cm^{-1} vw (ν C=C), 1481 cm^{-1} vw (δ OCH_2), 1447 cm^{-1} vw (δ_{as} CH_3), 1406 cm^{-1} w (ω OCH$_2$), 1372 cm^{-1} vvw (δ$_{as}$ CH$_3$), 1280 cm^{-1} w (=CH rock), 1200 cm^{-1} ms (ν P=O), 1167 cm^{-1} vw and 1091 cm^{-1} vw (CH$_3$ rock, characteristic of POEt), 1035 cm^{-1} s (ν P-O-C), 989 cm^{-1} s [ν P-O(H) and ν C-C of POEt, ca 980 shoulder (may also have some contribution from the *trans* =CH wag ?], 800 cm^{-1} w POC.

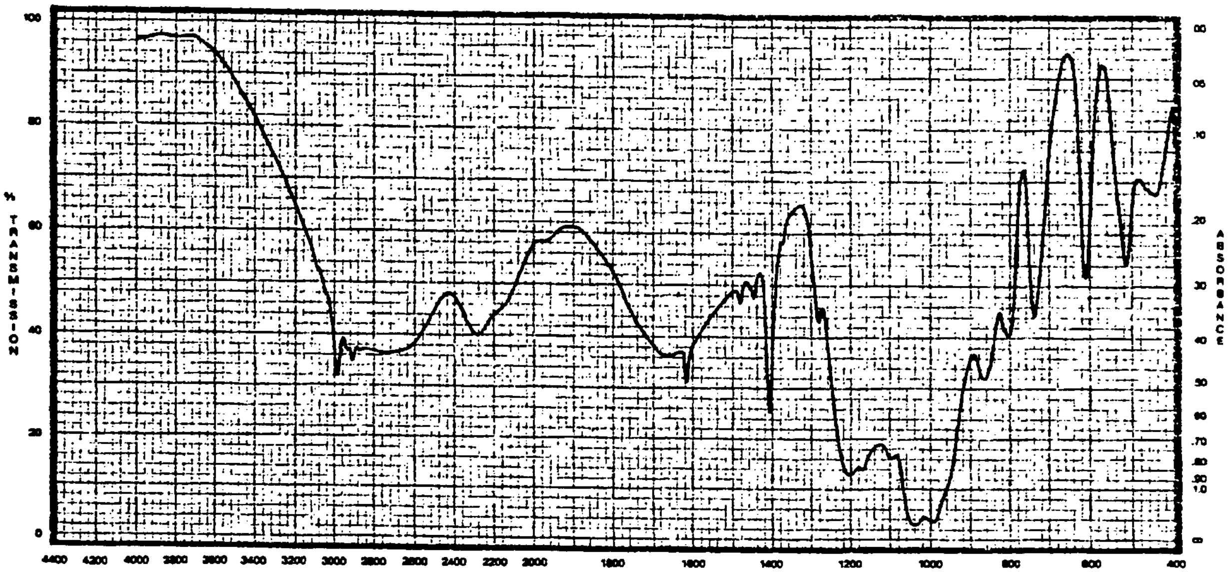

Figure 17A ETHYL VINYLPHOSPHONOFLUORIDATE, LIQUID, CF/CsI AFTER 7 DAYS

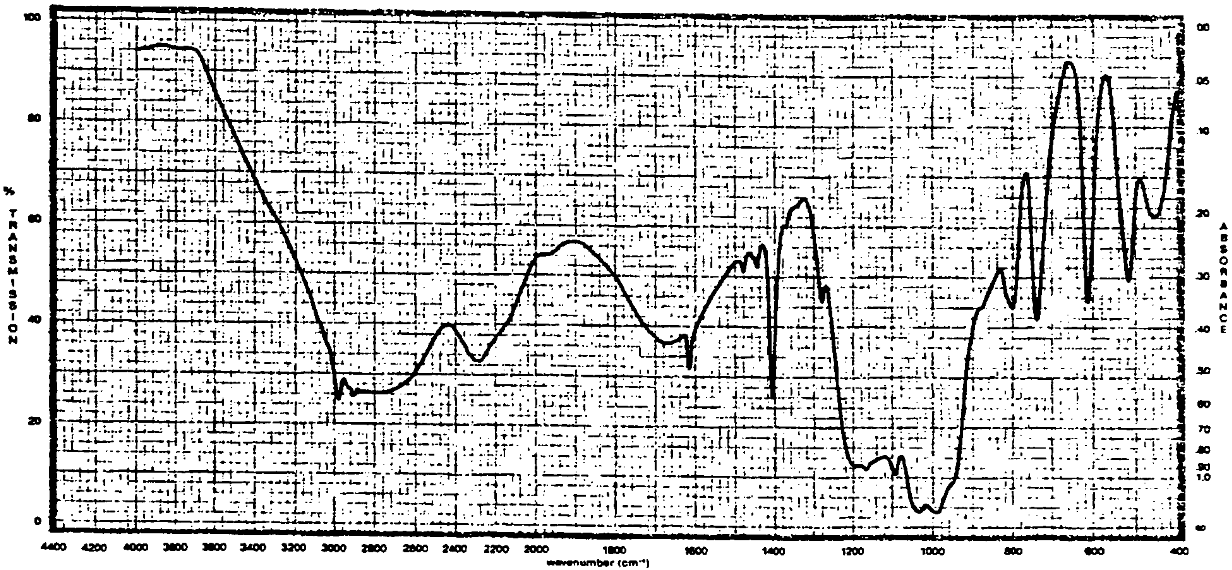

Figure 17B ETHYL VINYLPHOSPHONOFLUORIDATE, LIQUID, CF/CsI, AFTER 20 DAYS

3.1.8 Trimethylsilyl Methylphosphonocyanidate $CH_3P{=}O(C{\equiv}N)[O\text{-}Si(CH_3)_3]$

The infrared spectrum for trimethylsilyl methylphosphonocyanidate, is presented in ***Figure 18***. The bands made be assigned as follows: 2965 cm^{-1} m (ν_{as} CH_3), 2920 cm^{-1} w (ν_{sy} CH_3), 2202 cm^{-1} ms (ν C≡N), 2081 cm^{-1} vvw (ν C≡N from HCN, some broadening above the the 2965 cm^{-1} band may also be due to the presence of HCN), 1411 cm^{-1} w (δ_{as} P-CH_3 and δ_{as} Si-CH_3), 1312 cm^{-1} ms (δ_{sy} P-CH_3), 1272 and 1260 cm^{-1} s split band (the 1272 cm^{-1} band is probably the ν P=O since the calculated value[a] for this vibration would be 1274 cm^{-1}, while the 1260 cm^{-1} band may be assigned to the δ_{sy} Si-CH_3), 1048 cm^{-1} s (ν P-O-C), 889 cm^{-1} m (P-CH_3 rock), 853 cm^{-1} s and 783 cm^{-1} ms (Si-CH_3 rocking and ν Si-C), 764 cm^{-1} m (ν P-C ?), 596 cm^{-1} m (P-CN ?).

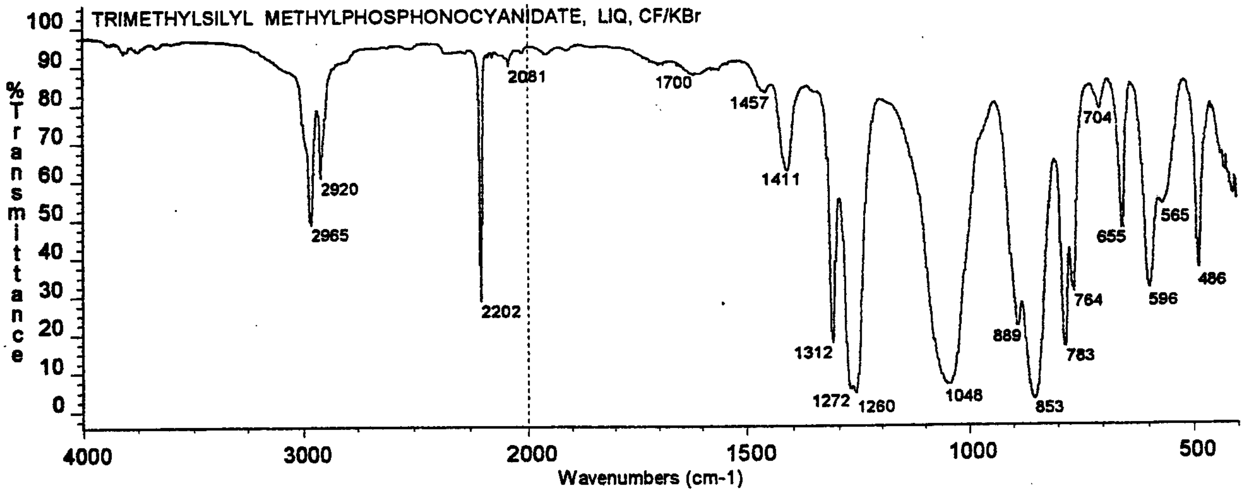

Figure 18 TRIMETHYLSILYL METHYLPHOSPHONOCYANIDATE, LIQUID, CF/KBr

The effect of atmospheric moisture on the thin film of trimethylsilyl methylphosphonocyanidate while between KBr windows is given in ***Figure 19***. As time progresses to 5 hours of exposure to atmospheric moisture, the infrared spectrum shows an increase in the intensities of the bands at 3074 cm^{-1} w and 2080 cm^{-1} w (H-C≡N) and a corresponding decrease in the intensity of the P-C≡N at 2202 cm^{-1}. A new band appears at 964 cm^{-1} which may be assigned to a pyro P-O-P moiety. No bands

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[a] The calculation of the phosphoryl frequency is described in L. C. Thomas, "Interpretation of the Infrared Spectra of Organophosphorus Compounds," Heyden, New York, 1974.

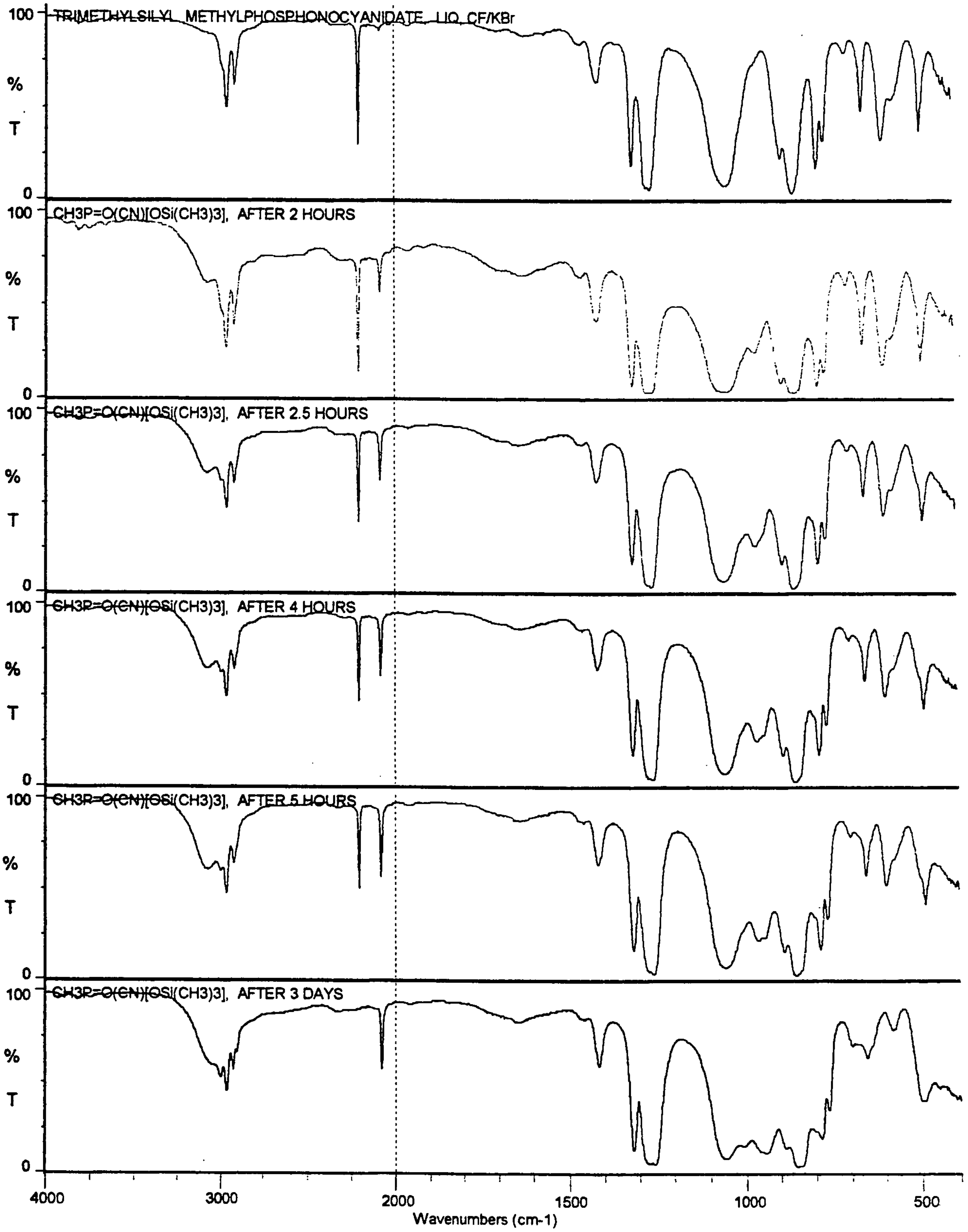

Figure 19 TRIMETHYLSILYL METHYLPHOSPHONOCYANIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

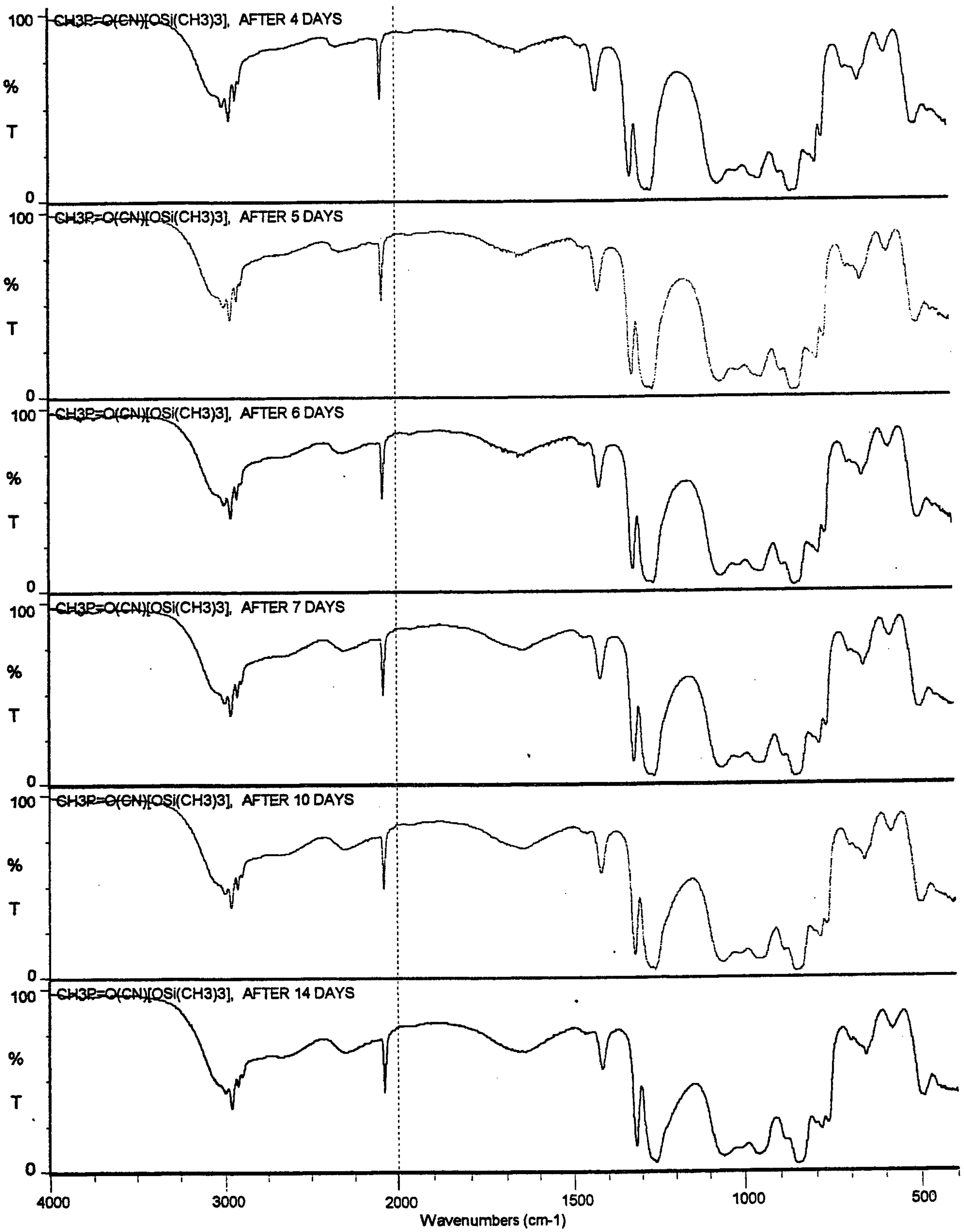

Figure 19 TRIMETHYLSILYL METHYLPHOSPHONOCYANIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

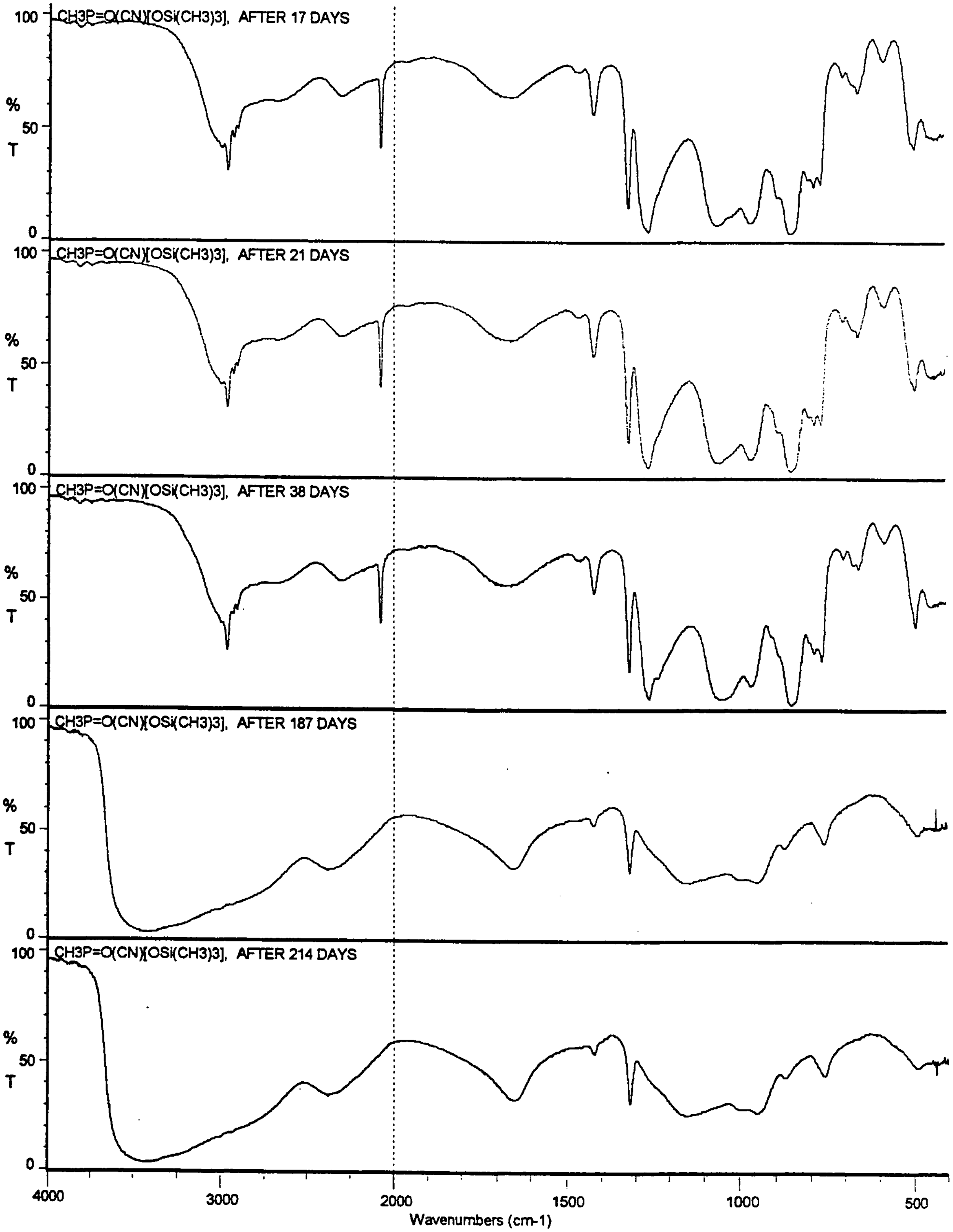

Figure 19 TRIMETHYLSILYL METHYLPHOSPHONOCYANIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

assignable to the P-OH group are yet visible in the spectrum. Thus, a pyro compound such as $[(CH_3)_3SiO\,]CH_3P(=O)\text{-}O\text{-}P(=O)CH_3[OSi(CH_3)_3\,]$ may be forming. As time progresses the P-C≡N band at 2202 cm^{-1} disappears and the band due to HCN is left at 2080 cm^{-1} . This is the case up to 38 days. However, since the 3 days time period, some bands due to the P-OH moiety have also been creeping into the spectra. At the 38 day mark two moieties seem to be predominant in the spectra, namely, a P-acid and the aforementioned pyro compound. The acid may be $CH_3\,P{=}O(OH)[OSi(CH_3)_3\,]$. Between the 38 day and the 187 day periods further hydrolysis of the compound(s) appears to have occurred to form a wet methylphosphonic acid, $CH_3P{=}O(OH)_2$. Compare the spectra after 187 or 214 days to ***Figure 20*** which is the spectrum of methylphosphonic acid to which some water had been added.

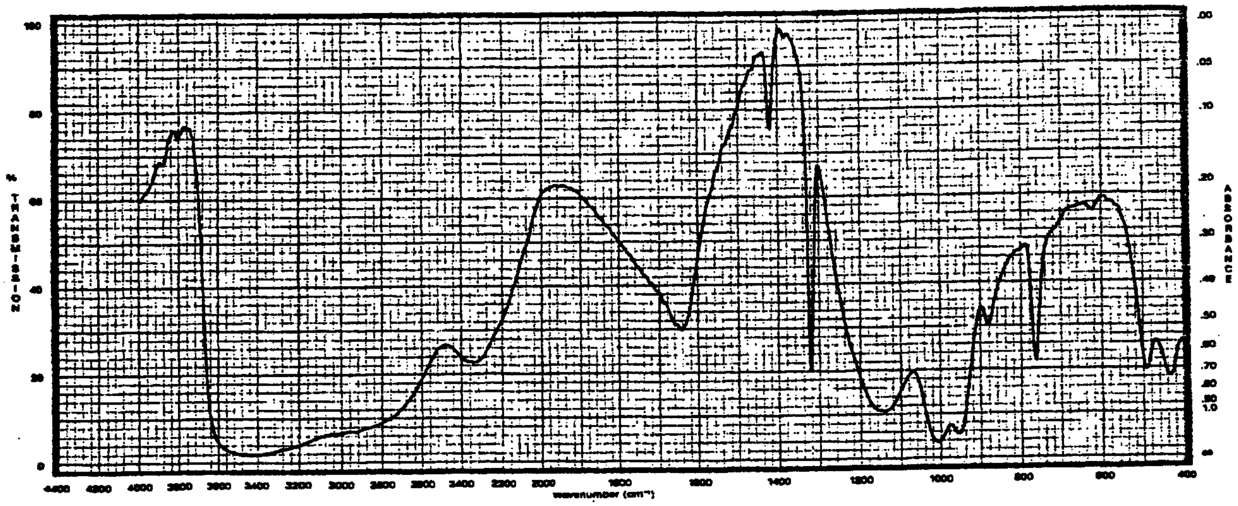

Figure 20 **WET METHYLPHOSPHONIC ACID, FILM BETWEEN KBr DISCS**

3.1.9 Ethyl N,N-Dimethylphosphoramidocyanidate (GA) $(CH_3)_2N\text{-}P{=}O(C{\equiv}N)(OCH_2CH_3)$

The infrared spectrum of **GA**, ethyl N,N-dimethylphosphoramidocyanidate, is given in ***Figure 21***. Band assignments for **GA** are as follows: 2988 cm^{-1} m, 2942 cm^{-1} m, 2912 cm^{-1} m, 2864 cm^{-1} w and 2826 cm^{-1} w (aliphatic ν CH), 2195 cm^{-1} m (ν C≡N), 1812 cm^{-1} vvw (1030 + 788 = 1818 ?), 1734 cm^{-1} vvw (1006 + 731 = 1737 ?), 1481 cm^{-1} m (δ OCH_2), 1459 cm^{-1} m (δ CH_3), 1394 cm^{-1} w (ω OCH_2, δ_{sy} CH_3), 1321 cm^{-1} ms [$PN(CH_3\,)_2$] , 1269 cm^{-1} s (ν P=O, 1181 cm^{-1} m [$PN(CH_3\,)_2$], 1165 cm^{-1} w and 1098 cm^{-1}

w (characteristic of POEt, CH_3 rock), 1068 cm^{-1} sh [$PN(CH_3)_2$], 1030 cm^{-1} s (ν P-O-C), 1006 cm^{-1} s (ν P-N-C), 974 cm^{-1} m (ν C-C of P-O-Et), 788 cm^{-1} m (POC), 731 cm^{-1} m (PNC), 595 cm^{-1} m (P-C≡N ?).

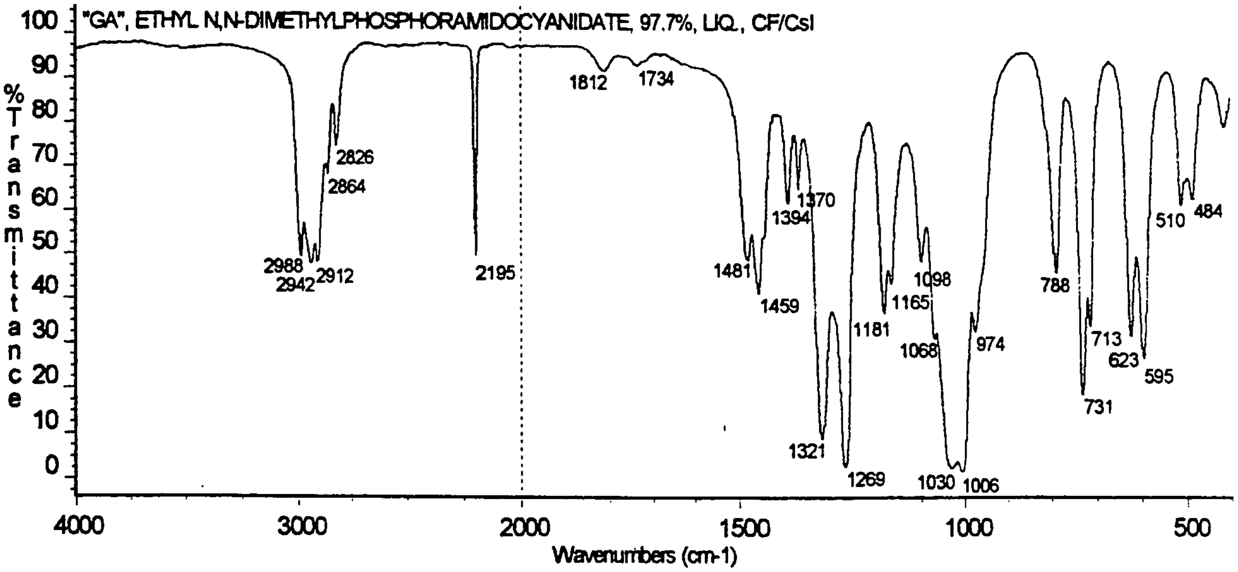

Figure 21 GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQ, CF/CsI

The effect of atmospheric moisture on the infrared spectra of GA is given in ***Figure 22***. As **GA** hydrolyzes there is a gradual decrease in the intensity of the ν C≡N band at 2195 cm^{-1}. After 14 days no ν C≡N is present in the infrared spectrum. Bands are now observed at 1315 cm^{-1} ms, 1188 cm^{-1} w, 1006 cm^{-1} s and 709 cm^{-1} m [$PN(CH_3)_2$]; 1265 cm^{-1} s (ν P=O); 1165 cm^{-1} vw (POEt), 1052 cm^{-1} ms (ν P-O-C, 985 cm^{-1} sh (ν CC of POEt) and 796 cm^{-1} w (POC). Bands at 1093 s and 613 w are due to the formation of what is believed to be cesium sulfate, Cs_2SO_4, from the cesium iodide windows. An infrared band at 932 cm^{-1} s is assigned to a P-O-P stretching vibration from a pyro moiety such as (EtO) $(CH_3)_2$ N-P(=O)-O-P(=O)N$(CH_3)_2$ (OEt), which we shall call **"GA PYRO"** for a short name, or more properly *sym*-bis(dimethylamido) diethyl pyrophosphate or bis(ethyl N,N-dimethylphosphoramidic) anhydride. The pyro band at 932 cm^{-1} shows up earlier between the 3 and 7 day time interval. The pyro compound appears to be present even after some 100 days. The infrared spectrum for an authentic sample of the **"GA PYRO"** in presented in ***Figure 23***. The spectrum for **GA PYRO** shows the following bands:

Text continues on page 49.

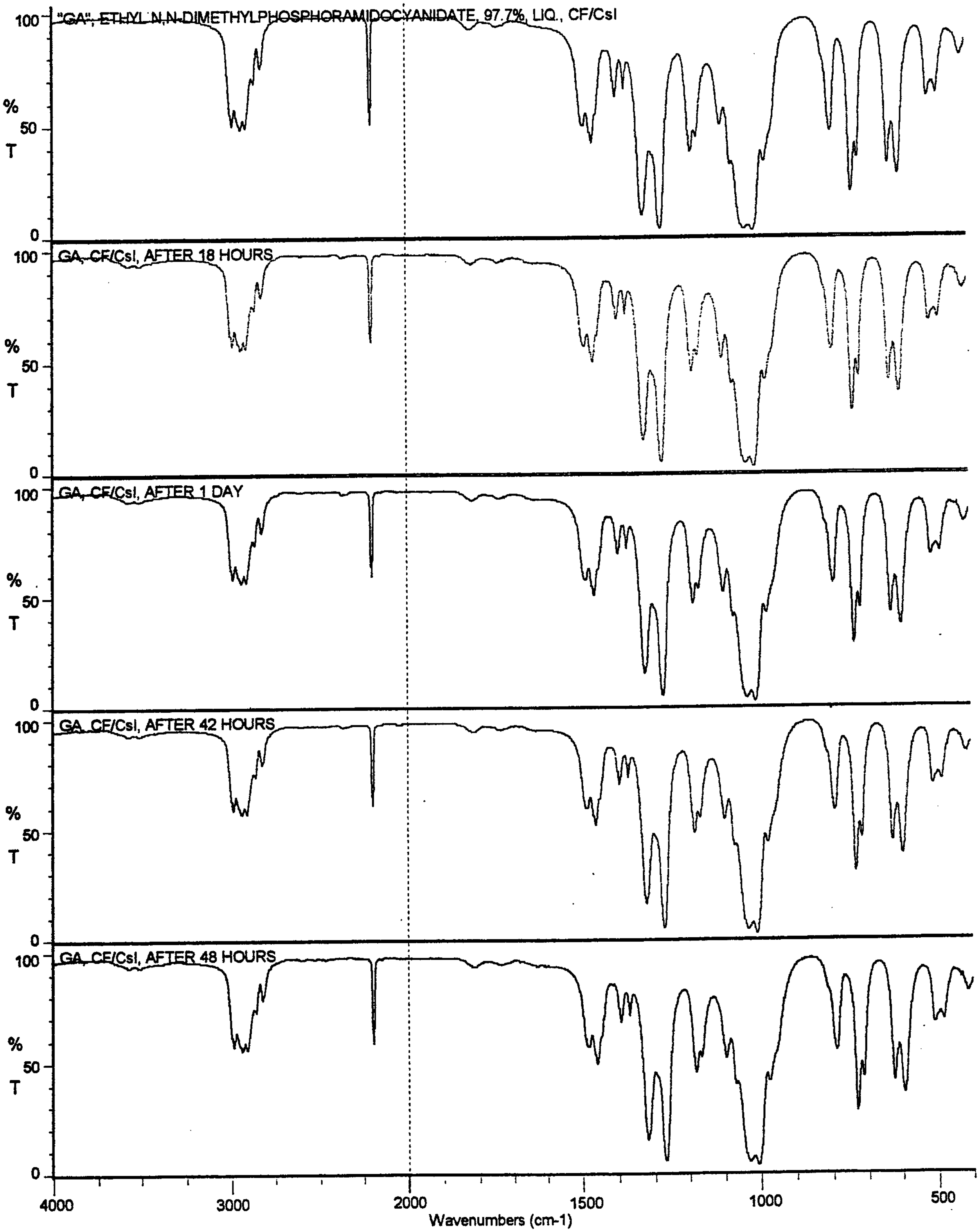

Figure 22 GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

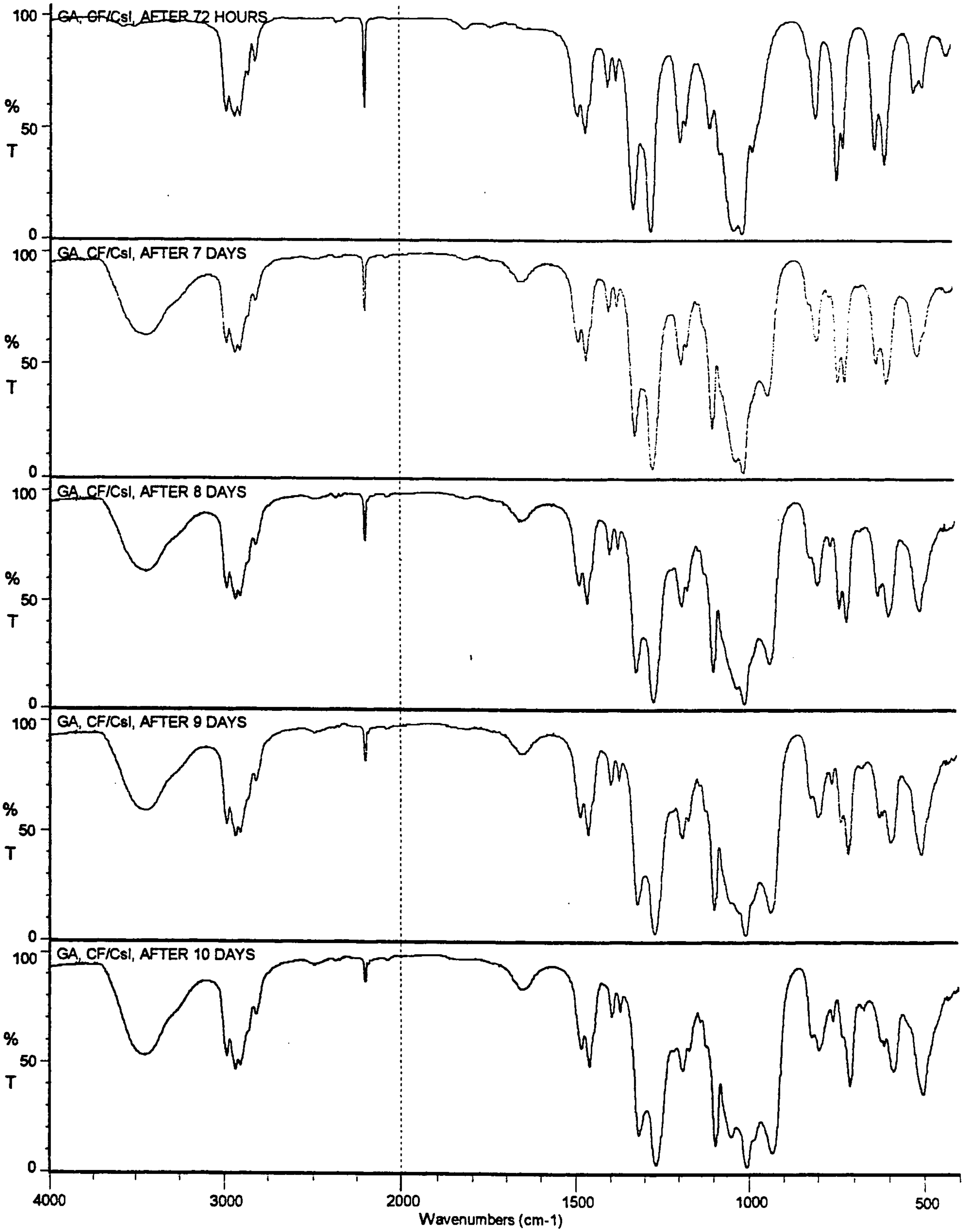

Figure 22 GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

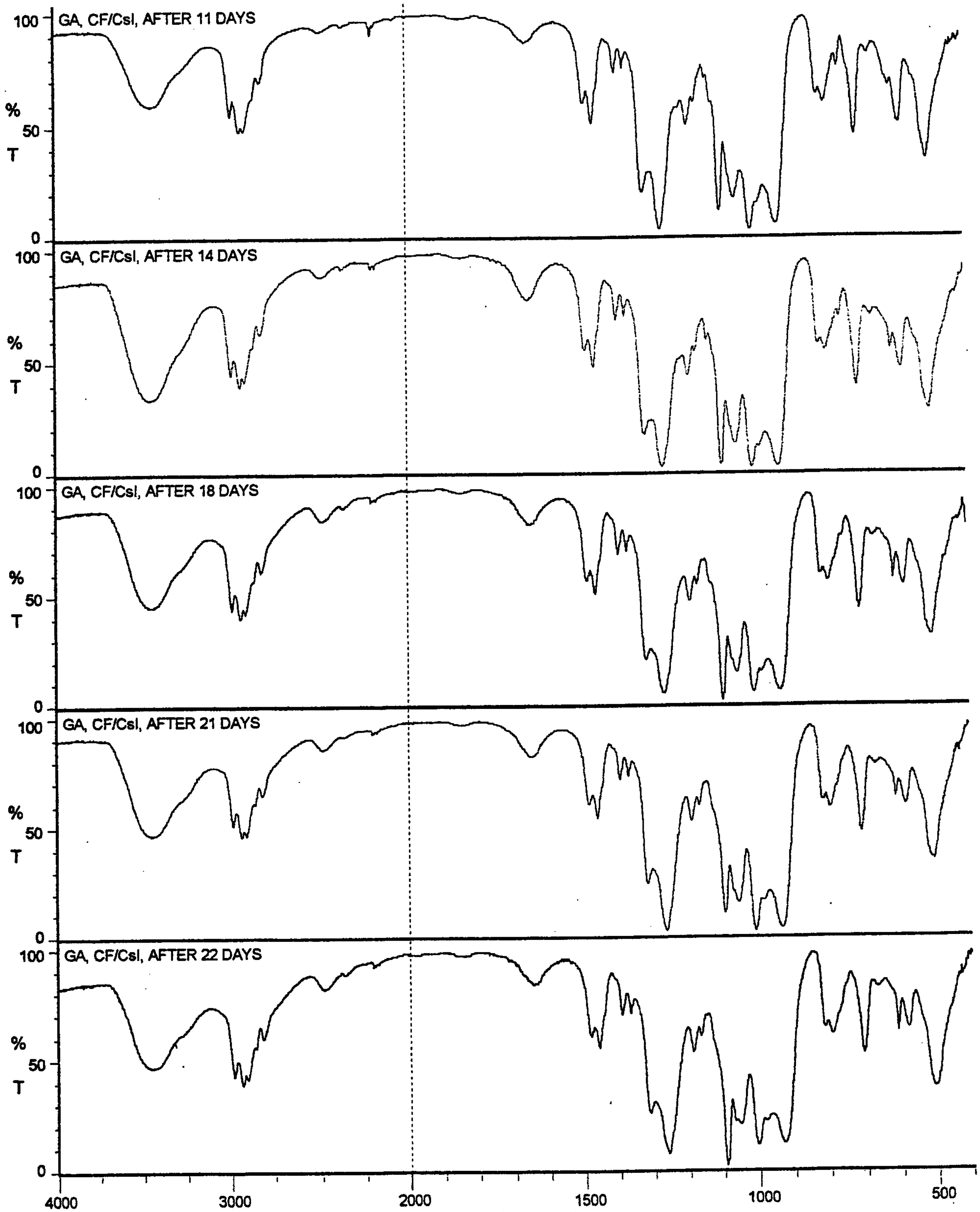

Figure 22 GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

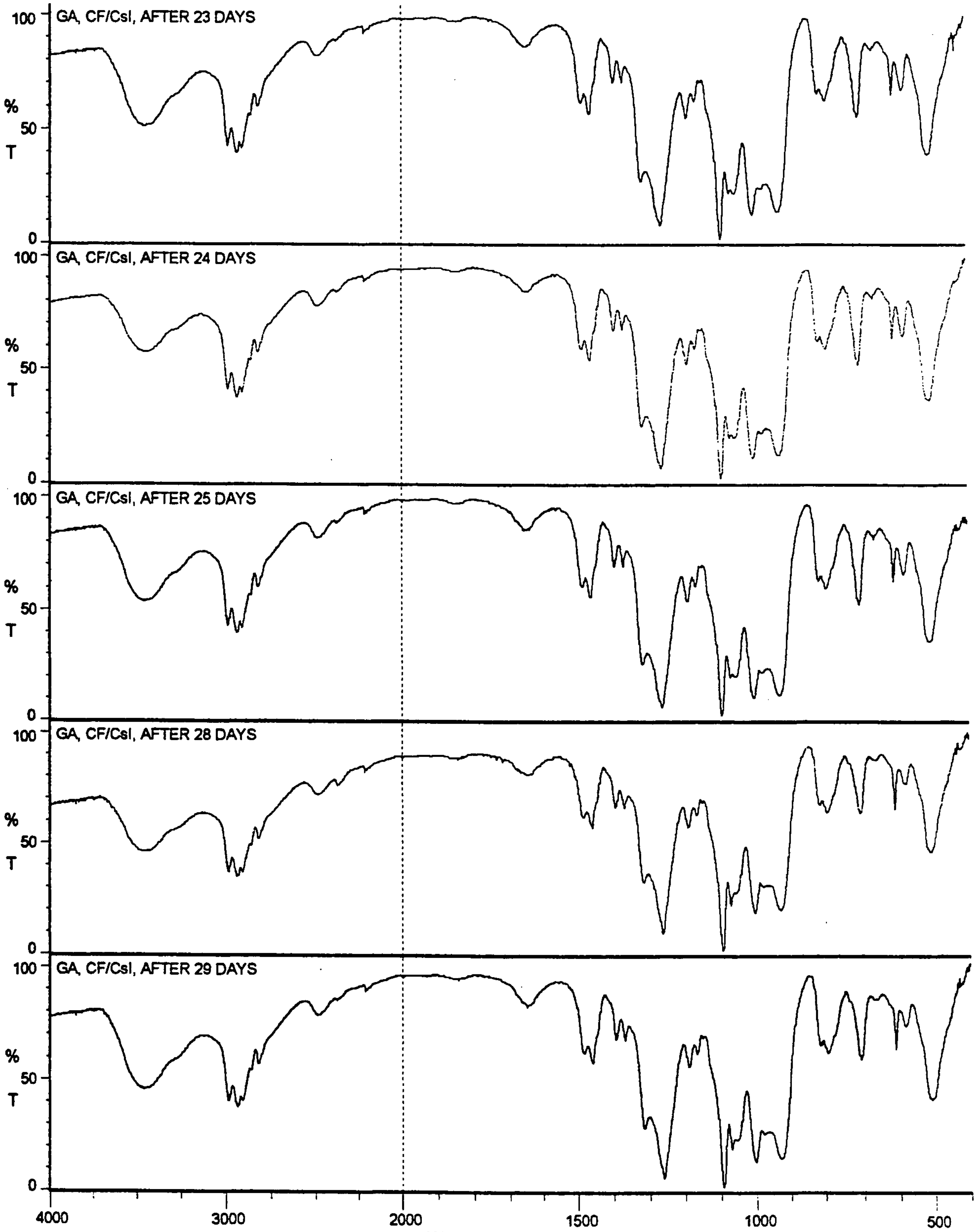

Figure 22 GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

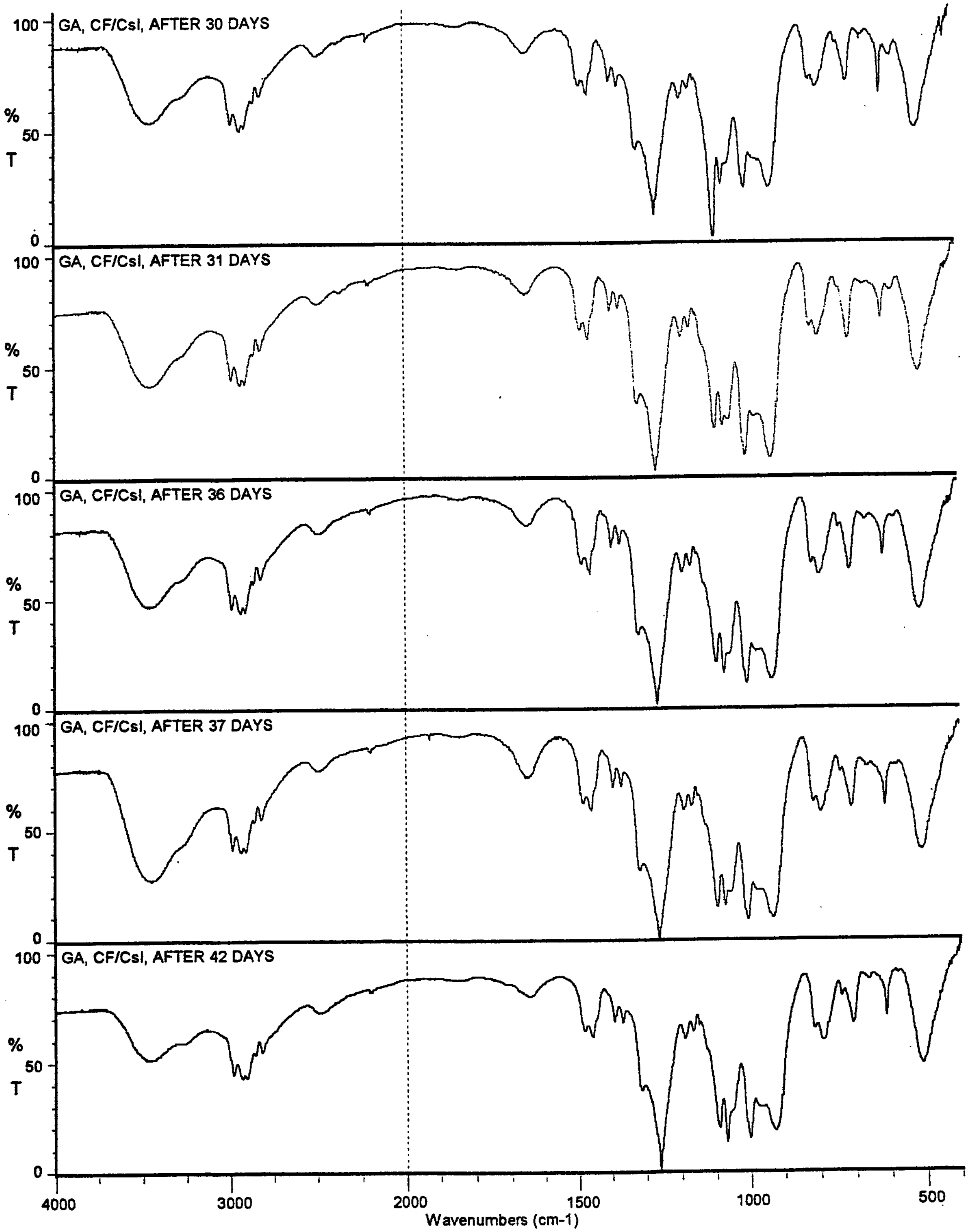

Figure 22 GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

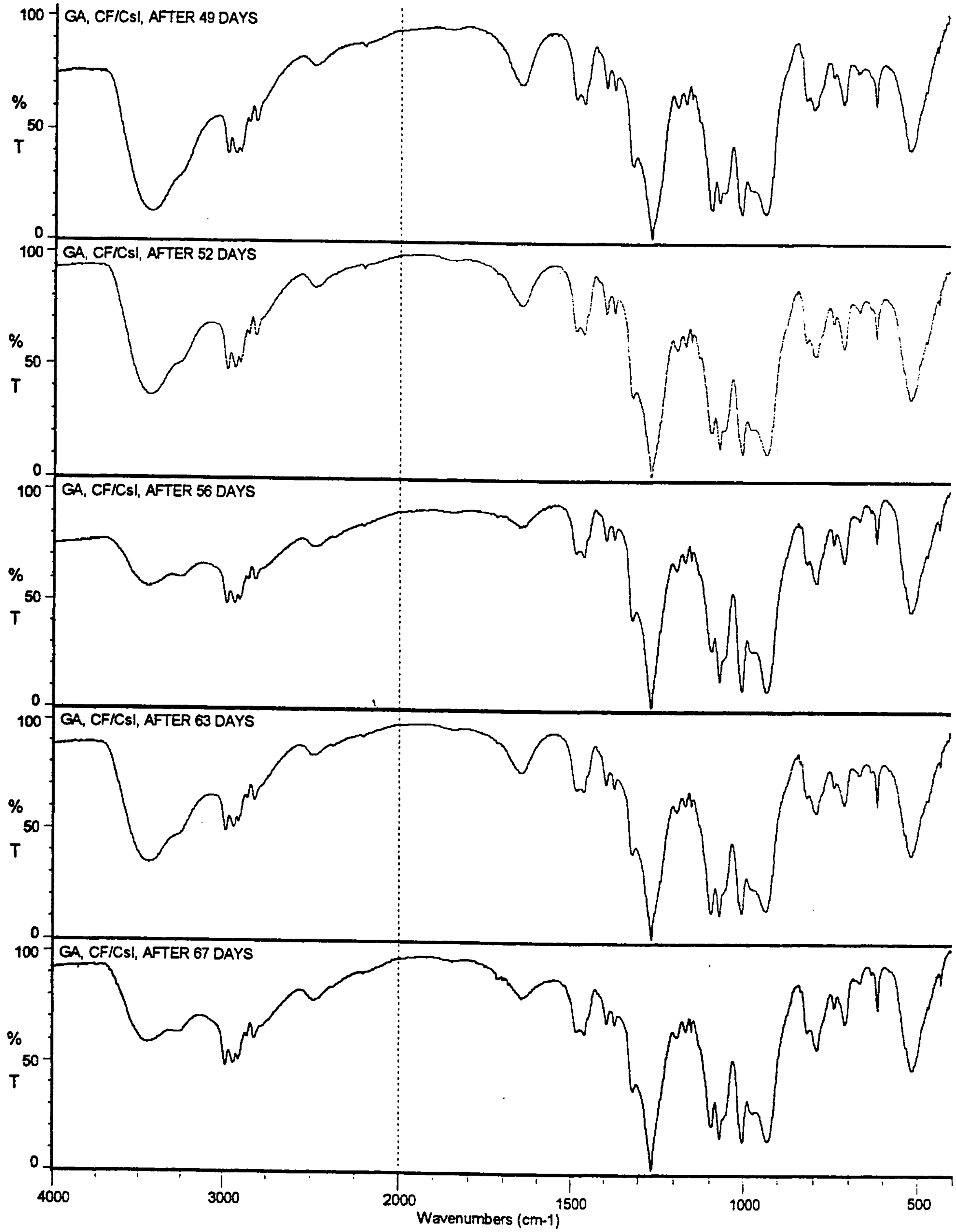

Figure 22 GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

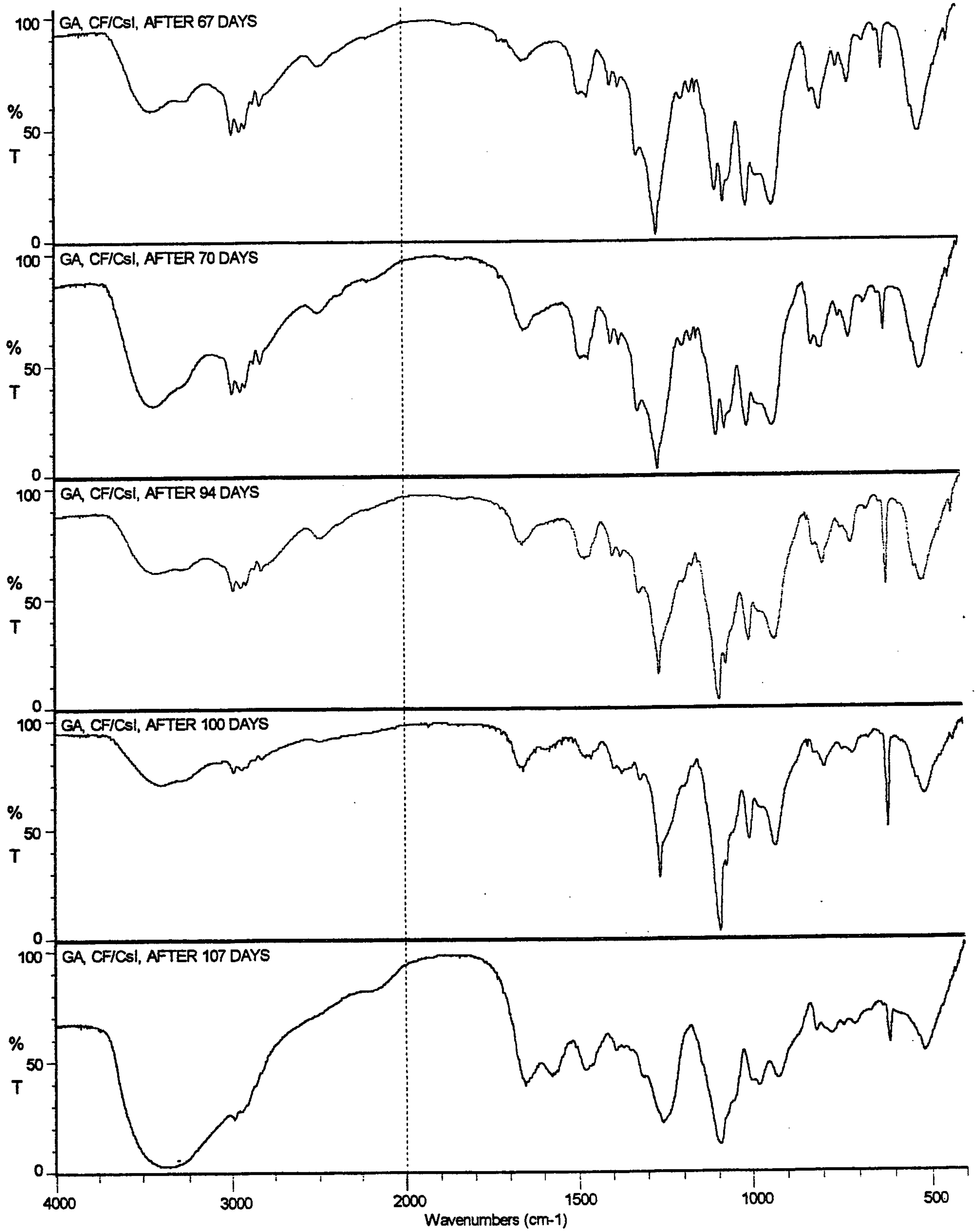

Figure 22 GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

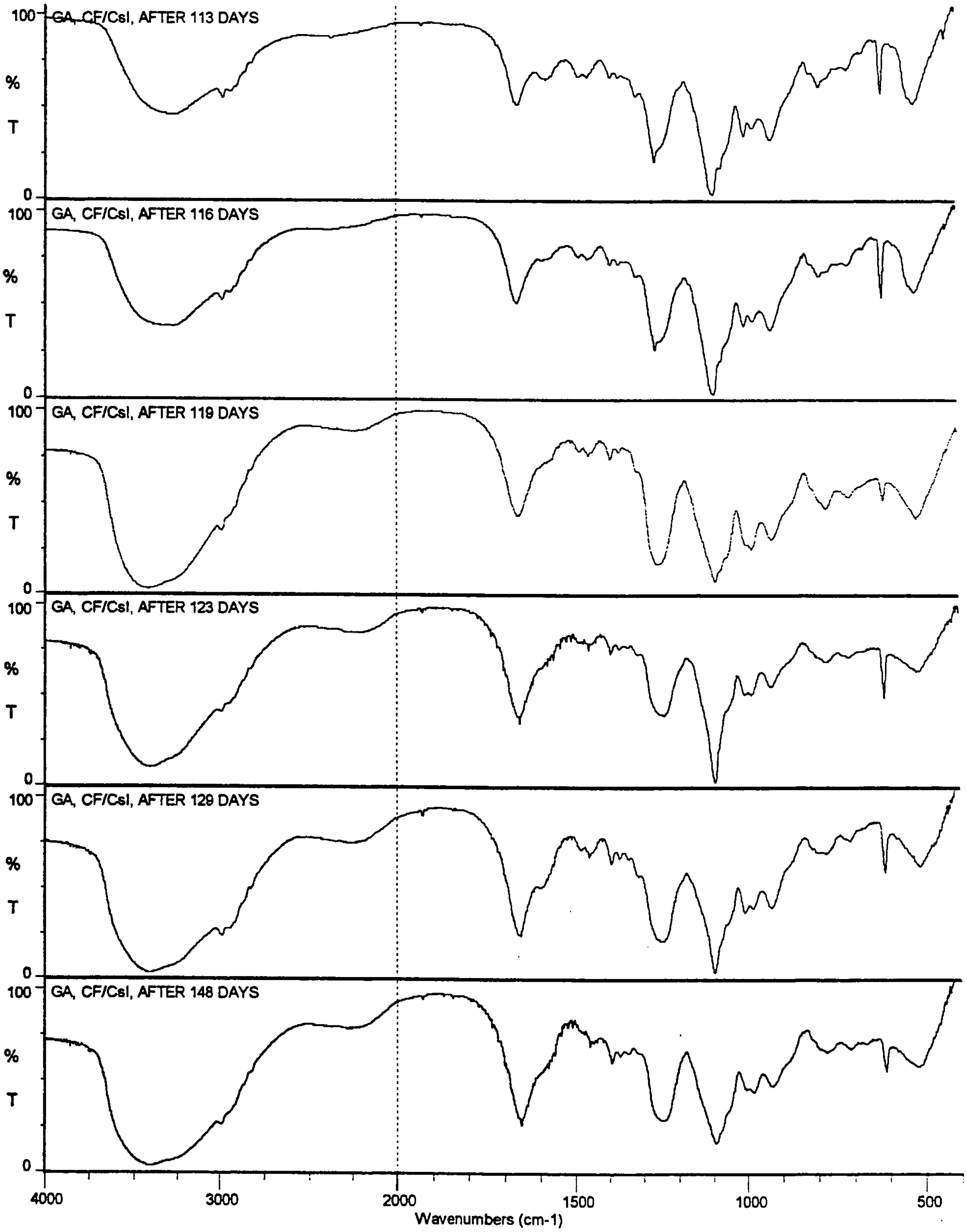

Figure 22 GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

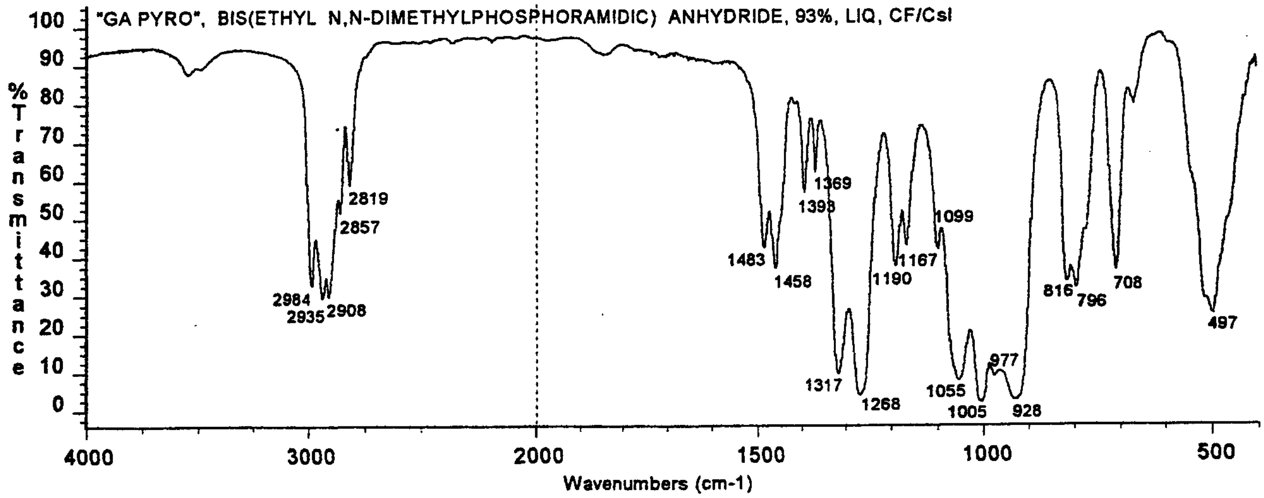

Figure 23 "GA PYRO", BIS(ETHYL N,N-DIMETHYLPHOSPHORAMIDIC ANHYDRIDE, 93%, LIQUID, CF/CsI

2984 cm^{-1} m, 2935 cm^{-1} m, 2908 cm^{-1} m, 2857 cm^{-1} w and 2819 cm^{-1} w (ν CH_3 and CH_2), 1483 cm^{-1} m (δ OCH_2), 1458 cm^{-1} m (δ CH_3), 1393 cm^{-1} w (ω OCH_2), 1369 cm^{-1} w (δ_{sy} CH_3), 1317 cm^{-1} ms [$P\text{-}N(CH_3)_2$], 1268 cm^{-1} s (ν P=O), 1190 cm^{-1} m [$P\text{-}N(CH_3)_2$], 1167 cm^{-1} w and 1099 cm^{-1} w (characteristic of POEt, CH_3 rock), 1055 cm^{-1} ms (ν P-O-C), 1005 cm^{-1} s (ν P-N-C), 977 cm^{-1} vw (ν C-C of POEt), 928 cm^{-1} s (ν P-O-P pyro moiety), 816 cm^{-1} m, 796 cm^{-1} m (POC), 708 m (PNC), 497 cm^{-1} m (δ P=O ?).

Figure 24 shows the effect of atmospheric moisture on the infrared spectrum of **GA PYRO**. The compound remains intact in excess of 154 days. At the 175 day mark there is some decrease in the intensities of the bands indicative of the $PN(CH_3)_2$ moiety (namely 1317, 1190, 1005 and 708 cm^{-1}). This decrease continues through the remainder of the observations until the last being at 212 days. After 212 days, some very weak absorption due to the $PN(CH_3)_2$ moiety is still visible at 1316, 1009 and 709 cm^{-1}. Bands are present at 1250 cm^{-1} (ν P=O), 1165 cm^{-1} vw (POEt), 1056 cm^{-1} s (ν P-O-C), 969 cm^{-1} sh (ν C-C of POEt), 923 cm^{-1} ms (ν P-O-P), 795 cm^{-1} w (POC). Bands at 1090 cm^{-1} s and 610 cm^{-1} w are probably due to Cs_2SO_4 from the CsI windows. Perhaps, another pyro compound such as (HO)(OEt)P(=O)-O-P=O(OH)(OEt) is being formed? The phosphoryl strectch of such a compound could occur near 1250 cm^{-1} (see the reference given in footnote[a]).

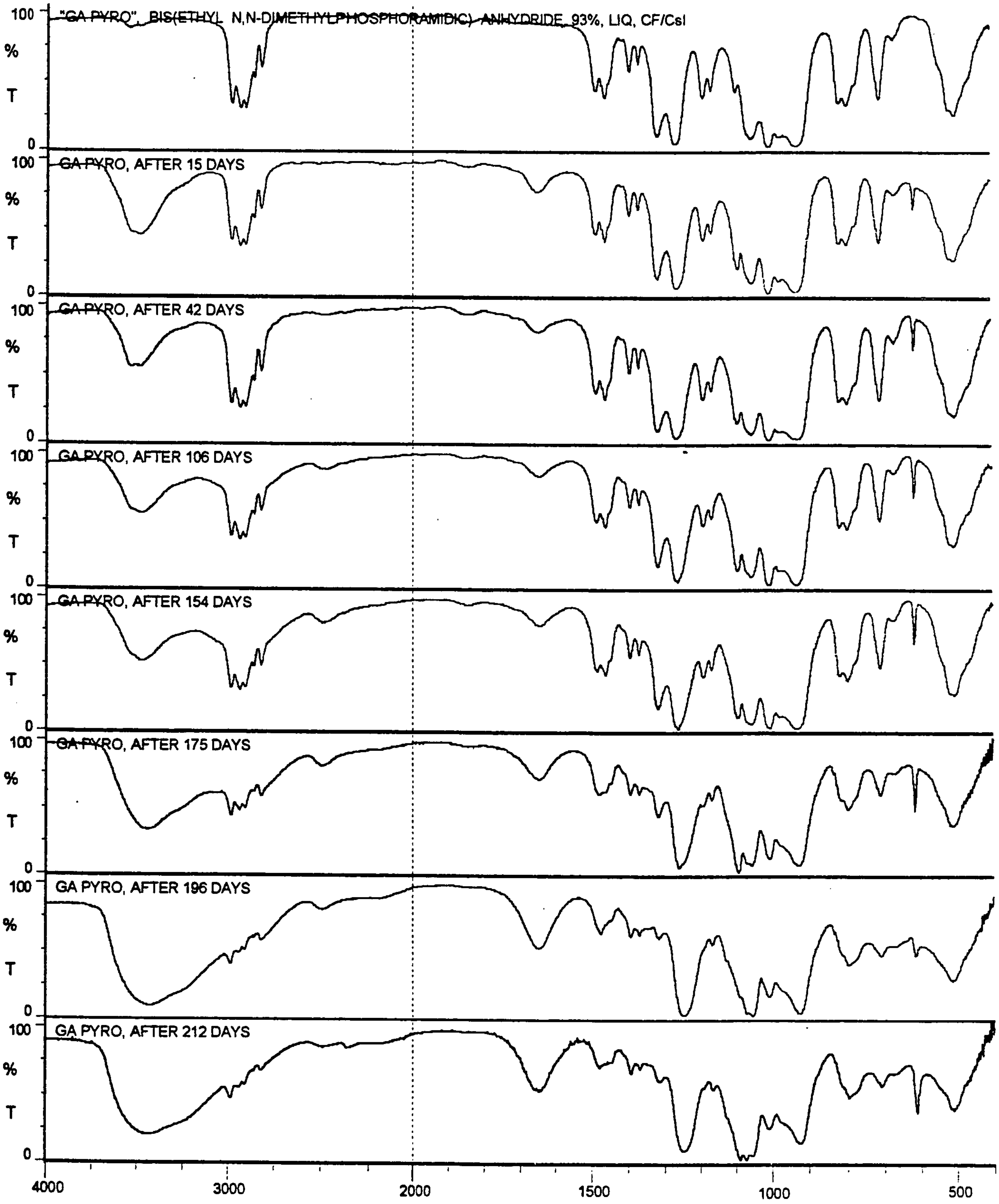

Figure 24 **EFFECT OF ATMOSPHERIC MOISTURE ON GA PYRO, LIQUID, CF/CsI**

3.1.10 Trimethylsilyl N,N-Dimethylphosphoramidofluoridate $(CH_3)_2NP{=}O(F)[OSi(CH_3)_3]$

The infrared spectrum of trimethylsilyl N,N-dimethylphosphoramidofluoridate is given is ***Figure 25***. The band assignments are as follows: 2963 cm^{-1} ms, 2905 cm^{-1} ms, 2862 cm^{-1} m and 2824 cm^{-1} m (ν CH), 1689 cm^{-1} w (The 855 cm^{-1} band is believed to be composed of two bands with contributions from both the Si(CH$_3$)$_3$ and ν P-F, ca. 859 and 830 cm^{-1} . The sum of these two bands would be ca. 1689 cm^{-1}), 1487 cm^{-1} m and 1459 cm^{-1} m (δ CH$_3$), 1420 cm^{-1} w (δ_{as} SiCH$_3$), 1321 cm^{-1} s [PN(CH$_3$)$_2$], 1286 cm^{-1} s (ν P=O, the calculated value for the ν P=O is 1302 cm^{-1} . The average of 1321 cm^{-1} and 1286 cm^{-1} is 1304 cm^{-1}), 1258 cm^{-1} s (δ_{sy} SiCH$_3$), 1192 cm^{-1} w [PN(CH$_3$)$_2$], 1050 cm^{-1} s (ν P-O-C), 1010 cm^{-1} s (ν P-N-C), 855 cm^{-1} s (probably-contribution from both the SiCH$_3$ rock and ν P-F), 764 cm^{-1} m [Si(CH$_3$)$_2$], 738 cm^{-1} or 661 cm^{-1} m [PN(CH$_3$)$_2$], 486 cm^{-1} ms (δ P=O ?).

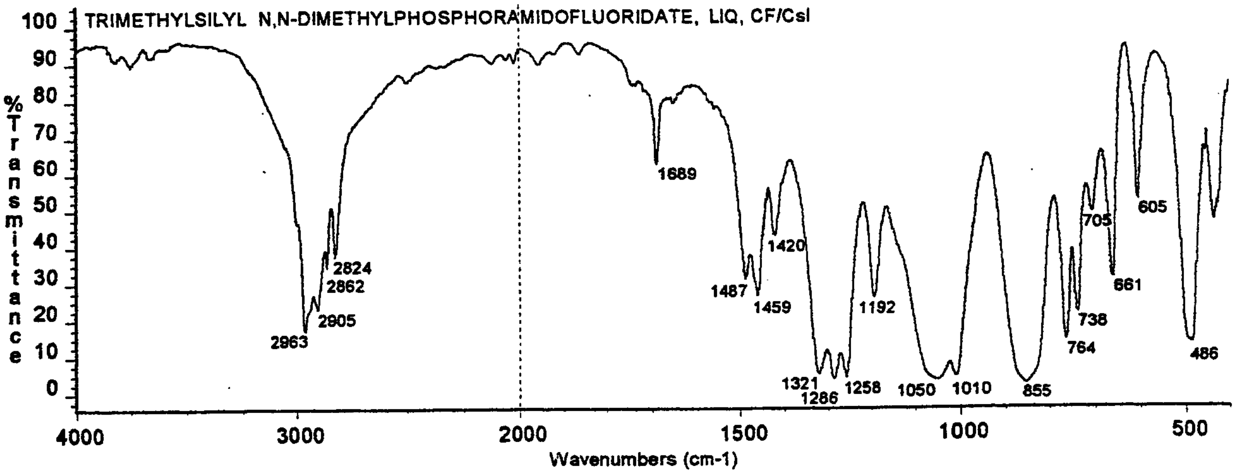

Figure 25A TRIMETHYLSILYL N,N-DIMETHYLPHOSPHORAMIDOFLUORIDATE, LIQUID, CF/CsI

The effect of atmospheric moisture on trimethylsilyl N,N-dimethylphosphoramidofluoridate is demonstrated in ***Figures 25A & B***. Even an soon as 1.5 hours changes are apparent in the infrared spectrum as evidenced by the new band near 2500 cm^{-1} and the broadening in the 3000 cm^{-1} region. After 19 hours dramatic changes are apparent, namely bands near 3070, 2800 and 2500 cm^{-1} (NH$_2^{\oplus}$), 1281 and 1103 cm^{-1} which may be assigned to the asymmetric and symmetric stretching of the PO$_2^-$ group. Bands due to the PN(CH$_3$)$_2$ (1321, 1192, 1010, 738 or 661 cm^{-1}) are now absent from the spectrum. The

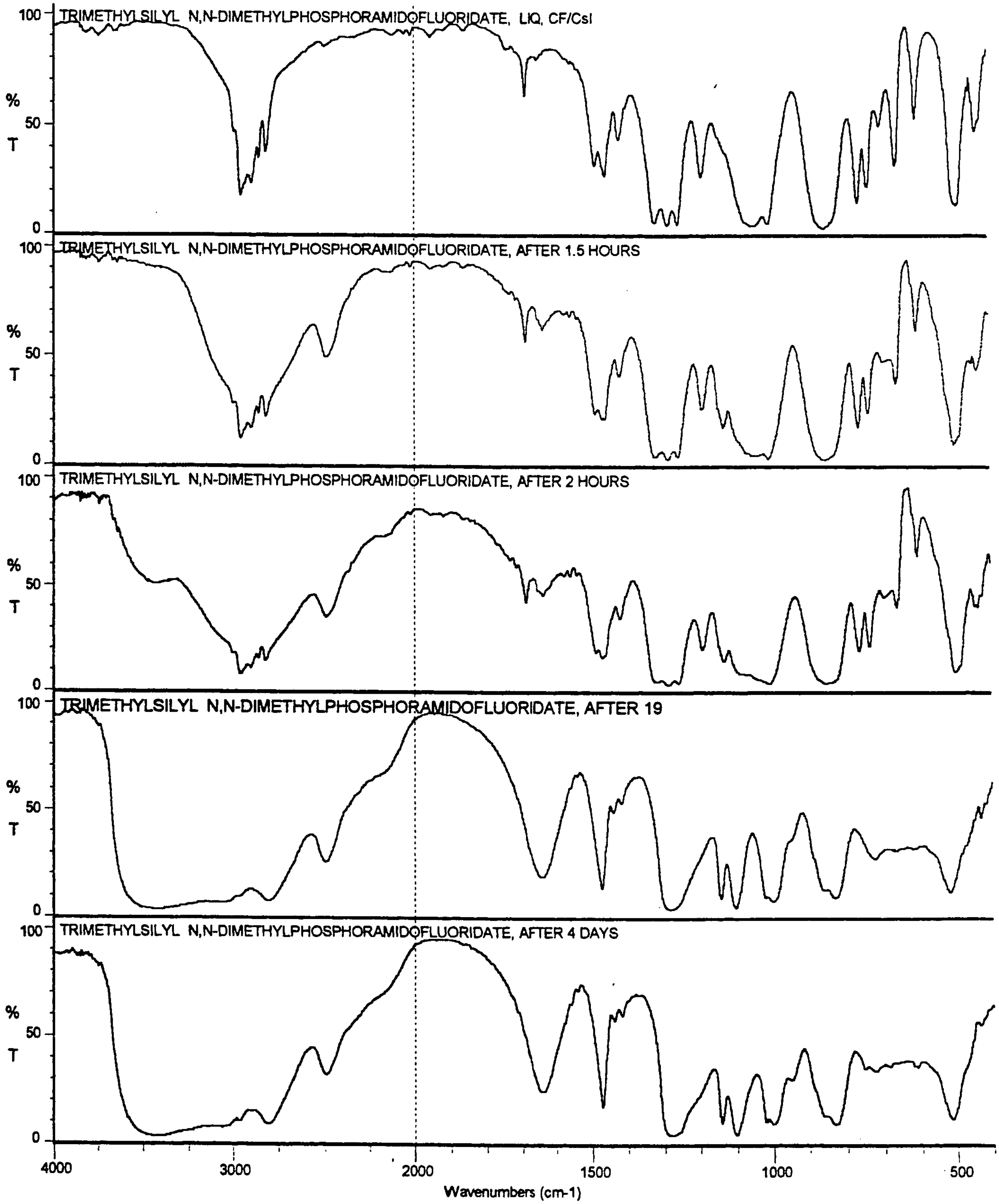

Figure 25B TRIMETHYLSILYL N,N-DIMETHYLPHOSPHORAMIDOFLUORIDATE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

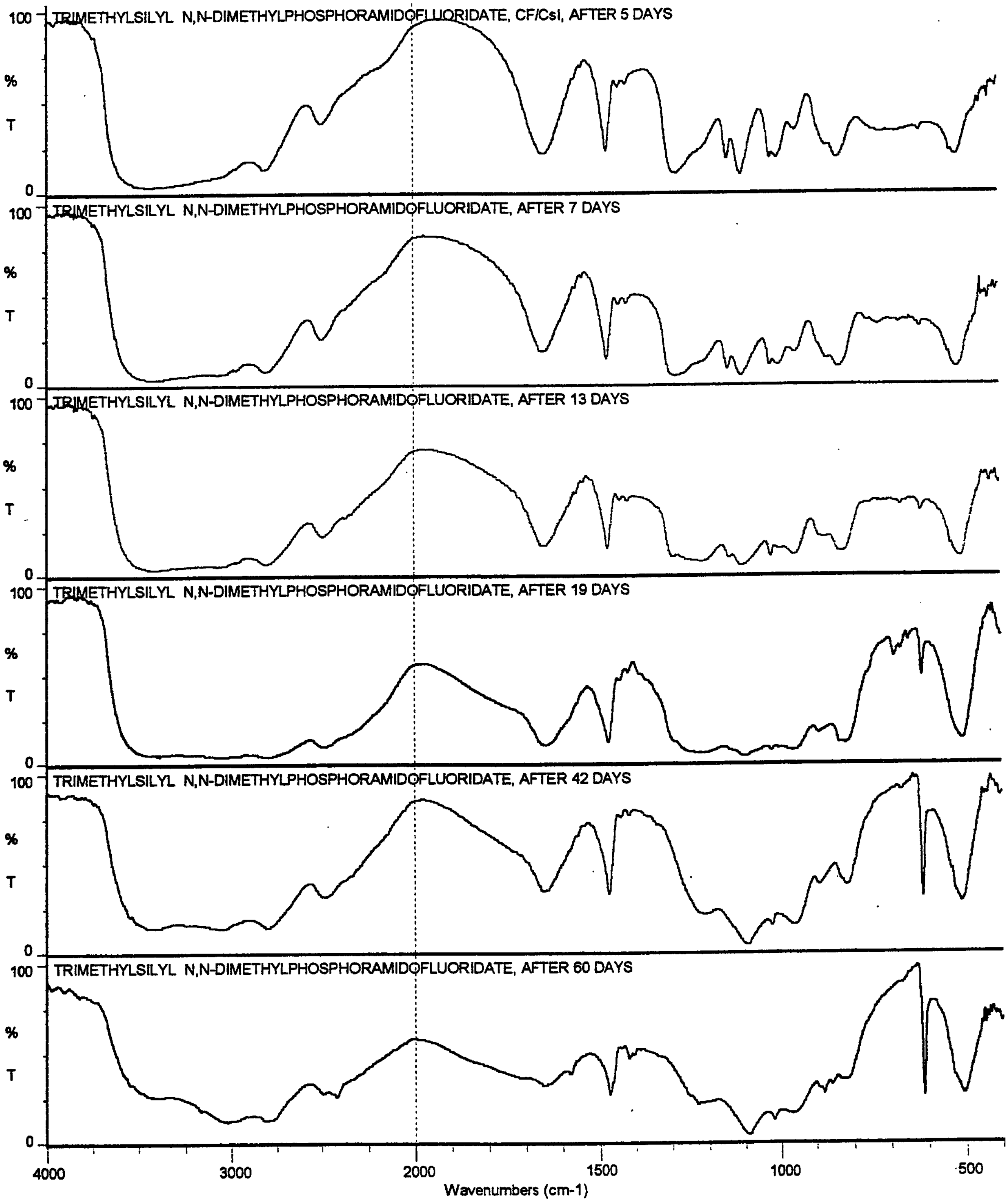

Figure 25B **TRIMETHYLSILYL N,N-DIMETHYLPHOSPHORAMIDOFLUORIDATE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE** (CONTINUED)

$Si(CH_3)_3$ group is still apparently present as the 1281 cm^{-1} may be partly due to this moiety. The bands at 859 and 830 cm^{-1} may still be due to the $Si(CH_3)_3$ and the P-F moieties. The band at 1000 cm^{-1} may be due to the P-OH group. The following compound may now be the prevalent species, $[HO\text{-}P(O_2)F]^- \, H_2N(CH_3)_2^{\oplus}$. The final compound after 42-60 days may result from the removal of the fluorine to give $[HOP(O_2)OH]^- \, H_2N(CH_3)_2^{\oplus}$. This is indicated by the drop in the ν_{as} PO_2^- from 1281 to 1209 cm^{-1} and the disappearance of the ν P-F band near 830 cm^{-1}. Also present during the 42-60 day period are bands at 1091 and 611 cm^{-1} which are believed to be due to the formation of Cs_2SO_4 from the cesium iodide windows.

3.2 Precursors of G-Agents

Methylphosphonous dichloride, **SW** CAS [676-83-5]

Phosphorus trichloride, **TH** CAS [7719-12-2]

Methylphosphonic chlorofluoride

Methylphosphonic dichloride, **DC**, **Dichlor** CAS [676-97-1]

Methyl methylphosphinate

Dimethyl phosphite CAS [868-85-9]

Trimethyl phosphite, **TMP** CAS [121-45-9]

Dimethyl methylphosphonate, **DMMP** CAS [756-79-6]

Hydrogen methyl methylphosphonate (methyl methylphosphonic acid)

Diisopropyl phosphite CAS [1809-20-7]

Triisopropyl phosphite CAS [116-17-6]

3,3-Dimethylbutanone-2 (pinacolone) CAS [75-97-8]

3.2.1 Methylphosphonous Dichloride (dichloromethylphosphine) SW $CH_3P(Cl)_2$

The infrared spectrum of methylphosphonous dichloride (**SW**), $CH_3P(Cl)_2$, is give in ***Figure 26***. The band assignments are as follows: 2992 cm^{-1} vvw, 2925 cm^{-1} vvw, 2905 cm^{-1} vvw (ν CH_3), 1405 cm^{-1}

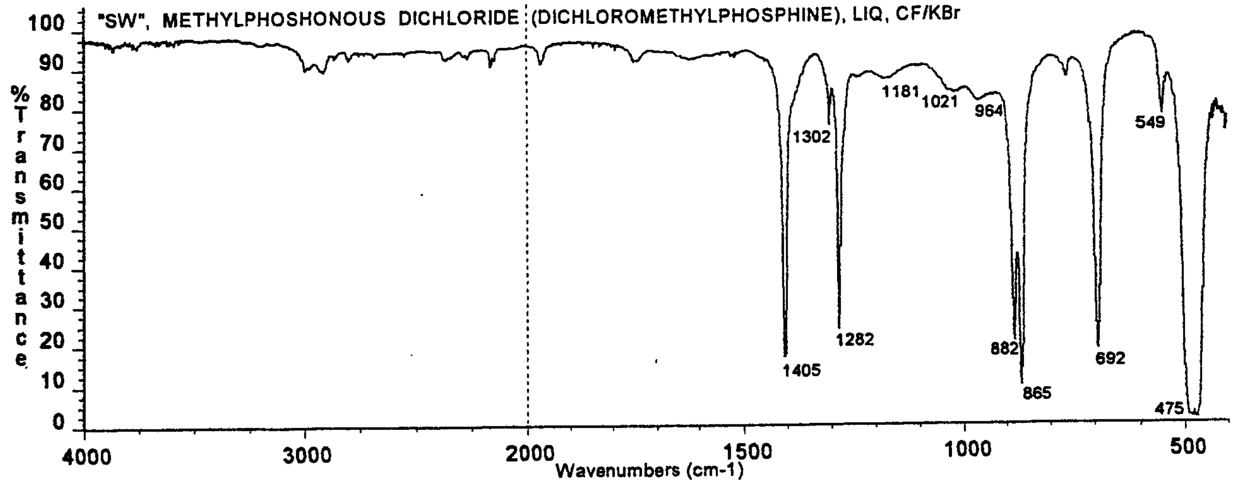

Figure 26 METHYLPHOSPHONOUS DICHLORIDE (SW), LIQUID, CF/KBr

m (δ_{as} P-CH$_3$), 1282 cm^{-1} m δsy P^{+3}-CH$_3$ (a very weak band at 1302 cm^{-1} is probably due to the δ_{sy} P^{+5}-CH$_3$), 1181 cm^{-1} vw broad ν P=O of an acid, hydrolysis product. The bands at 1021 and 964 cm^{-1} are also probably due to the ν P-O(H) and the ν P-O-P of a pyro moiety present as an impurity because of hydrolysis. The medium bands at 882 and 865 cm^{-1} are due to the P-CH$_3$ rocking vibration. The medium band at 692 cm^{-1} can be assigned to ν P-C. The strong band at 475 cm^{-1} is assigned to ν PCl$_2$.

The effect of atmospheric moisture on the spectrum of methylphosphonous dichloride is given in ***Figure 27***. As time progressed to 75 minutes, the spectrum showed the following: ca 2750, 2250 and 1680 cm^{-1} w broad (P-OH), ca 2430 cm^{-1} vw (ν P-H), 1405 vw cm^{-1} (δ_{as} P-CH$_3$), 1308 cm^{-1} w δ_{sy} P^{+5}CH$_3$ (the 1281 cm^{-1} δ_{sy} P^{+3}-CH$_3$ band is decreasing in intensity), 1180 cm^{-1} m (ν P=O), 1015 cm^{-1} s (P-H deformation), 961 cm^{-1} ν P-O(H), 882 cm^{-1} w P-CH$_3$ rock and 691 cm^{-1} ν P-C. The band at 473 cm^{-1} is decreasing in intensity and is assigned to the PCl$_2$ stretching vibration. As time passed the hydrolysis became more complete and the resultant spectrum resembled that of a phosphinic acid, namely methylphosphinic acid,CH$_3$P=O(H)(OH). The sample of **SW** left exposed to atmospheric moisture *overnight* is somewhat wetter than the 105 minute sample and thus shows a lower ν P=O (1180 to 1143 cm^{-1}). Thus the hydrolysis of **SW** may be represented by: CH_3PCl_2 -2 HOH-> CH_3P-O-H(OH) → CH_3P=O(H)(OH) + 2HCl.

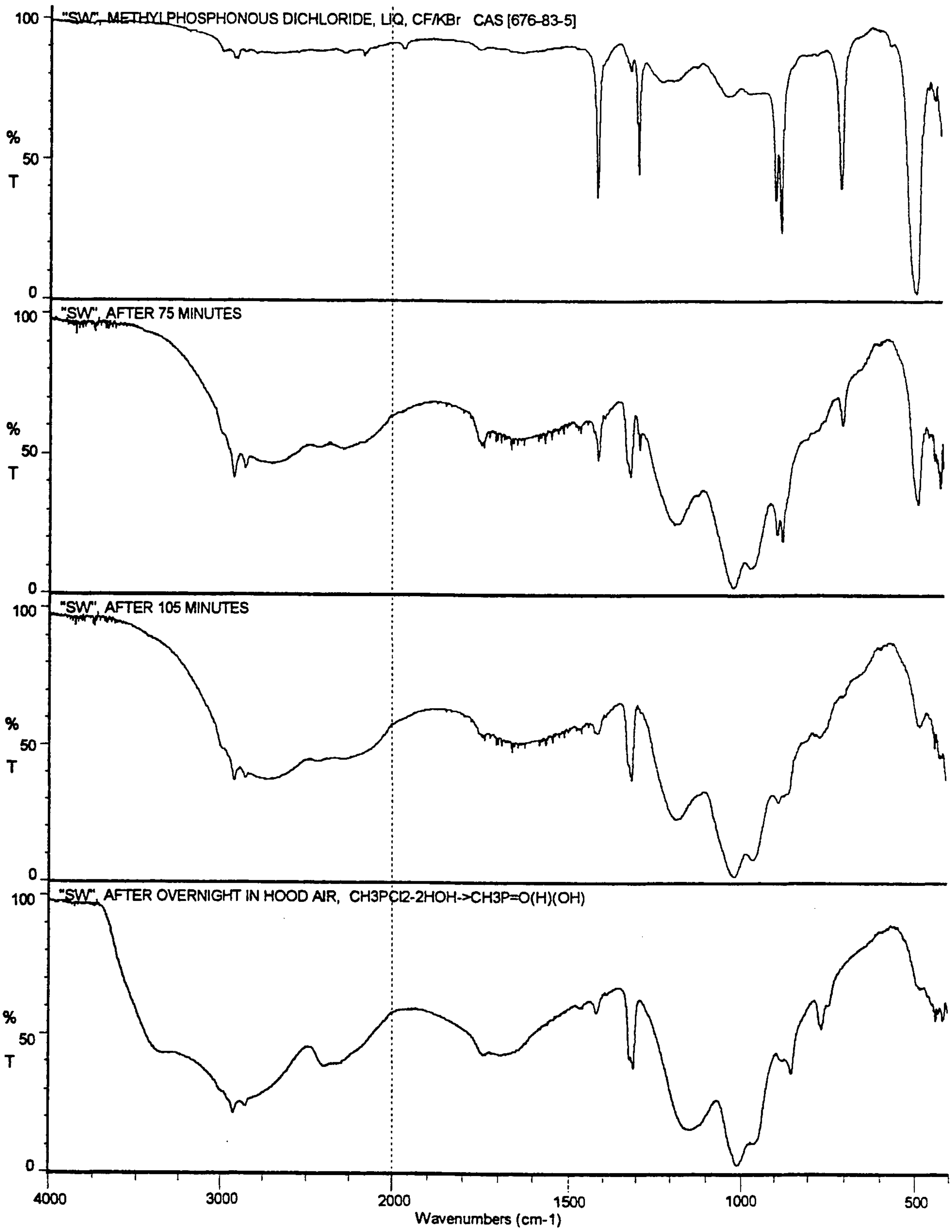

Figure 27 **EFFECT OF ATMOSPHERIC MOISTURE ON METHYLPHOSPHONOUS DICHLORIDE (SW), LIQUID, CF/KBr**

3.2.2 Methylphosphonic Dichloride (DC, Dichlor)

The infrared spectrum of methylphosphonic dichloride, $CH_3P{=}O(Cl)_2$, is given in ***Figure 28***. The bands may be assigned as follows: 3005 and 2919 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 1405 cm^{-1} w (δ_{as} P-CH_3), 1384 cm^{-1} vw (KNO_3 from the KBr windows), 1305 cm^{-1} m (δ_{sy} P-CH_3), 1271cm^{-1} s (ν P=O), 968 cm^{-1} vvw (ν P-OH or ν P-O-P ?), 895 cm^{-1} m (P-CH_3 rock), 764 cm^{-1} m (ν P-C), 539 cm^{-1} ms and 493 cm^{-1} m (ν_{as} and ν_{sy} P-Cl_2).

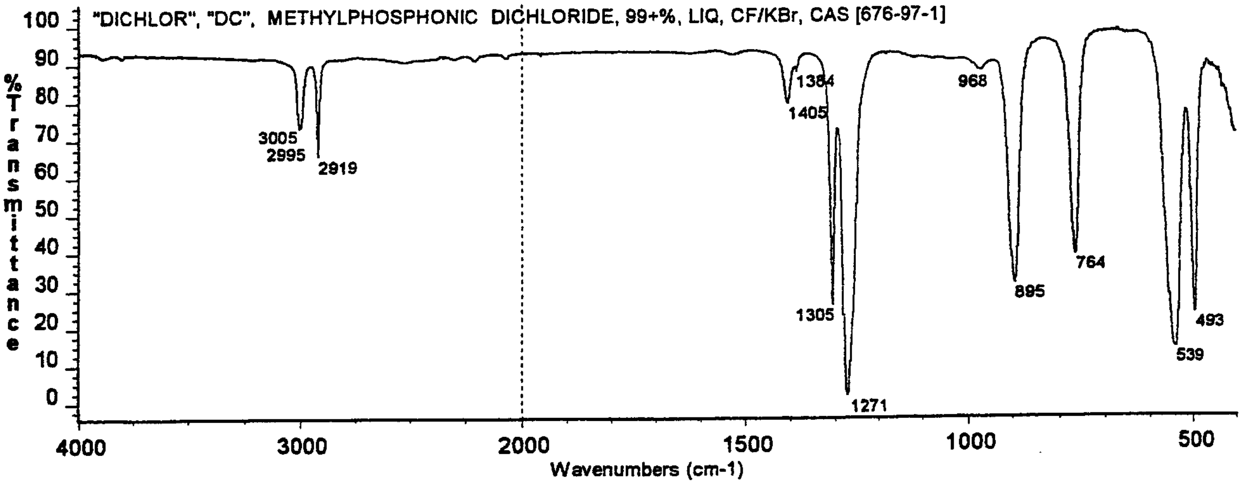

Figure 28 METHYLPHOSPHONIC DICHLORIDE (DICHLOR, DC), 99^{+}%, LIQUID, CF/KBr

The effect of atmospheric moisture on the infrared spectrum of methylphosphonic dichloride is given in ***Figure 29***. After an exposure of 22 hours to atmospheric moisture, the spectrum of **Dichlor** shows broad weak bands near 2800, 2340, 1650 cm^{-1} and a strong band at 1008 cm^{-1} due to the acid POH moiety. The PCl_2 bands at 546 and 495 cm^{-1} have become much weaker. The P=O stretching region shows multiple bands at 1270, 1256, 1242 cm^{-1} and some broad diffuse absorption near 1150 cm^{-1}. The first band 1270 cm^{-1} being from the **Dichlor**, while the other bands may be due to methylphosphonic anhydride (a pyro compound) and methylphosphonic acid as well as other intermediates. The infrared spectra after 3 and 14 days show mainly the presence of a very wet methylphosphonic acid (**MPA**), $CH_3\,P{=}O(OH)_2$. An infrared spectrum for a sample of water and **MPA** was reproduced earlier as ***Figure 20***.

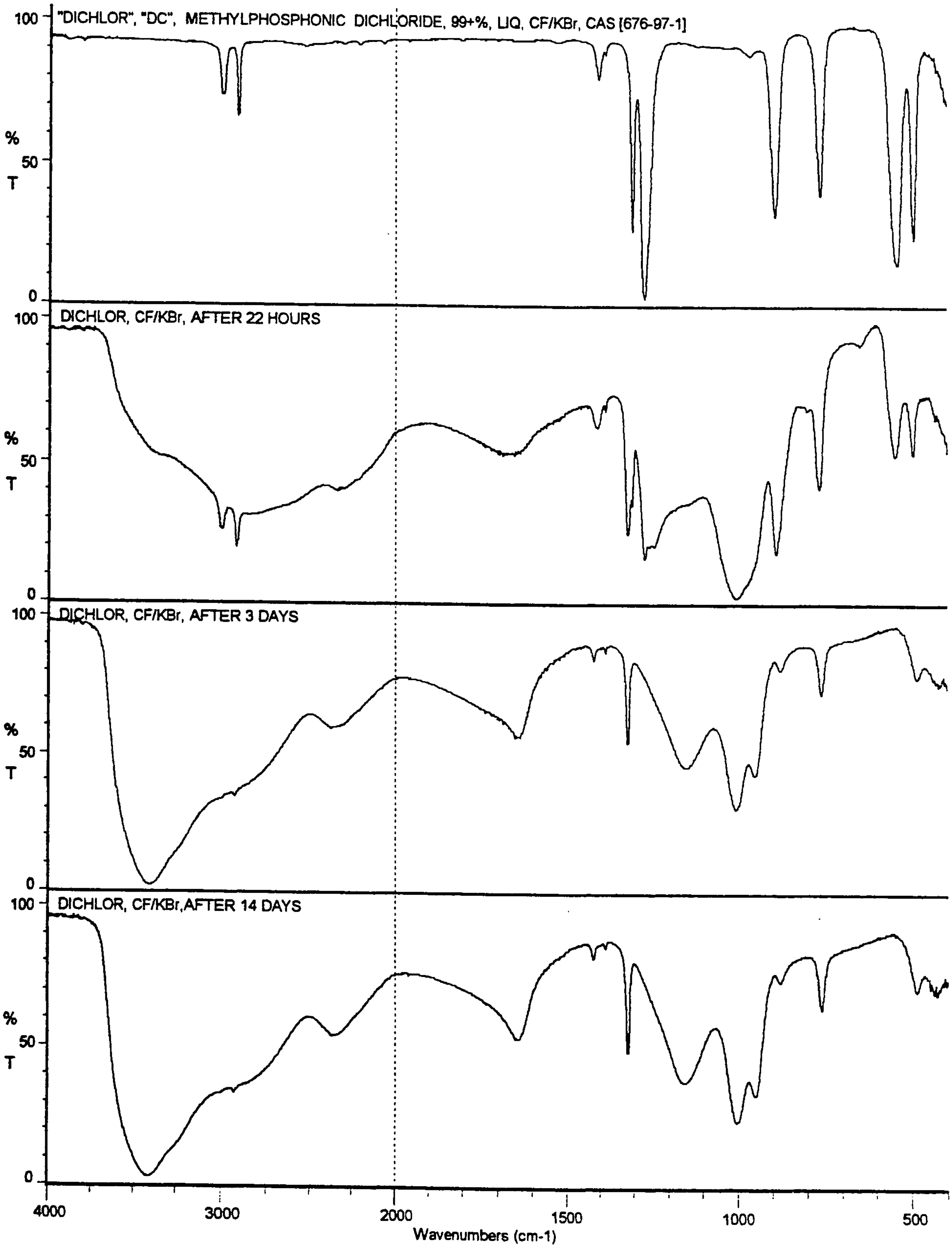

Figure 29 METHYLPHOSPHONIC DICHLORIDE, (DICHLOR, DC), LIQUID, CF/KBr, EXPOSED TO ATMOSPHERIC MOISTURE

3.2.3 Methylphosphonic Chlorofluoride $CH_3P=O(Cl)(F)$

The infrared spectrum of methylphosphonic chlorofluoride, $CH_3P=O(Cl)(F)$. is reproduced in ***Figure 30***. Band assignments are as follows: 3009 w and 2927 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 2567 cm^{-1} vw broad (POH), 1409 cm^{-1} w (δ_{as} P-CH_3), 1384 cm^{-1} vvw (KNO_3 from the KBr windows), 1319 cm^{-1} s (δ_{sy} P-CH_3), 1292 cm^{-1} s (ν P=O), 1006 cm^{-1} w (ν P-OH), ca 950 cm^{-1} sh (ν P-O-P pyro ?), 922 cm^{-1} s and 901 cm^{-1} ms (P-CH_3 antisymmetrical and symmetrical rocking respectively), 858 cm^{-1} ms (ν P-F), 762 cm^{-1} s (ν P-C), ca 655 cm^{-1} vvw (pyro ?), 541 cm^{-1} s (ν P-Cl), 423 cm^{-1} ms (P-F bending).

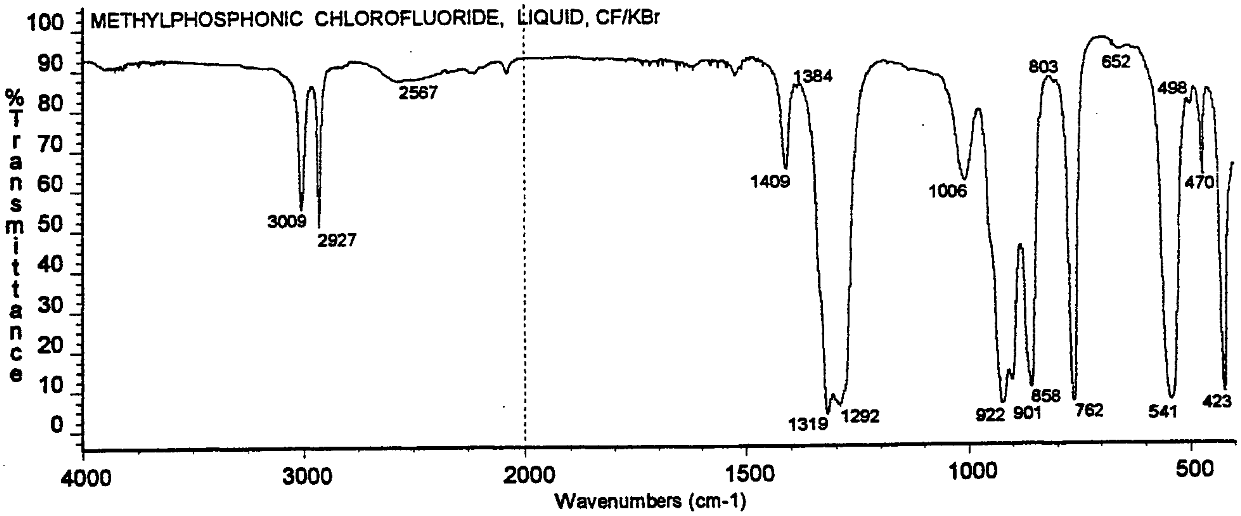

Figure 30 METHYLPHOSPHONIC CHLOROFLUORIDE, LIQUID, CF/KBr

The effect of atmospheric moisture on the infrared spectra of methylphosphonic chlorofluoride is given in ***Figure 31***. After 1 day in moist air the liquid film showed mainly the **Fluoro Acid**, methylphosphonofluoridic acid, $CH_3P=O(F)(OH)$, with some residual ν P-F still visible at 855 cm^{-1}. Over the period of 4 to 12 days, the spectrum is mainly that of a very wet specimen of methylphosphonic acid (**MPA**), $CH_3P=O(OH)_2$. This last spectrum (after 12 days) may be compared to ***Figure 20*** which is the infrared spectrum of an authentic but very wet sample of **MPA**. The hydrolysis of methylphosphonic chlorofluoride may be summarized as follows:

$CH_3P=O(Cl)(F)$ -HOH-> $CH_3P=O(F)(OH)$ + HCl ↑ -HOH-> $CH_3P=O(OH)_2$ + HF ↑

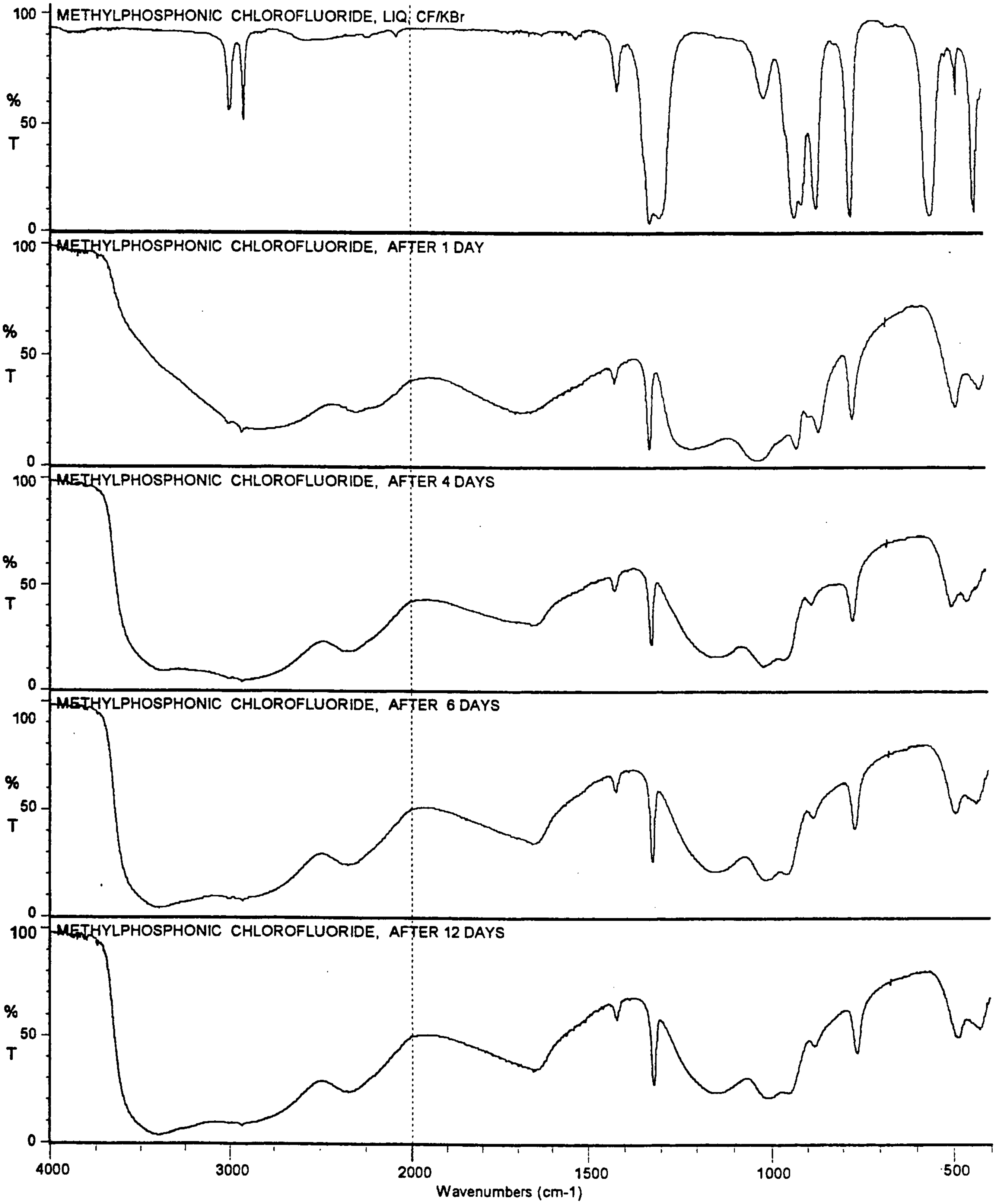

Figure 31 EFFECT OF ATMOSPHERIC MOISTURE ON METHYLPHOSPHONIC CHLOROFLUORIDE, LIQUID, CF/KBr

3.2.4 Phosphorus Trichloride (TH) PCl_3

The infrared spectrum of phosphorus trichloride (**TH**) is reproduced in ***Figure 32***. The infrared spectrum of phosphorus trichloride (**TH**) showed the following bands: 1384 cm^{-1} (KNO_3 from the KBr windows), 1301 cm^{-1} (ν P=O possibly from $POCl_3$, which has a ν P=O of 1298 cm^{-1}), 991 cm^{-1} (ν P-OH ?), 485 cm^{-1} (ν PCl_3).

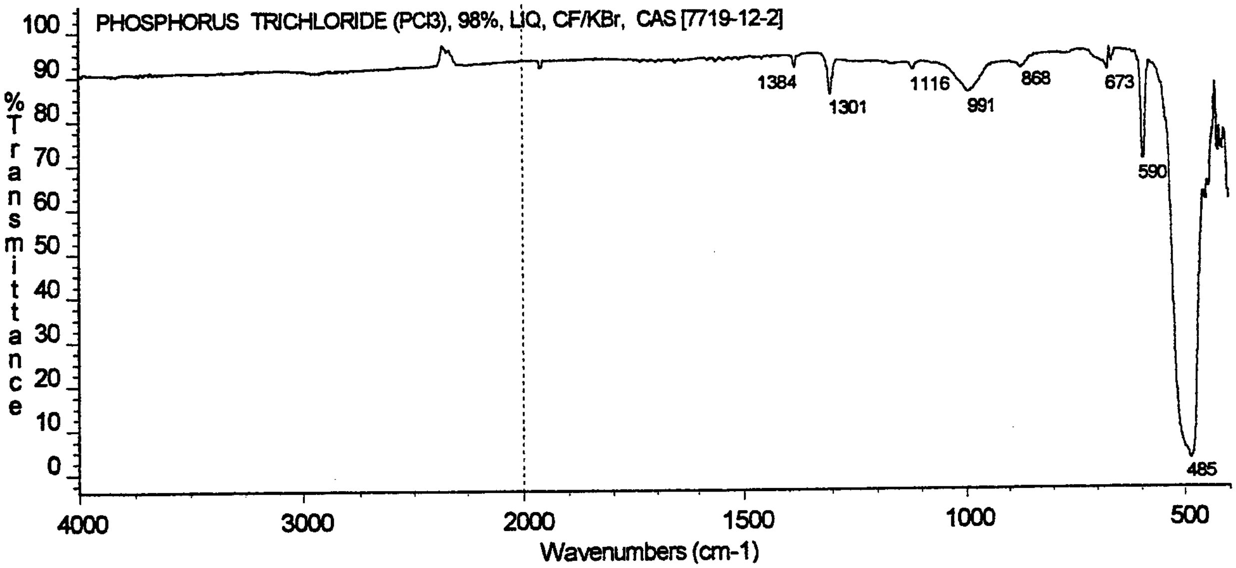

Figure 32 PHOSPHORUS TRICHLORIDE (TH), 98%, LIQUID, CF/KBr

The effect of atmospheric moisture on the infrared spectrum of phosphorus trichloride (**TH**) is presented in ***Figure 33***. After 30 minutes, the presence of a P-acid moiety is evident by the bands at 2799, 2451, ca 1650, 1159, 1005 and 937 cm^{-1} . The 2451 cm^{-1} band may also be due to the ν P-H of a compound such as $H\text{-}P{=}O(OH)_2$, phosphorous acid (H_3PO_3). After 60 minutes the PCl_3 band, which was at 485 cm^{-1} , is gone. The final product(s) ater 5 days may be a combination of products such as $H\text{-}P{=}O(OH)_2$, and $HO\text{-}P{=}O(OH)_2$. The former compound arising from the hydrolysis of PCl_3 , while the latter compound (phosphoric acid, H_3PO_4) coming from the oxidation of PCl_3 followed by hydrolysis:

PCl_3 -HOH-> $H\text{-}O\text{-}P(Cl)_2$ --> $H\text{-}P{=}O(Cl)_2$ -HOH-> $H\text{-}P{=}O(HO)(Cl)$ -HOH-> $H\text{-}P{=}O(OH)_2$

PCl_3 -[O]-> $O{=}P(Cl)_3$ -HOH-> $HO\text{-}P{=}O(Cl)_2$ -HOH-> $HO\text{-}P{=}O(OH)(Cl)$ -HOH-> $P{=}O(OH)_3$

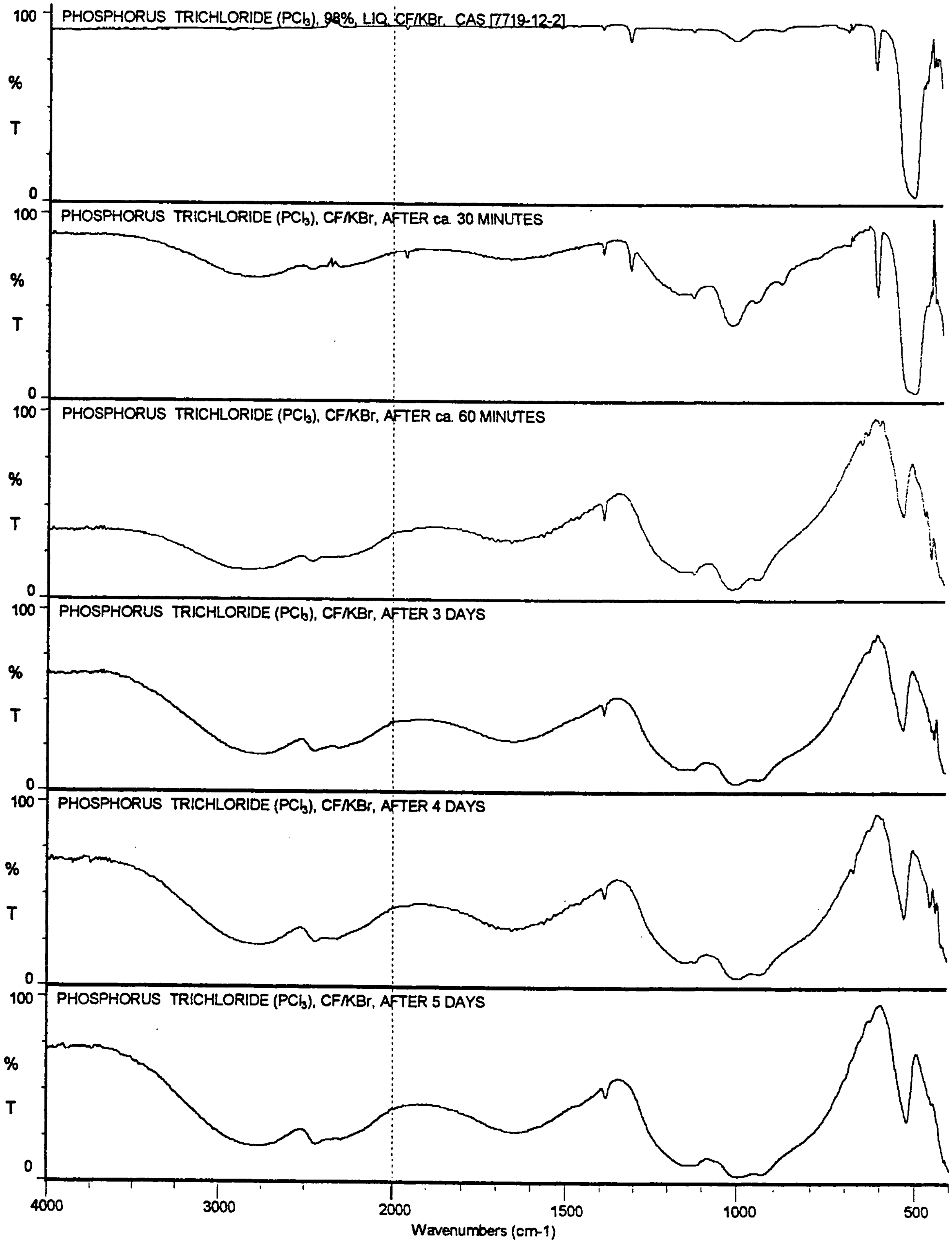

Figure 33 EFFECT OF ATMOSPHERIC MOISTURE ON PHOSPHORUS TRICHLORIDE, LIQUID, CF/KBr

3.2.5 Dimethyl Phosphite $H\text{-}P{=}O(OCH_3)_2$

The infrared spectrum of dimethyl phosphite, $H\text{-}P{=}O(OCH_3)_2$, is given in ***Figure 34***. The band assignments are as follows: 3000 cm^{-1} vw, 2958 cm^{-1} w (ν_{as} CH_3), 2854 cm^{-1} w (ν_{sy} CH_3), 2428 cm^{-1} vw (ν P-H), 1465 cm^{-1} w (δ CH_3), 1384 cm^{-1} vvw (KNO_3 from the KBr windows), 1267 cm^{-1} s (ν P=O), 1187 cm^{-1} w (CH_3 rock, characteristic of $POCH_3$), 1082 m and 1045 cm^{-1} ms (ν P-O-C), 977 cm^{-1} s (P-H deformation), 825 m and 780 cm^{-1} w (POC), 546 cm^{-1} w (P=O deformation).

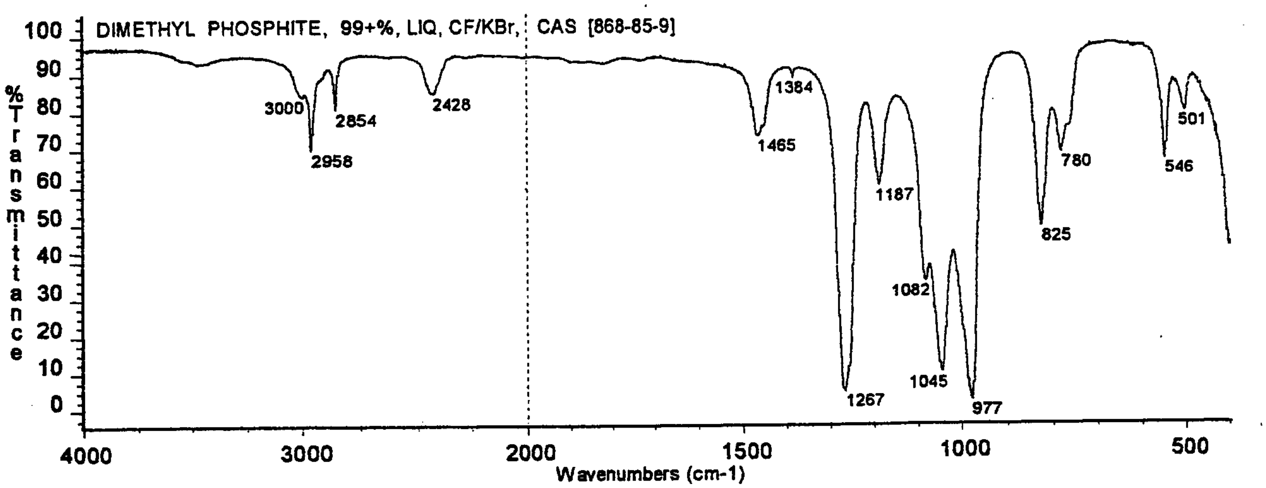

Figure 34 DIMETHYL PHOSPHITE, 99^{+}%, LIQUID, CF/KBr

The effect of environmental moisture of the infrared spectrum of dimethyl phosphite is illustrated in ***Figure 35***. The infrared spectrum remains essentially the same up to the time of 44 hours of exposure to atmospheric moisture. New weak bands appear near 3494 and 1650 cm^{-1} due to the adsorbtion of water by the compound. A dramatic change is visible in the infrared spectrum after 6 days have elapsed. Bands indicative of the P-acid moiety are evident near 2800 w, 2300 w, 1650 w, 1010 s and 939 cm^{-1} w (P-OH), 2430 cm^{-1} w (ν P-H), 1150 cm^{-1} m (ν P=O), 525 cm^{-1} w (P=O deformation). No bands appear to be present from the OCH_3 groups, as these appear to have been hydrolyzed off. The spectrum stays essentially the same up to the 41 day mark, with just a slight increase in the amount of adsorbed water. The final spectrum appears to be consistent with that expected for the compound, phosphorous acid, $P(OH)_3$, that is $H\text{-}P{=}O(OH)_2$.

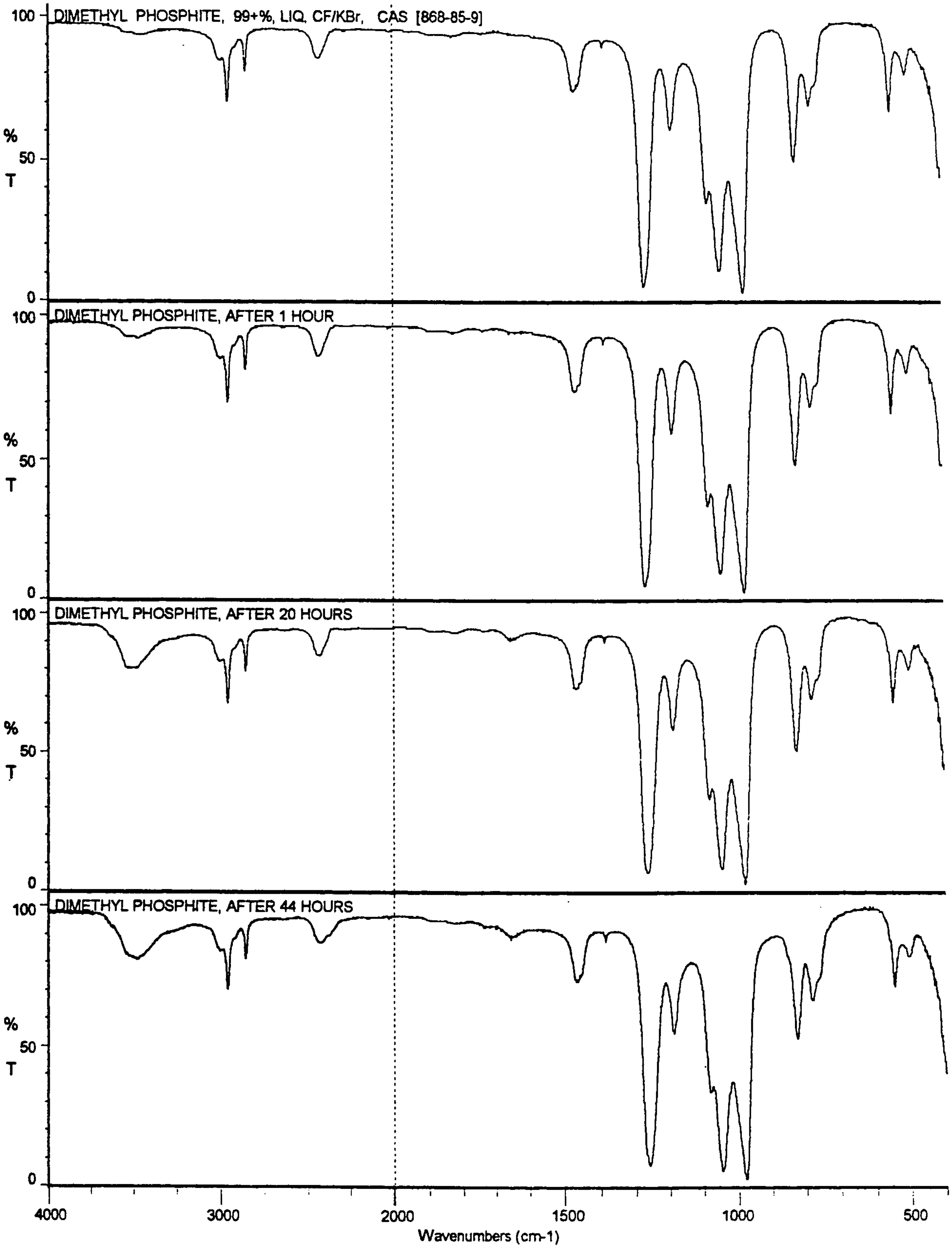

Figure 35 EFFECT OF ATMOSPHERIC MOISTURE ON DIMETHYL PHOSPHITE, LIQUID, CF/KBr

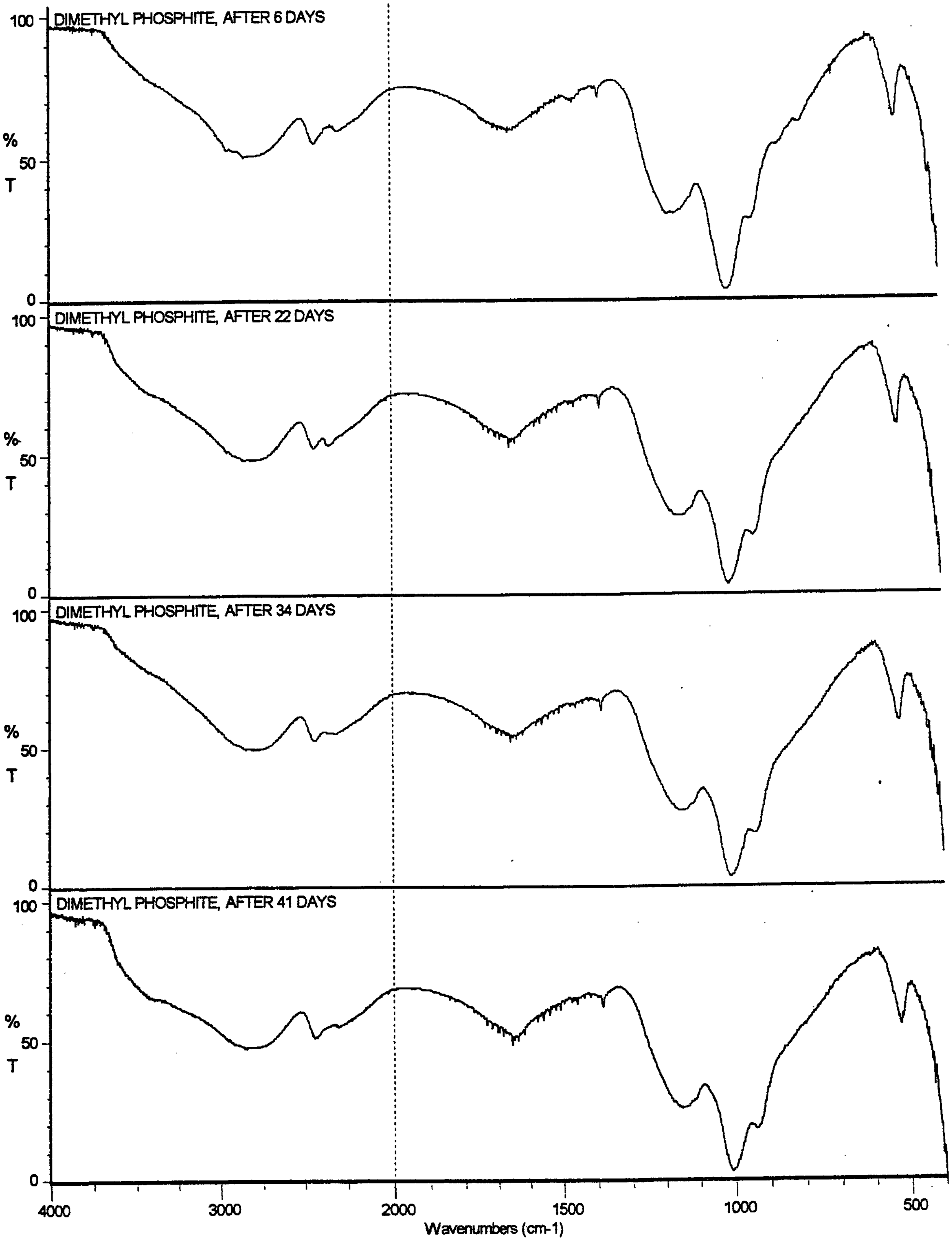

Figure 35 EFFECT OF ATMOSPHERIC MOISTURE ON DIMETHYL PHOSPHITE, LIQUID, CF/KBr (CONTINUED)

3.2.6 Trimethyl Phosphite (TMP) $P(OCH_3)_3$

The infrared spectrum of trimethyl phosphite (TMP) is reproduced in ***Figure 36***. The band assignments are as follows: 2986 cm^{-1} vw, 2946 cm^{-1} w (ν_{as} CH$_3$), 2836 cm^{-1} w (ν_{sy} CH$_3$), 1458 cm^{-1} vw (δ CH$_3$), 1384 cm^{-1} vvw (KNO$_3$ from the KBr windows), 1181 cm^{-1} w (CH$_3$ rock, characteristic of POCH$_3$), 1057 cm^{-1} sh and 1013 cm^{-1} s (ν P-O-C), 768 cm^{-1} sh and 729 cm^{-1} m (POC), 513 cm^{-1} vw (POC).

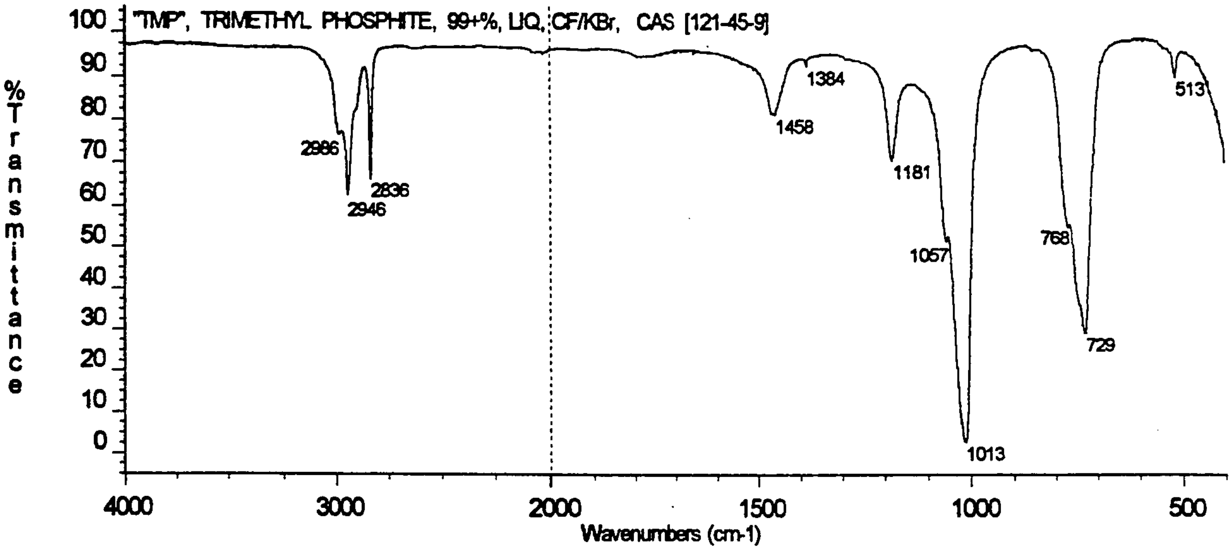

Figure 36 TRIMETHYL PHOSPHITE, 99$^+$%, LIQUID, CF/KBr

The effect of the environment on the infrared spectrum of a film of liquid trimethyl phosphite between KBr windows is presented in ***Figure 37***. After 2.5 hours the liquid film shows the beginnings of a band near 1280 cm^{-1} and one near 852 cm^{-1}. These are due to a ν P=O and a POC vibration respectively. The P^{+3} compound is being oxidized to a P^{+5} compound, namely trimethyl phosphate, $O{=}P(OCH_3)_3$. This conversion is more predominant after one day. The band in the 1 day spectrum at 1384 cm^{-1} is due to KNO$_3$ from the KBr windows used to support the liquid film. Thus the resultant spectrum for trimethyl phosphite exposed to the atmosphere (over a period of 1 day) is not one of hydrolysis but one of oxidation to trimethyl phosphate. The sample also appears to be evaporating, so any longer exposure times are not practical.

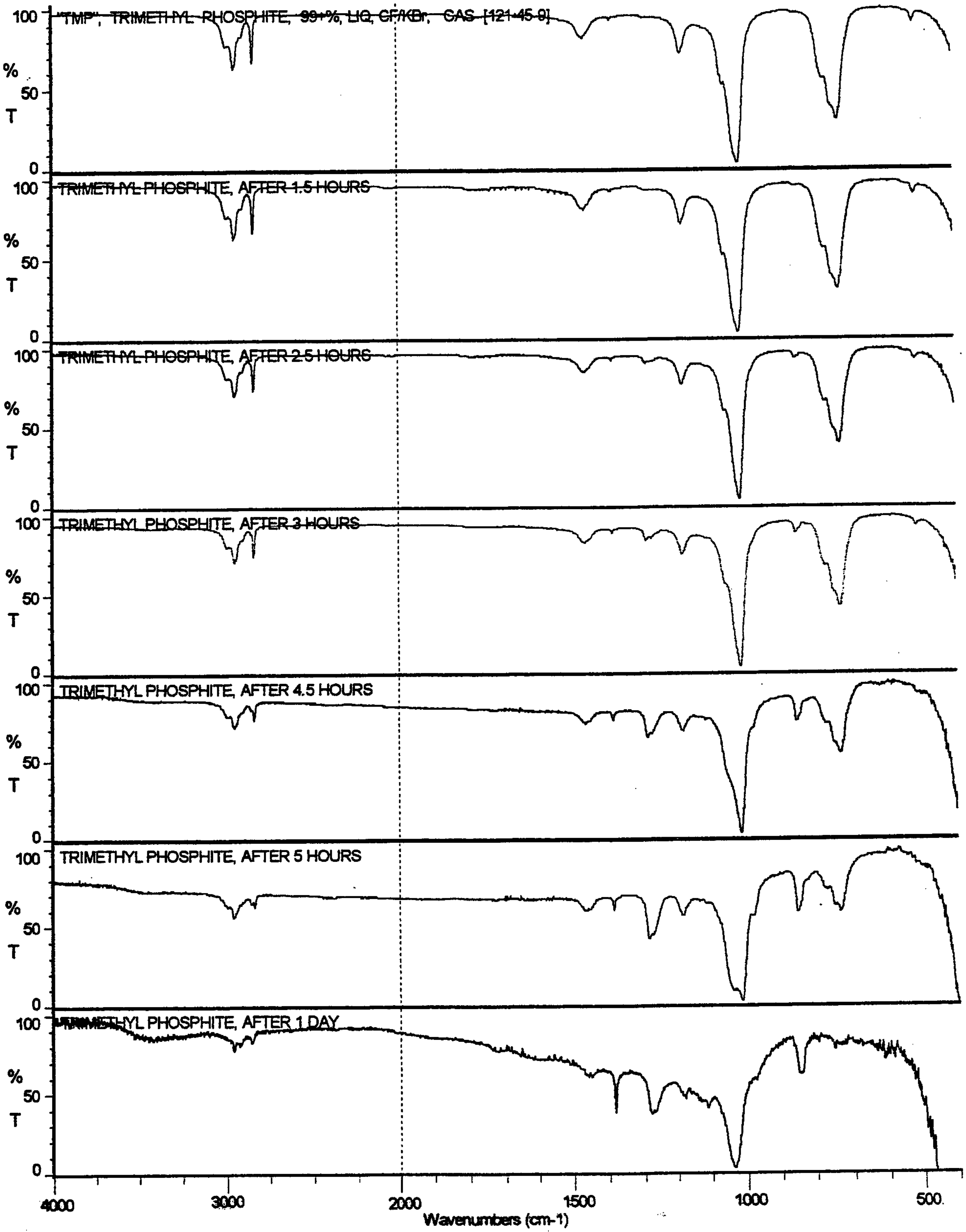

Figure 37 EEFECT OF THE ENVIRONMENT ON TRIMETHYL PHOSPHITE, LIQUID, CF/KBr

3.2.7 Diisopropyl Phosphite $HP{=}O[OCH(CH_3)_2]_2$

The infrared spectrum of diisopropyl phosphite is give in ***Figure 38***. The band assignments are as follows: 3446 cm^{-1} vw (H_2O), 2981m, 2936 w and 2878 cm^{-1} vw (ν_{as} and ν_{sy} CH_3 and ν CH), 2423 cm^{-1} w (ν P-H), 1468 cm^{-1} w and 1456 cm^{-1} sh (δ_{as} CH_3), 1387 and 1377 cm^{-1} m (doublet, δ_{sy} CH_3), ca 1354 cm^{-1} sh (δ C-H), 1259 cm^{-1} ms (ν P=O), 1179 w, 1143 w and 1110 cm^{-1} m (a triplet characteristic of P-O-isopropyl), 974 cm^{-1} s (ν P-O-C and P-H deformation ?), 768 cm^{-1} w (POC), 555 cm^{-1} w (δ P=O).

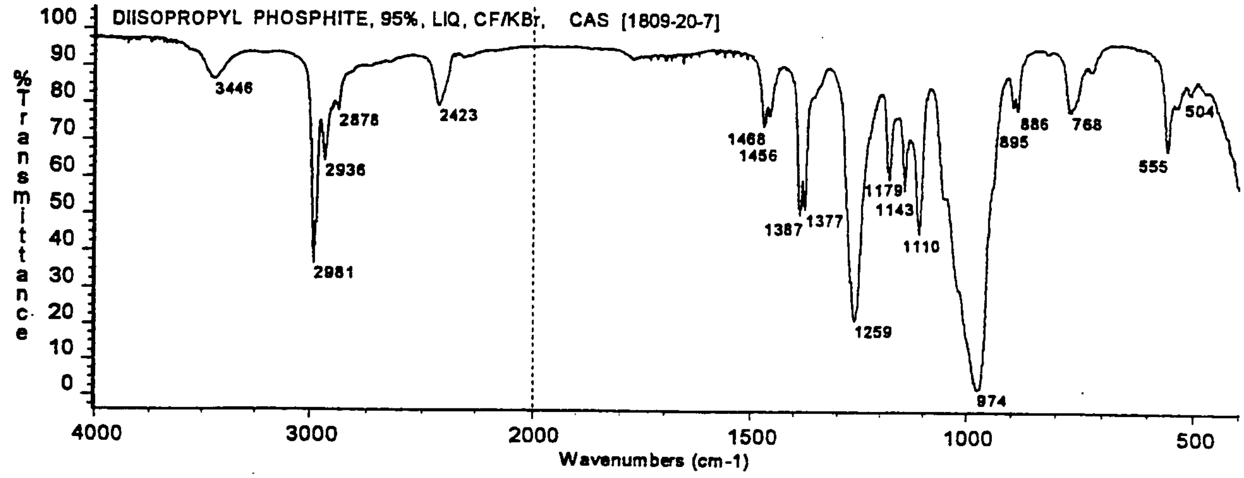

Figure 38 DIISOPROPYL PHOSPHITE, 95%, LIQUID, CF/KBr

The effect of atmospheric moisture on diisopropyl phosphite is represented by the infrared spectra reproduced in ***Figure 39***. After the first day the compound has picked up some water as evidenced by the bands at 3452 and 1653 cm^{-1}. The ν P=O has also decreased in value from 1259 to 1252 cm^{-1} due to the water. After 6 days the spectrum resembles that of a P-acid with bands at ca 2700, 2280, 1675, 1225, and 1000 cm^{-1} being due entirely or in part to the POOH moiety. The ν P-H is still visible at 2423 cm^{-1}. At the 13 day mark the bands due to isopropyl moiety have become much weaker. One of the O-isopropyl groups has been hydrolyzed off to leave the resultant compound, H-P=O(OH)(O-isopropyl). As time progresses the bands assignable to the isopropyl moiety have almost completely disappeared from the infrared spectra. The resultant compound after the 98th day appears to be almost entirely phosphorous acid, H_3PO_3, that is, $H{-}P{=}O(OH)_2$. The hydrolysis may be represented as follows: $HP{=}O(O\text{-}iPr)_2$ -HOH-> $HP{=}O(OH)(O\text{-}iPr)$ -HOH-> $HP{=}O(OH)_2$.

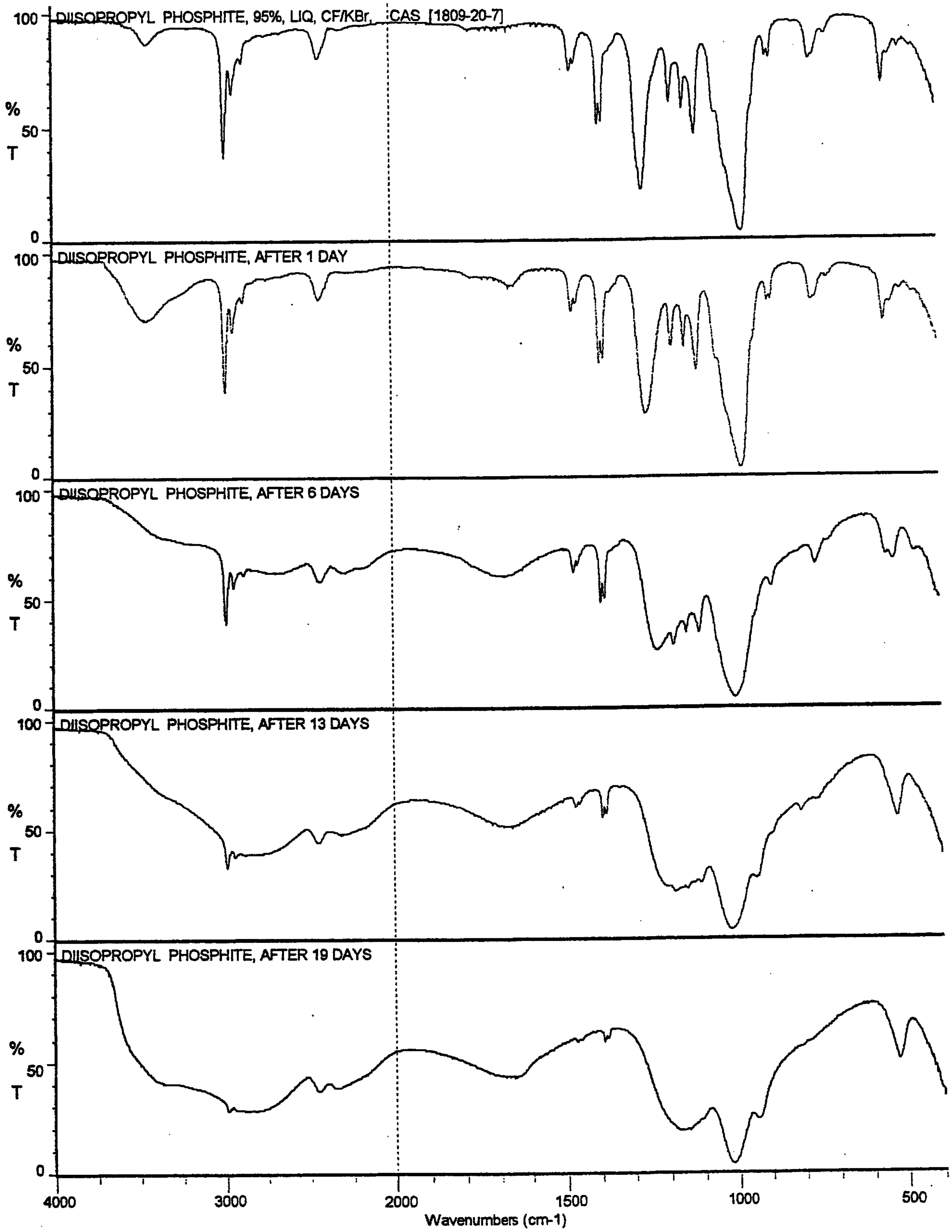

Figure 39 EFFECT OF ATMOSPHERIC MOISTURE ON DIISOPROPYL PHOSPHITE, LIQUID, CF/KBr

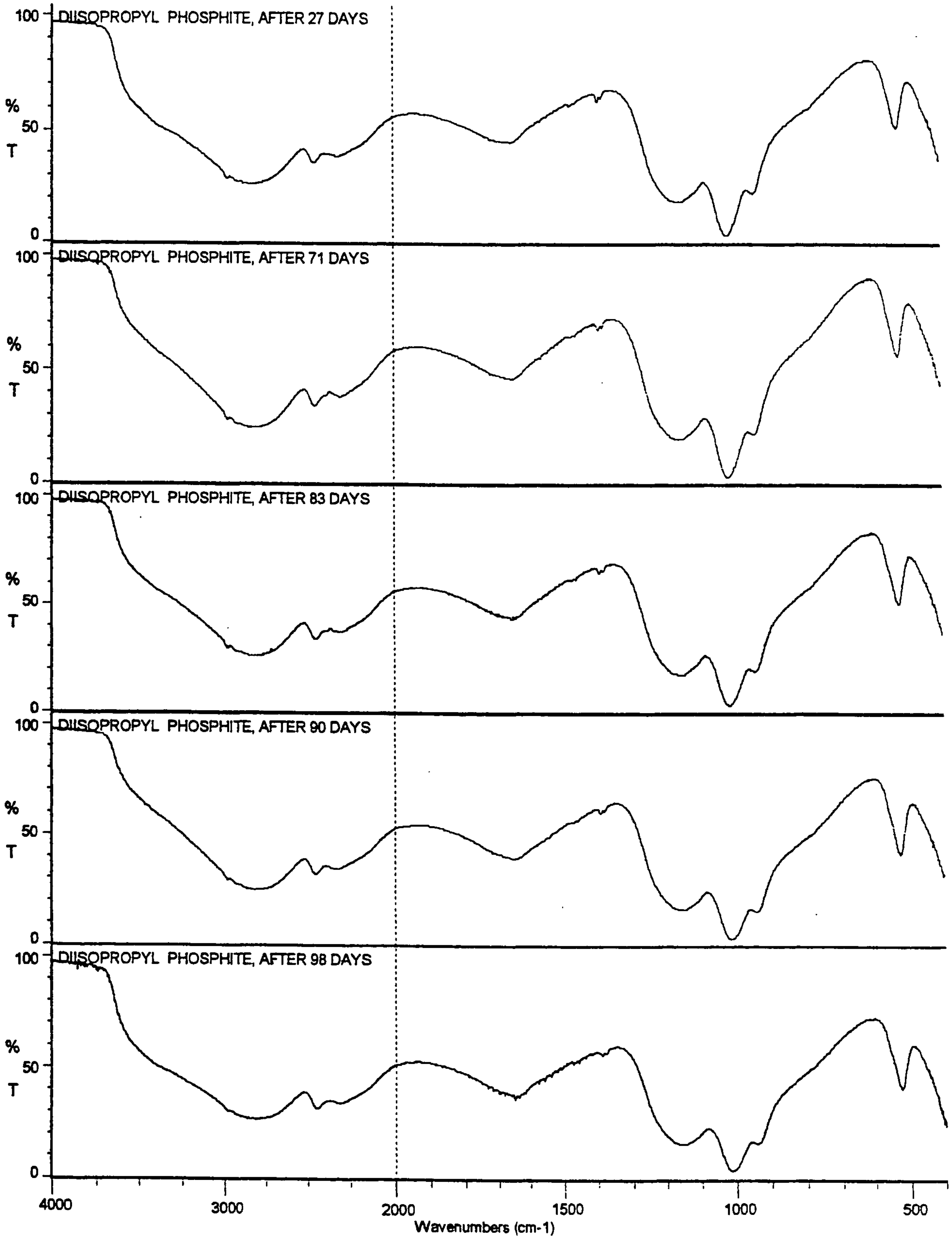

Figure 39 EFFECT OF ATMOSPHERIC MOISTURE ON DIISOPROPYL PHOSPHITE, LIQUID, CF/KBr (CONTINUED)

3.2.8 Triisopropyl Phosphite $P[O\text{-}CH(CH_3)_2]_3$

The infrared spectrum of triisopropyl phosphite is given in ***Figure 40***. The band assignments are as follows: 2974 cm^{-1} ms, 2932 cm^{-1} m, and 2876 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 1466 and 1453 cm^{-1} w (δ_{as} CH_3), 1383 and 1371 cm^{-1} m doublet (δ_{sy} CH_3), 1351 cm^{-1} w (δ C-H), 1280 and 1263 cm^{-1} vw (ν P=O of triisopropyl phosphate ?), 1176 cm^{-1} m, 1138 cm^{-1} m and 1109 cm^{-1} ms (characteristic of P-O-isopropyl), 1000 cm^{-1} m and 957 cm^{-1} ms (ν P-O-C), 858 cm^{-1} ms (CH_3 rock of isopropyl group), 771 amd 741 cm^{-1} m (POC), 541 cm^{-1} w (P=O deformation ?).

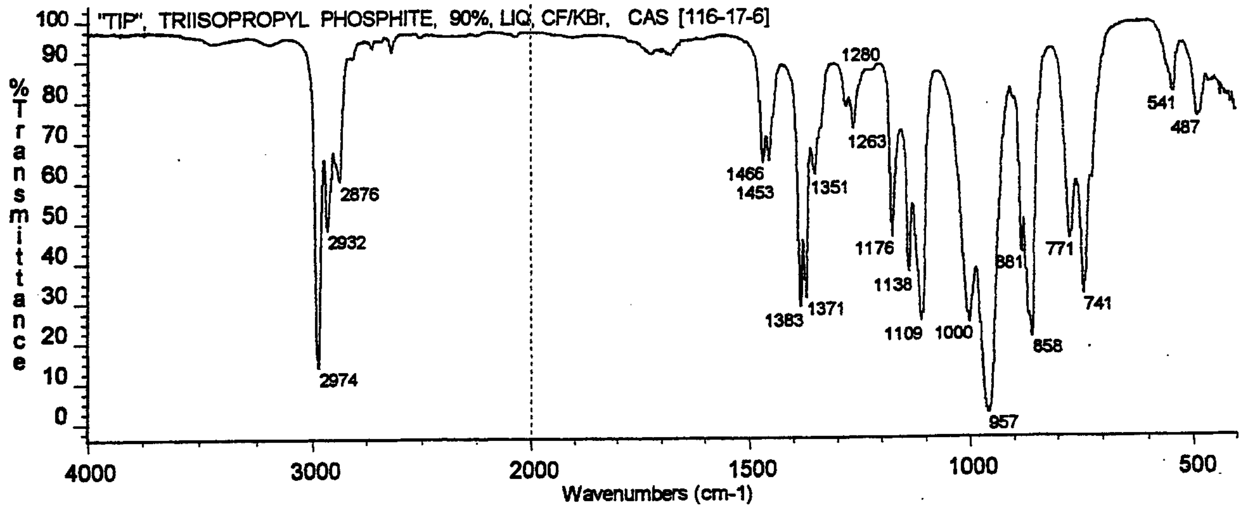

Figure 40 TRIISOPROPYL PHOSPHITE, 90%, LIQUID, CF/KBr

The effect of atmospheric moisture on triisopropyl phosphite is presented in ***Figure 41***. After 19 hours of exposure to atmospheric moisture the infrared spectrum show a very weak band at 2425 cm^{-1} due to P-H stretching. The bands at 1278 and 1262 cm^{-1} are increasing in intensity. Apparently two effects are occurring. On the one hand, hydrolysis is occurring to produce possibly $H\text{-}P\text{=}O(O\text{-}iPr)_2$, while concurrently oxidation is causing the formation of $O\text{=}P(O\text{-}iPr)_3$. However, after 7 days have elapsed, the P-H stretching band at 2425 cm^{-1} seems to have disappeared from the spectrum. The bands at 1275 and 1261 cm^{-1} are still present and are assigned to the P=O stretching of trisopropyl phosphate. By the eighth day, the P=O stretching band has a low frequency component near 1230 cm^{-1}, which may be the beginning of P-acid formation. There appears to be some very weak diffuse absorption near 3000 and

2300 cm^{-1} which could be indicative of P-OH formation.

Thus, some of the compound appears to undergo hydrolysis as follows: $P(O\text{-}iPr)_3$ -HOH-> $H\text{-}P{=}O(O\text{-}iPr)_2$. The rest of the compound oxidizes and then may hydrolyze as follows: $P(O\text{-}iPr)_3$ -[O]-> $O{=}P(O\text{-}iPr)_3$ ~HOH~> $HO\text{-}P{=}O(O\text{-}iPr)_2$. The sample appears to be evaporating with the passage of time, so that the diisopropyl phosphite formed disappears leaving the triisopropyl phosphate formed, which then begins to hydrolyze to form the P-acid.

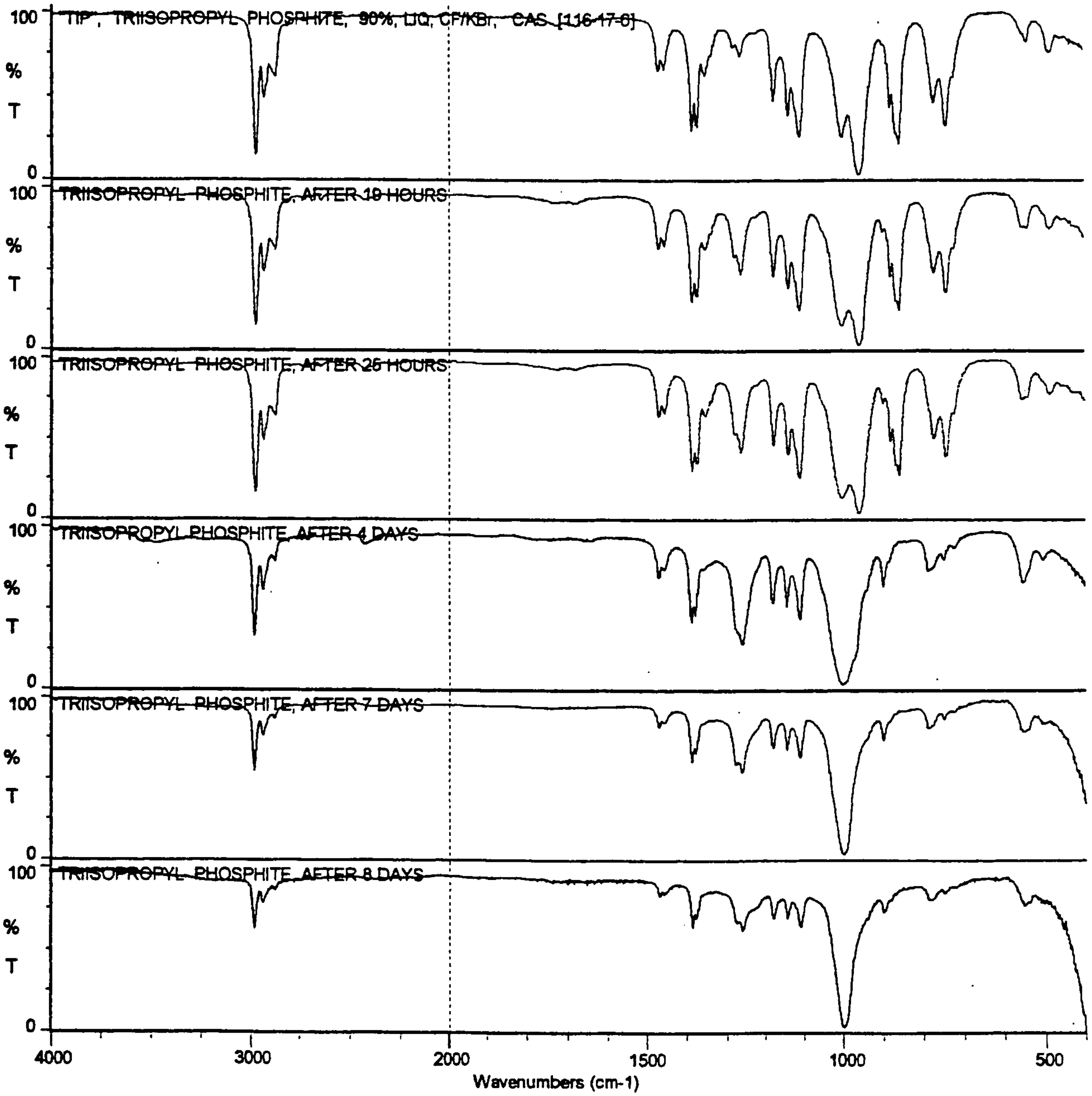

Figure 41 EFFECT OF ATMOSPHERIC MOISTURE ON TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr

Some time later, another sample of triisopropyl phosphite was determined as a liquid film between KBr windows (discs). The effect of the environment on this sample is given in ***Figures 42A*** through ***42F***. The infrared spectrum given in ***Figure 42A*** is similar to that given in ***Figure 40***. Both

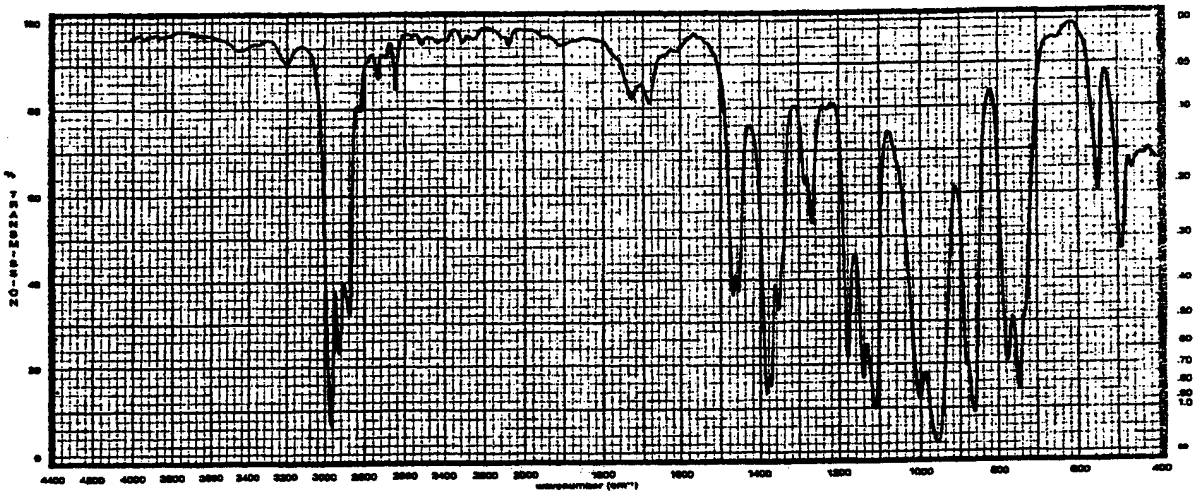

Figure 42A TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr

figures show the presence of P=O streching near 1275 and 1260 cm^{-1} that is attributed to triisopropyl phosphate, O=P(O-iPr)$_3$. This is still the picture after 5 hours of exposure to the environment. However, after 22 hours, the spectrum (***Figure 42 C***) shows a new band at 2426 cm^{-1} due to the ν P-H, and a band

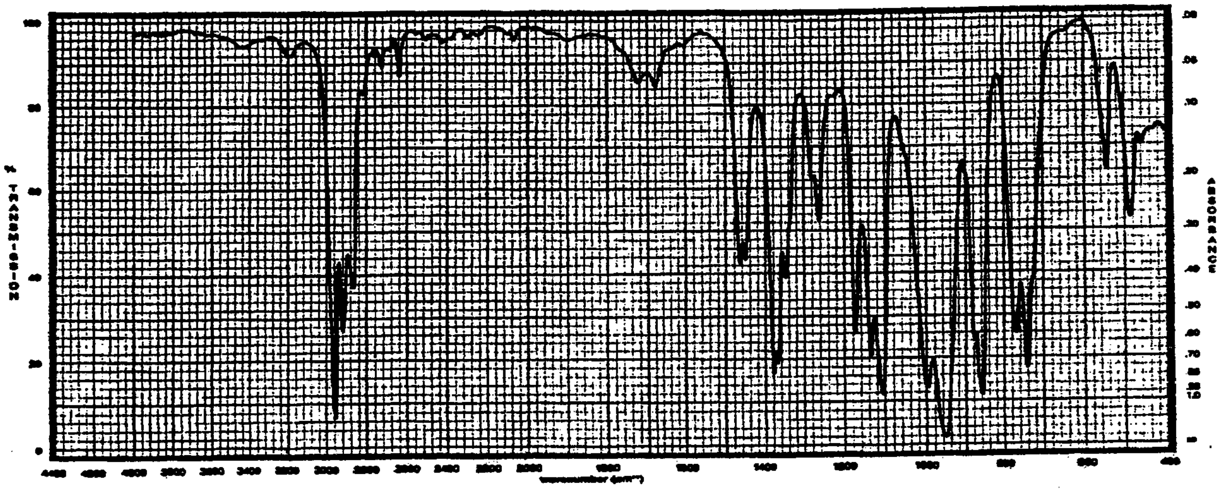

Figure 42 B TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr, AFTER 5 HOURS OF ENVIRONMENTAL EXPOSURE

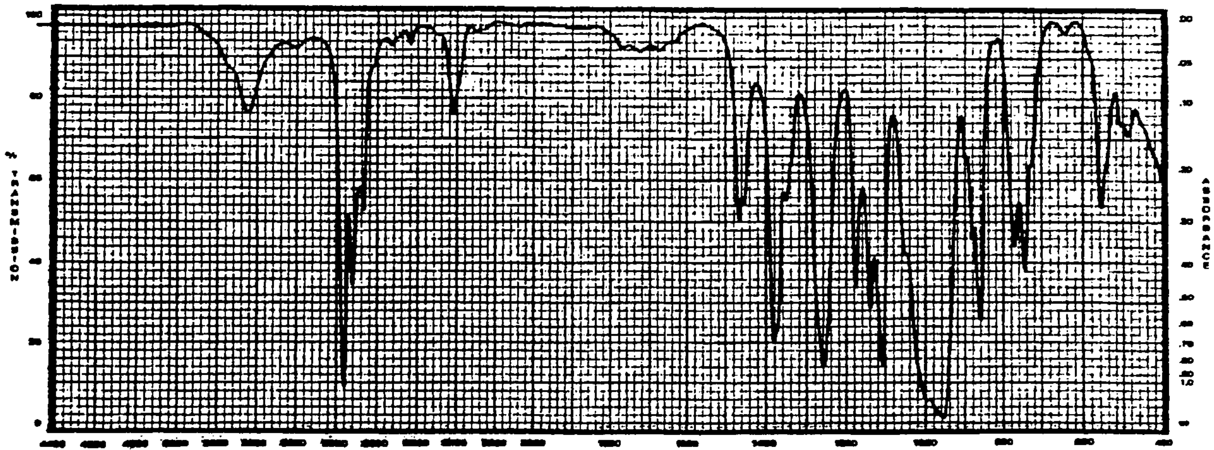

Figure 42 C TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr, AFTER 22 HOURS OF ENVIRONMENTAL EXPOSURE

at 1260 cm^{-1} due to a P=O stretching vibration., as well as bands at 1179, 1143 and 1110 cm^{-1} (characteristic of P-O-iPr). These bands are believed to be from diisopropyl phosphite, H-P=O(O-iPr)$_2$, formed as a result of hydrolysis. The infrared spectra for the period 70 hours (***Figure 42D***) to 4 days (***Figure 42E***) still show the presence of diisopropyl phosphite (see ***Figure 38*** for comparison to an authentic diisopropyl phosphite). At the 7 day mark the infrared spectrum (***Figure 42F***) is totally different from the spectra that preceded it. An examination of the sample between the KBr discs showed only a small spot of sample remaining. Apparently the sample present at the 4 day mark (diisopropyl phosphite) evaporated leaving behind a sample believed to be triisopropyl phosphate. This new compound would result from the oxidation of the original triisopropyl phosphite.

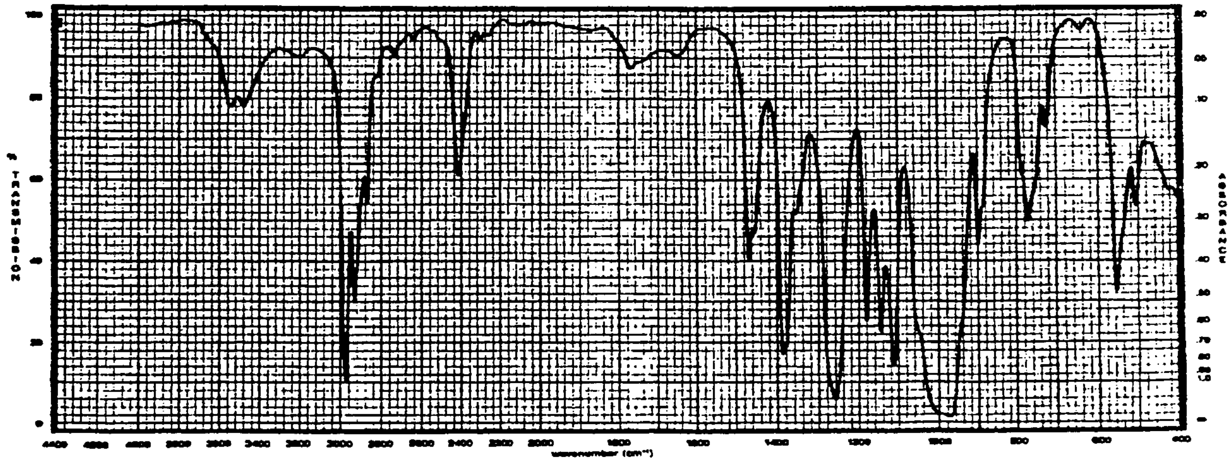

Figure 42D TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr, AFTER 70 HOURS OF ENVIRONMENTAL EXPOSURE

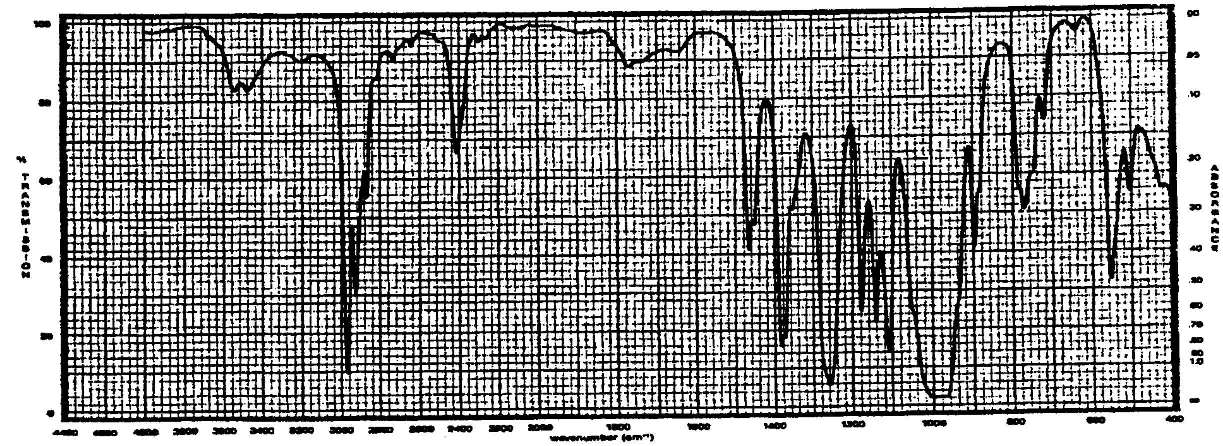

Figure 42E TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr, AFTER 4 DAYS OF ENVIRONMENTAL EXPOSURE

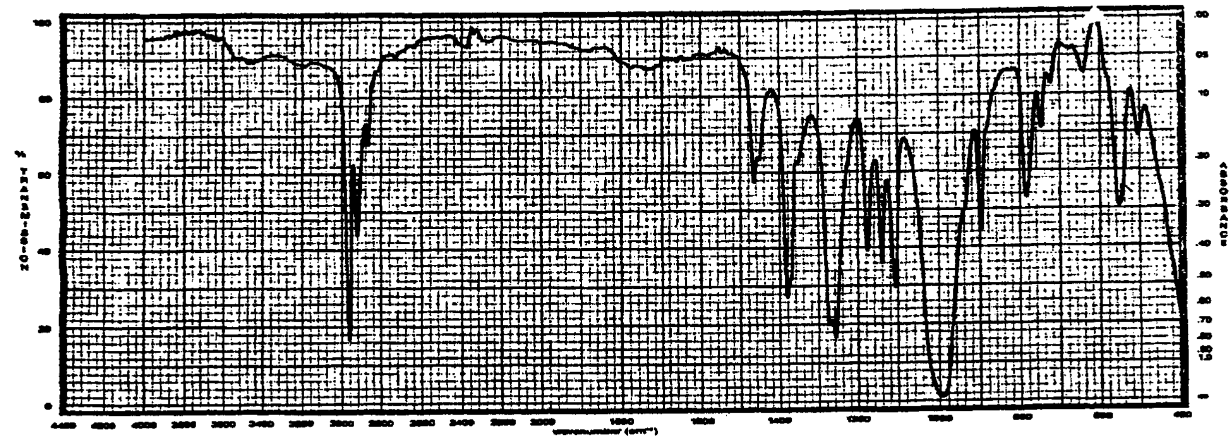

Figure 42F TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr, AFTER 7 DAYS OF ENVIRONMENTAL EXPOSURE

3.2.9 Dimethyl Methylphosphonate (DMMP) $CH_3P{=}O(OCH_3)_2$

The infrared spectrum of dimethyl methylphosphonate (**DMMP**) is given in ***Figure 43***. The band assignments are as follows: 2994 cm^{-1} vw and 2926 vw cm^{-1} (ν_{as} and ν_{sy} CH_3), 2956 cm^{-1} w and 2852 cm^{-1} w (ν_{as} and ν_{sy} OCH_3), 1465 cm^{-1} w (δ OCH_3), 1420 cm^{-1} vw (δ_{as} P-CH_3), 1313 cm^{-1} m (δ_{sy} P-CH_3), 1245 cm^{-1} ms (ν P=O), 1185 cm^{-1} w (CH_3 rock, characteristic of $POCH_3$), 1058 cm^{-1} sh and 1032 cm^{-1} s (ν P-O-C), 914 cm^{-1} m (P-CH_3 rock), 819 cm^{-1} m and 788 cm^{-1} m (POC), 713 cm^{-1} w (ν P-C), 501 cm^{-1} w (P=O deformation ?).

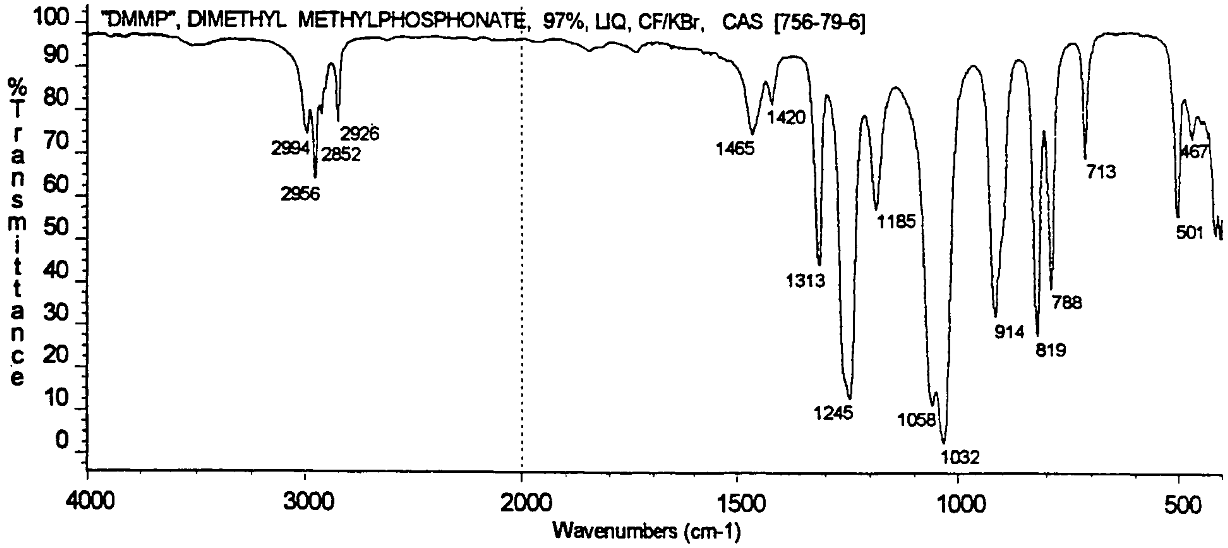

Figure 43 DIMETHYL METHYLPHOSPHONATE (DMMP), 97%, LIQUID, CF/KBr

The effect of atmospheric moisture on a thin liquid film of dimethyl methylphosphonate (DMMP) between KBr windows is given in ***Figure 44***. As the 7th day period is approached, the sample has picked up water. This is evidenced by the bands near 3470 and 1650 cm^{-1} and the decrease in the P=O stretching vibration from 1246 to 1238 cm^{-1}. Very weak broad bands are also visible near 2800 and 2370 cm^{-1} that indicate the presence of a P-acid (i.e., POOH). These acid bands become increasingly stronger as time passes. At the 14 day mark, POH bands are quite evident at ca 2800, 2370, 1650 and 995 cm^{-1}. The P=O stretching band has decreased to ca 1200 cm^{-1}; the $POCH_3$ moiety is still present as indicated by the bands at 1187 and 1037 cm^{-1}. The resident species may now be methyl hydrogen methylphosphonate (or methyl methylphosphonic acid), $CH_3P{=}O(OH)(OCH_3)$.[b] During the 22d through 81st day time period, the compound may be hydrolyzing further as indicated by the slight broadening of the band below 1186 cm^{-1}. A new compound such as methylphosphonic acid, $CH_3P{=}O(OH)_2$, may be forming. The hydrolysis of dimethyl methylphosphonate may be represented as follows: $CH_3P{=}O(OCH_3)_2$ -HOH-> $CH_3P{=}O(OH)(OCH_3)$ -HOH-> $CH_3P{=}O(OH)_2$.

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[b] An infrared spectrum for this compound is reproduced in "Chemical and Instrumental Verification of Organophosphorus Warfare Agents", p 76, Figure 8.27. Prepared for The Ministry for Foreign Affairs of Fnland by the Advisory Board for Disarmament, Helsinki, 1977.

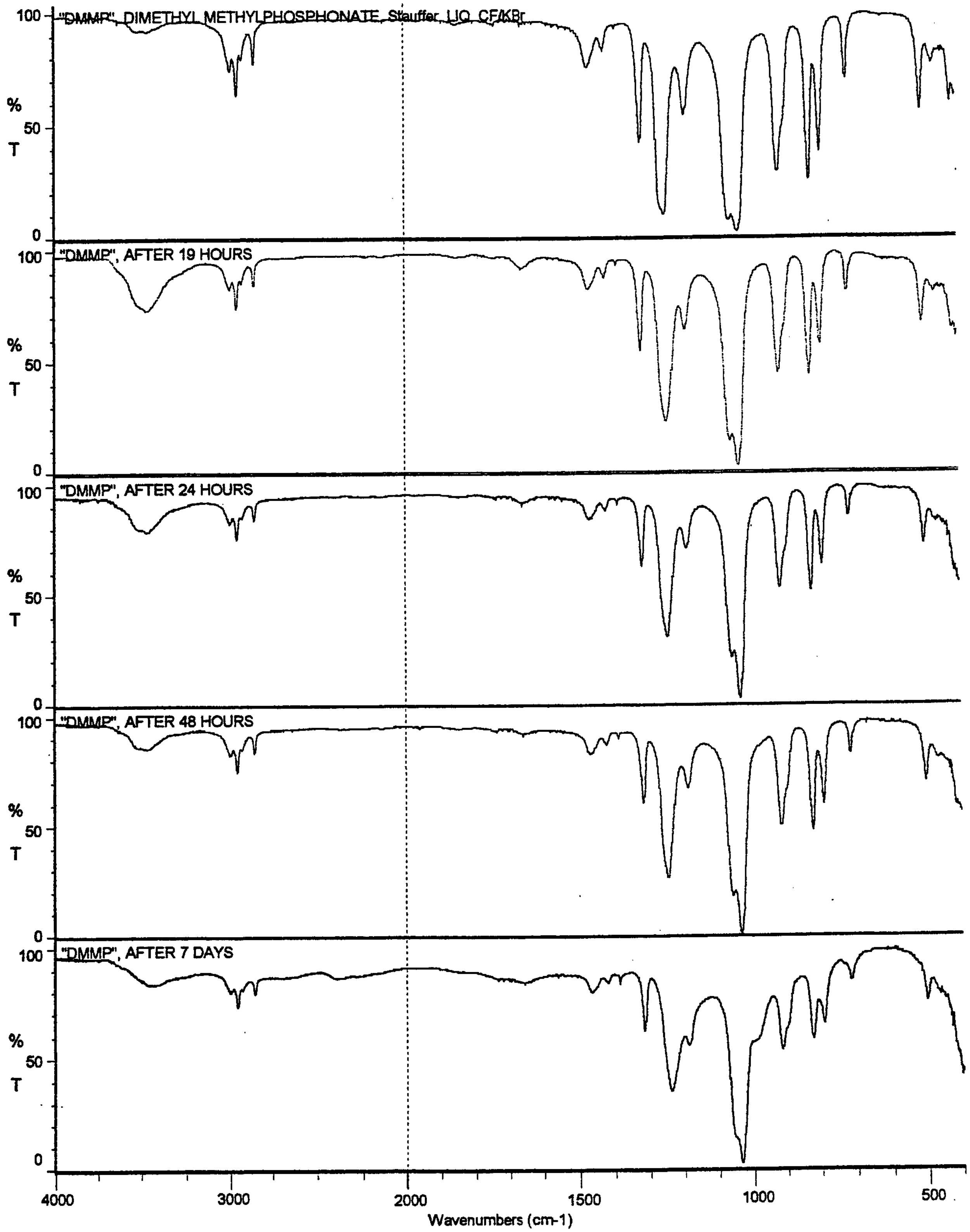


Figure 44 EFFECT OF ATMOSPHERIC MOISTURE ON DIMETHYL METHYLPHOSPHONATE (DMMP), LIQUID, CF/KBr

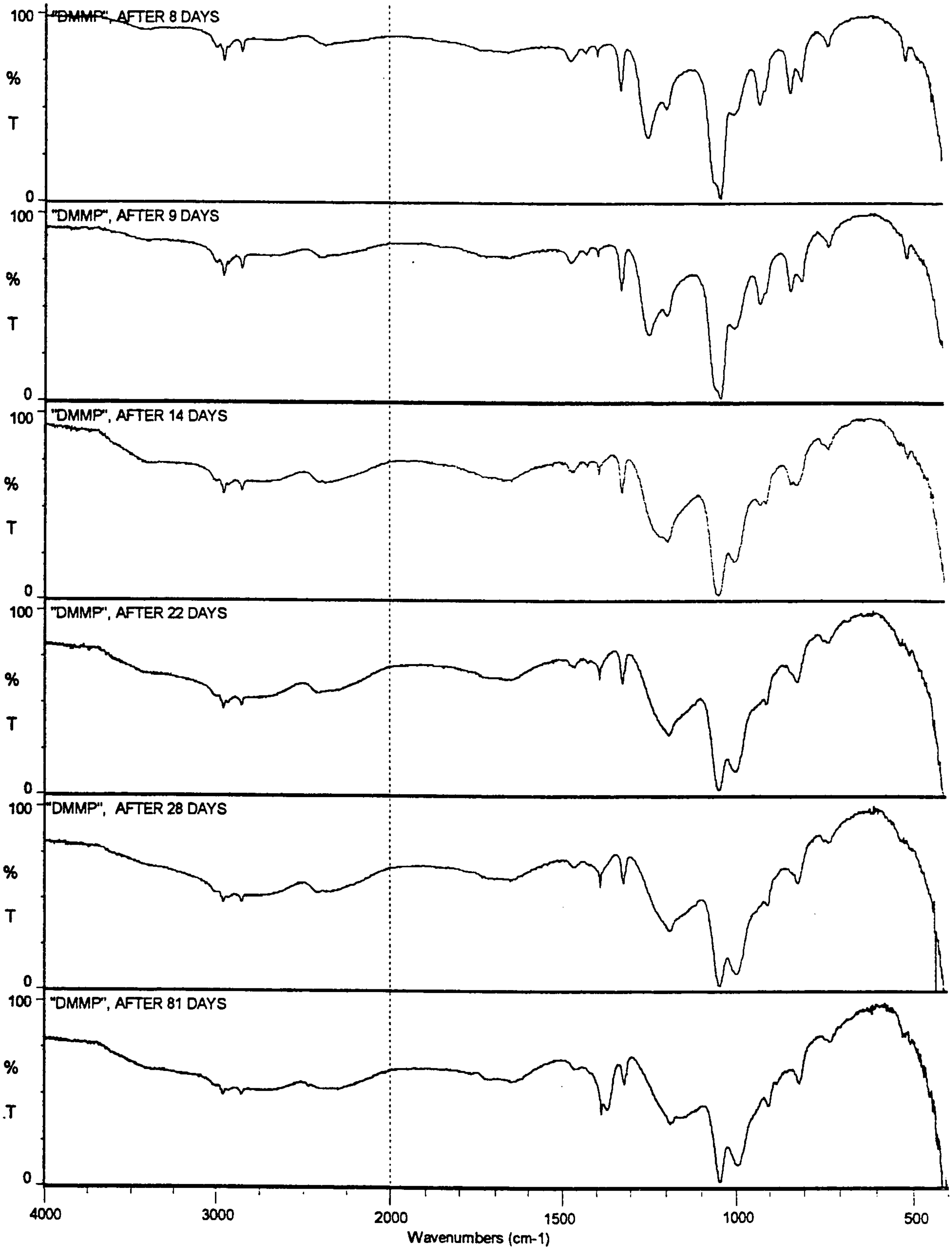


Figure 44 EFFECT OF ATMOSPHERIC MOISTURE ON DIMETHYL METHYLPHOSPHONATE (DMMP), LIQUID, CF/KBr (CONTINUED)

3.2.10 3,3-Dimethylbutanone-2 (Pinacolone) CH_3-C(=O)-C$(CH_3)_3$

The infrared spectrum of 3,3-dimethylbutanone-2 or *t*-butyl methyl ketone (**pinacolone**), is given in ***Figure 45***. The band assignments are as follows: 3398 cm^{-1} vw (overtone of ν P=O, 2 x 1709 = 3418 cm^{-1}), 2971 cm^{-1} ms, 2909 cm^{-1} w and 2873 cm^{-1} m (ν CH_3), 1709 cm^{-1} s (ν C=O), 1478 cm^{-1} m and 1466 cm^{-1} sh (δ_{as} CH_3), 1429 cm^{-1} w (δ_{as} CH_3-C=O), 1394 cm^{-1} w (δ_{sy} CH_3 *t*-butyl), 1366 and 1355 cm^{-1} ms (δ_{sy} CH_3 of *t*-butyl and CH_3-C=O), 1274 cm^{-1} m and 1223 cm^{-1} vw (*t*-butyl ?), 1137 cm^{-1} ms (ketone ν C-C-C), 954 cm^{-1} m (CH_3 rock), 554 cm^{-1} m (C=O deformation ?).

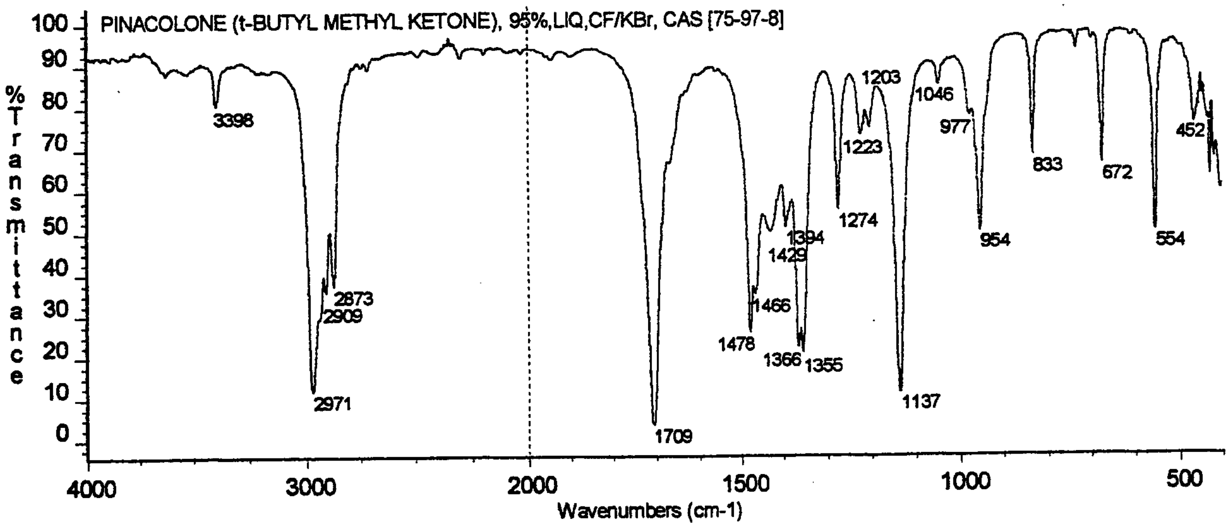


Figure 45 PINACOLONE (3,3-DIMETHYLBUTANONE-2), 95%, LIQUID, CF/KBr

3.3 Decomposition Products of G-Agents

Isopropyl methylphosphonic acid (isopropyl hydrogen methylphosphonate), **IMPA, GB Acid**, CAS [5514-35-2]

Methyl phosphonic acid (**MPA**), CAS [993-13-5]

Methyphosphonic anhydride

Mehylphosphonic difluoride (**DF, Difluor**), CAS [676-99-3]

Methylphosphonofluoridic acid (**Fluoro Acid**), CAS [1511-67-7]

Diisopropyl methylphosphonate (**DIMP**), CAS [1445-75-6]

2-Propanol (isopropyl alcohol, isopropanol), CAS [67-63-0]

Cyclohexyl methylphosphonic acid (cyclohexyl hydrogen methyphosphonate), **GF Acid**, CAS [1932-60-1]

Pinacolyl methylphosphonic acid (1,2,2-trimethylpropyl hydrogen methylphosphonate), **GD Acid**, CAS [616-52-4]

Dipinacolyl methylphosphonate [bis(1,2,2-trimethylpropyl) methylphosphonate], CAS [7040-58-6]

Pinacolyl alcohol (3,3-dimethyl-2-butanol or 1,2,2-trimethyl-1-propanol), CAS [464-07-3]

2-Methylcyclohexyl methylphosphonic acid (2-methylcyclohexyl hydrogen methylphosphonate), **EA 1356 Acid**

3.3.1 Isopropyl Methylphosphonic Acid (Isopropyl Hydrogen Methylphosphonate), IMPA

$CH_3P{=}O(OH)[OCH(CH_3)_2]$

The infrared spectrum of isopropyl methylphosphonic acid (**IMPA**, **GB Acid**) or isopropyl hydrogen methylphosphonate is given in ***Figure 46***. The band assignments are as follows: 2981 cm^{-1} m, 2934 cm^{-1} w and 2878 cm^{-1} vw (ν CH_3), 2639 cm^{-1}, 2292 cm^{-1} and 1685 cm^{-1} (all weak and broad, characteristic of the acid POH), 1469 cm^{-1} vw and 1457 cm^{-1} sh (δ_{as} CH_3), 1420 cm^{-1} vw (δ_{as} P-CH_3), 1376 and 1387 cm^{-1} weak doublet (characteristic of isopropyl group, δ_{sy} CH_3), ca 1350 cm^{-1} sh (δ -CH), 1313 cm^{-1} m (δ_{sy} P-CH_3), 1203 cm^{-1} ms (ν P=O), 1179 cm^{-1}, 1143 cm^{-1} and 1108 cm^{-1} (weak triplet of bands characteristic of P-O-isopropyl), 1004 cm^{-1} s (ν P-O-C and ν P-OH), 906 cm^{-1} w (P-CH_3 rock), 877 cm^{-1} vw (isopropyl CH_3 rock), 783 cm^{-1} w (POC), 730 cm^{-1} vw (ν P-C), 510 cm^{-1} w (P=O deformation ?).

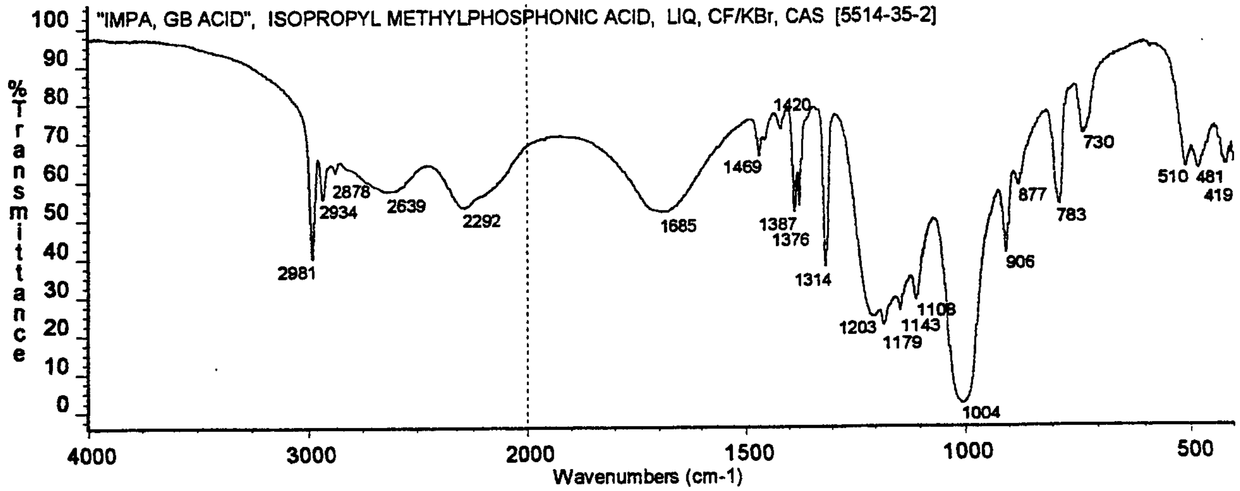


Figure 46 ISOPROPYL METHYLPHOSPHONIC ACID (IMPA), LIQUID, CF/KBr

3.3.2 Methylphosphonic Acid (MPA) $CH_3P{=}O(OH)_2$

The infrared spectrum of methylphosphonic acid (MPA) is given in ***Figure 47***. The band assignments are as follows: 3013 and 2934 cm^{-1} vvw (ν_{as} and ν_{sy} CH_3), 2744 cm^{-1} m broad, 2337 cm^{-1} m and ca 1630 cm^{-1} vw (characteristic of POH), 1534 cm^{-1} vvw (2 x 767 = 1534 cm^{-1}), 1423 and 1415 cm^{-1} vw (δ_{as} P-CH_3), 1323 cm^{-1} m (δ_{sy} P-CH_3), 1260 cm^{-1} m (P-OH in-plane bend ?), 1155 cm^{-1} m (ν P=O ?), 1011 and 954 cm^{-1} s (ν_{as} and ν_{sy} P-OH), 891 cm^{-1} vw (P-CH_3 rock ?), 767 cm^{-1} ms (ν P-C), 495 m and 458 s cm^{-1} (P=O deformation ?).

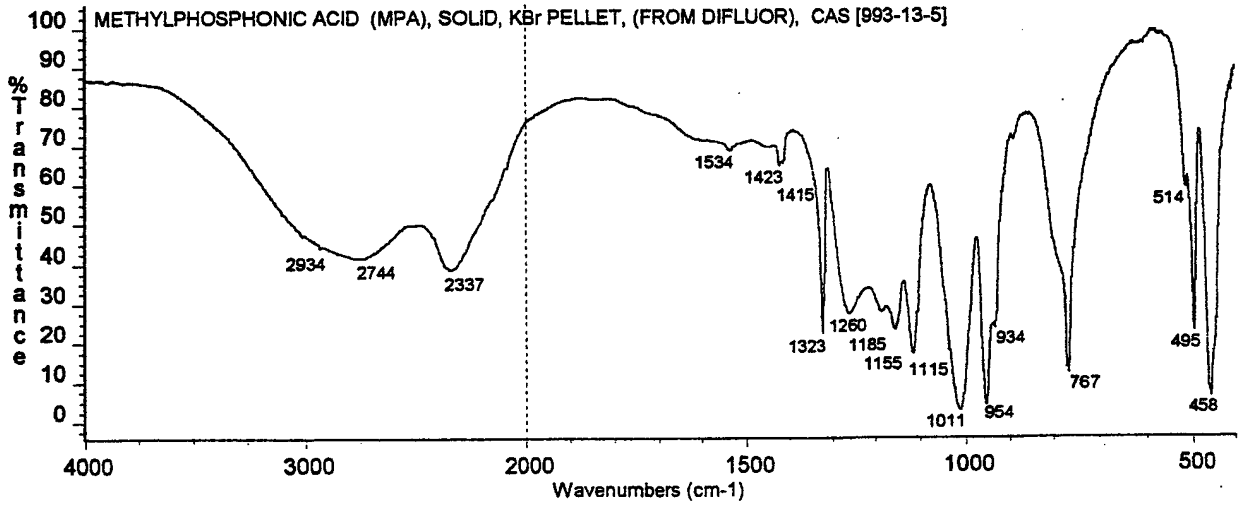


Figure 47 METHYLPHOSPHONIC ACID (MPA), SOLID, KBr PELLET

If the KBr pellet containing methylphosphonic acid is reground and repressed a number of times, one begins to see changes occurring in the infrared spectrum with each remaking of the pellet. This effect is illustrated in ***Figure 48***. The resultant infrared spectra, after the sixth and seventh regrindings and repressings of the KBr pellets, show that the compound is no longer methylphosphonic acid but more probably the salt of the acid. The infrared spectrum now shows a strong band at 1093-1083 cm^{-1} (ν_{as} PO_3^{-2}) and a much weaker band near 950 cm^{-1} (ν_{sy} PO_3^{-2}). Other bands at 2995 cm^{-1} vvw, 2928 cm^{-1} vvw, 1420 cm^{-1} vvw, 1312 cm^{-1} w, 874 cm^{-1} vvw and 771 cm^{-1} w are due to the P-CH_3 group. Therefore, with increased grinding of the sample/KBr matrix changes occur to produce a salt of methylphosphonic acid [CH_3-P=O$(OH)_2$ $\rightarrow$ CH_3-PO$(O^- K^+)_2$]. This example illustrates the care that must be exercised in the grinding of samples for use in the KBr pellet technique.

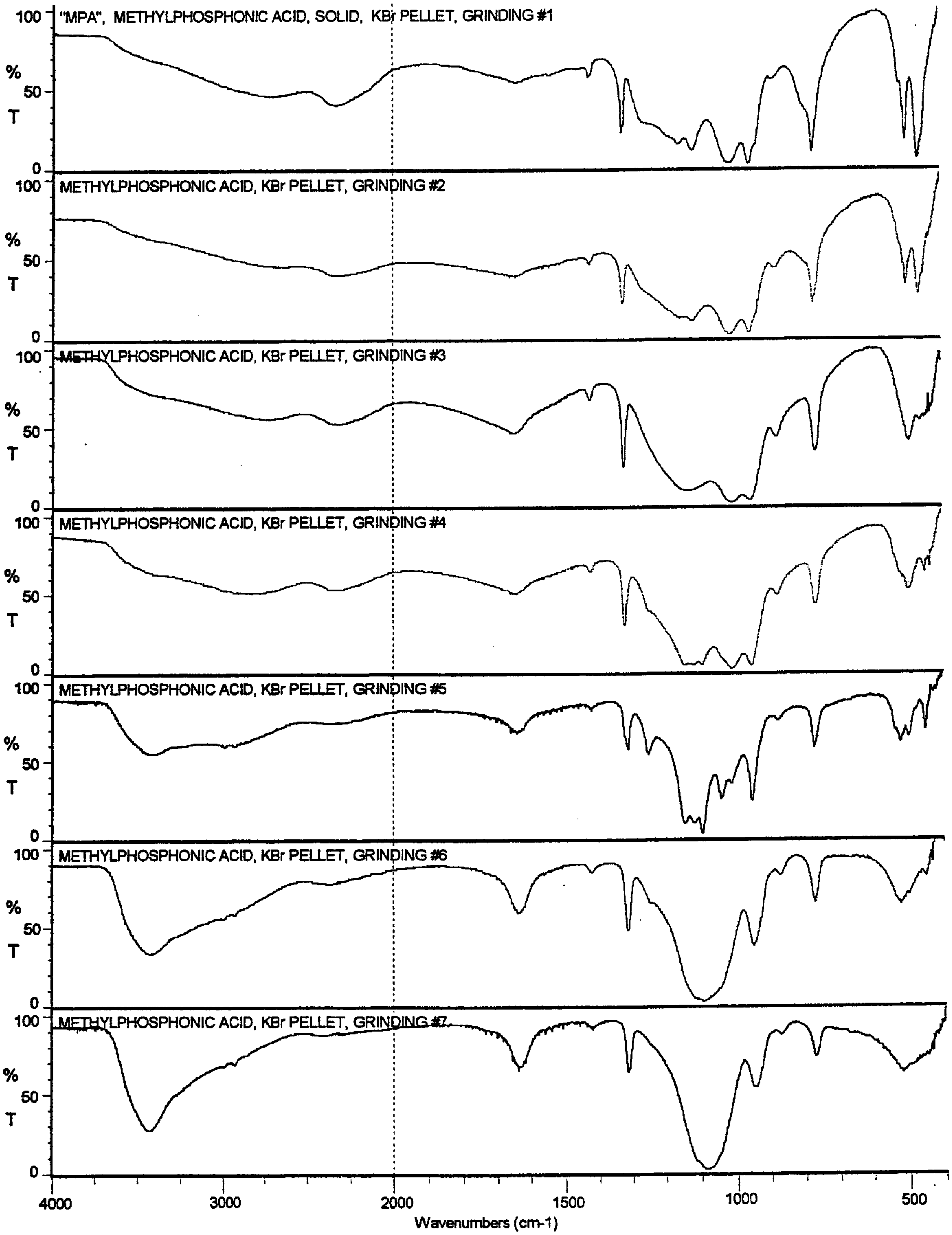


Figure 48 EFFECT OF GRINDING ON THE METHYLPHOSPHONIC ACID/KBr MATRIX

3.3.3 Methylphosphonic Anhydride $CH_3P{=}O(OH){-}O{-}P{=}O(OH)CH_3$

The infrared spectrum of methylphosphonic anhydride is reproduced in ***Figure 49***. The band assignments are as follows: 3006 cm^{-1} vw and 2929 cm^{-1} vw (ν_{as} and ν_{sy} CH_3), 2633 cm^{-1}, 2305 cm^{-1} and 1679 cm^{-1} all weak and broad (POH), 1424 cm^{-1} vw (δ_{as} P-CH_3), 1311 cm^{-1} m (δ_{sy} P-CH_3), 1213 cm^{-1} ms (ν P=O), 1009 cm^{-1} ms (ν P-OH), 951 cm^{-1} ms (ν P-O-P), 775 s (ν P-C), 525 w, 504 m, 468 m, 445 ms cm^{-1} (P=O deformations ?).

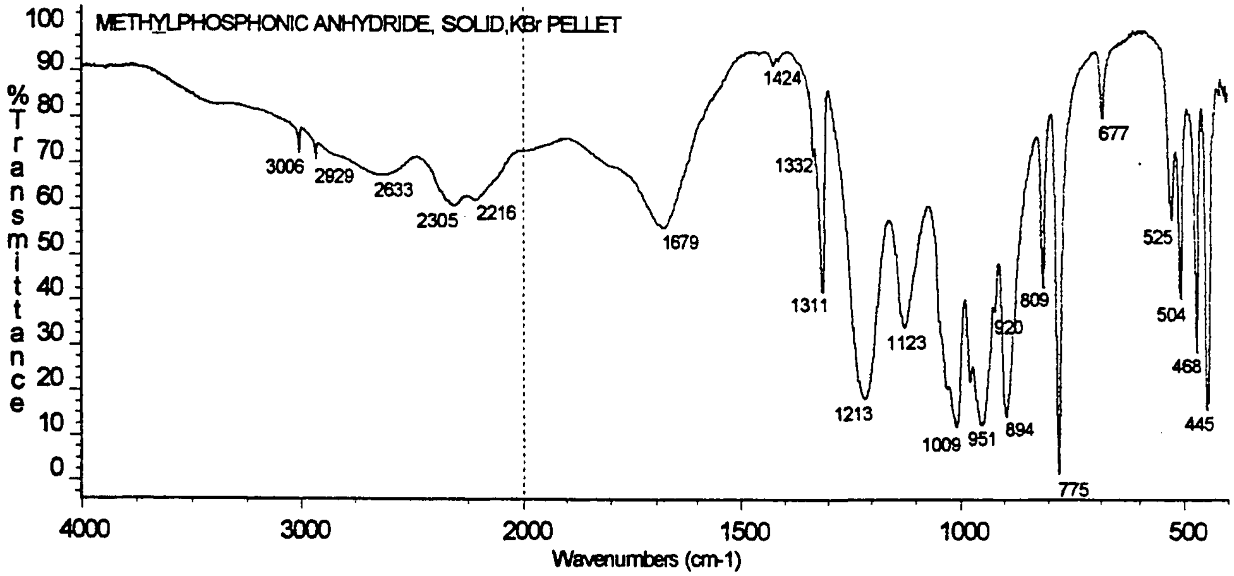


Figure 49 METHYLPHOSPHONIC ANHYDRIDE, SOLID, KBr PELLET

In ***Figure 50***, the effect of grinding on the solid/KBr matrix is illustrated. The top most spectrum is from a freshly prepared pellet. The next spectrum is from another freshly prepared pellet. Note the differences in the band intensities between the two spectra. The third spectrum down shows the previous pellet reground and repressed. Note this spectrum appears to lie between the two previous spectra. The last spectrum in the group, shows the effect of moisture on the pellet after it had been sitting in the air for 6 days. This last pellet now seems to resemble the spectrum for methylphosphonic acid (***Figure 48***, grinding #3).

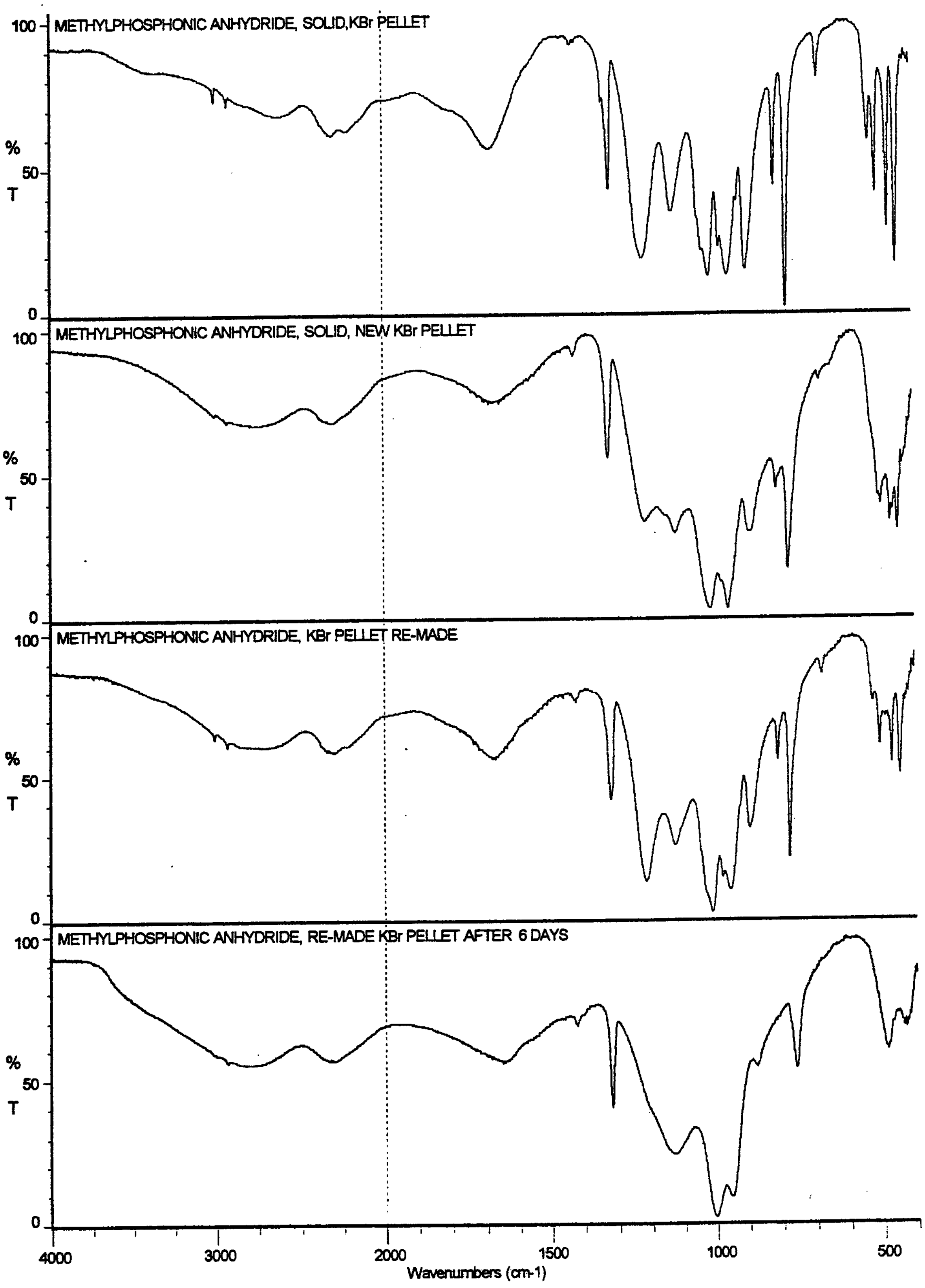


Figure 50 EFFECT OF GRINDING ON THE METHYLPHOSPHONIC ANHYDRIDE/KBr MATRIX

3.3.4 Methylphosphonic Difluoride (DF, Difluor) $CH_3P{=}OF_2$

The infrared spectrum of methylphosphonic difluoride (**DF**, **Difluor**) is given in ***Figure 51***. The band assignments are as follows: 3013 cm^{-1} w and 2937 cm^{-1} w (ν_{as} and ν_{sy} P-CH_3), 1506 cm^{-1} vw (2 x 755 cm^{-1} = 1510 cm^{-1}), 1418 cm^{-1} w (δ_{as} P-CH_3), 1336 cm^{-1} s (ν P=O), 1312 cm^{-1} s (δ_{sy} P-CH_3), 944 cm^{-1} sh and 926 cm^{-1} s (P-CH_3 rock), 882 cm^{-1} ms and 857 cm^{-1} m (ν_{as} and ν_{sy} PF_2), 755 cm^{-1} m (ν P-C), 469 cm^{-1} ms (PF_2 deformation ?), 415 and 407 cm^{-1} m (P=O deformation, PF_2 deformation ?).

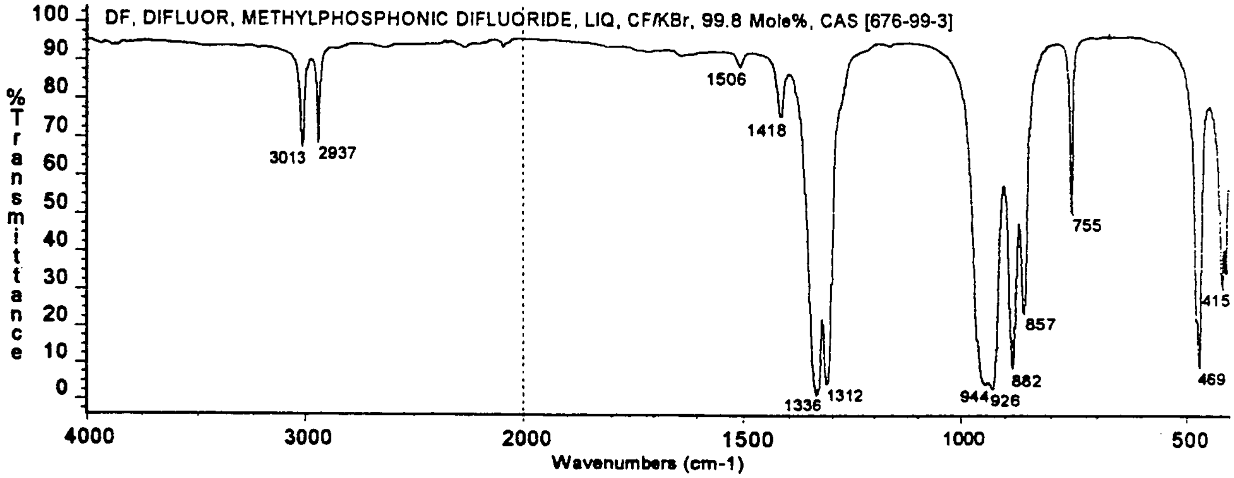


Figure 51 METHYLPHOSPHONIC DIFLUORIDE (DF, DIFLUOR), 99.8 MOLE%, LIQUID, CF/KBr

The effect of atmospheric moisture on the infrared spectrum of a thin liquid film of **Difluor** between KBr windows is given in ***Figures 52A*** through ***52E***. The infrared spectrum for a typical munition sample of **Difluor** (somewhat dark in color) is given in ***Figure 52A***. The presence of an acid moiety is

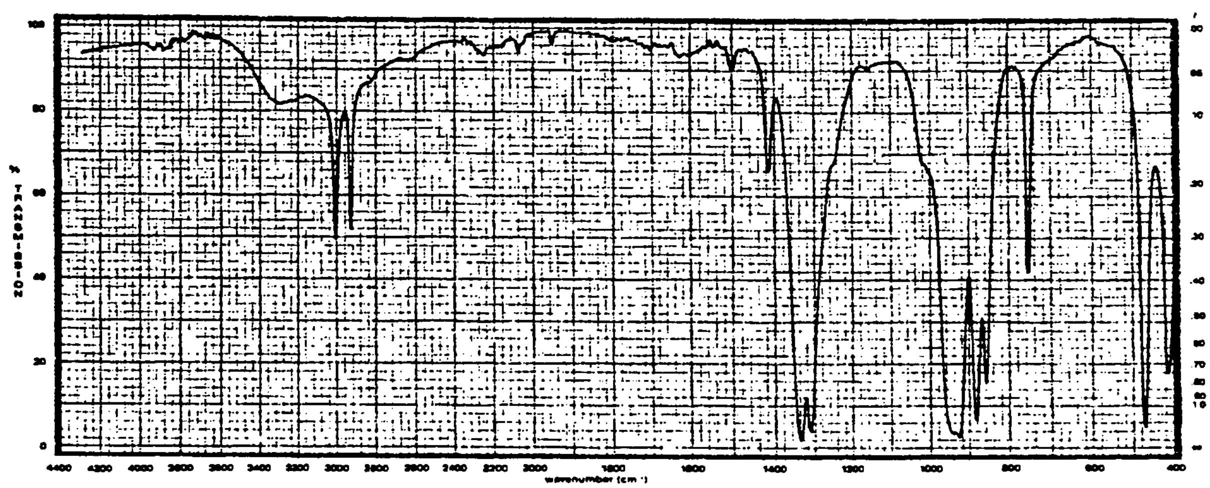


Figure 52A DIFLUOR, LIQUID (SOMEWHAT DARK), CF/KBr

evidenced by the inflections occurring near 1260 cm^{-1} (ν P=O) and 1020 cm^{-1} (ν P-OH). There is also some broadening of the area around 3000 cm^{-1} (POH) and some absorption is evident near 3300 cm^{-1} (H_2O). The sample, after sitting in the air for 30 minutes, ***Figure 52B***, shows bands in the 3000 and 2300 cm^{-1} areas as well as those near 1260 and 1020 cm^{-1} beginning to become more predominant. The sample of **Difluor** is beginning to undergo hydrolysis to the **Fluoro Acid**, methylphosphonofluoridic acid $(CH_3)P{=}O(OH)(F)$. This is even more evident after 120 minutes (***Figure 52C***). After an atmospheric exposure of 120 minutes, the sample shows more intense bands near 3000, 2300 and 1650 cm^{-1} due to the POH group. Bands near 1230 cm^{-1} (ν P=O) and 1020 cm^{-1} (ν P-OH) indicate the formation of a P-acid, namely the **Fluoro Acid**. After a period of 330 minutes, the infrared spectrum (***Figure 52D***) showed

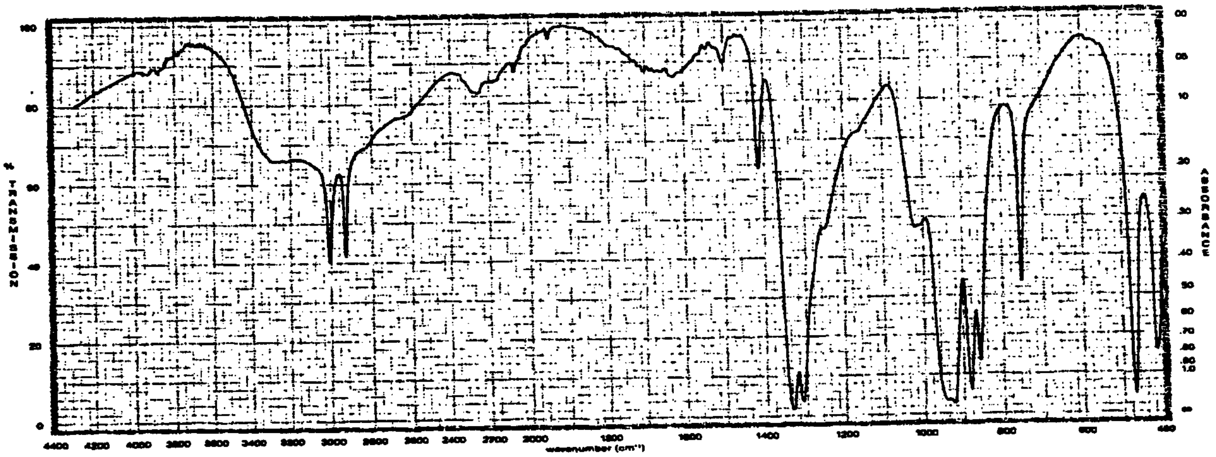


Figure 52B DIFLUOR, LIQUID, CF/KBr, AFTER 30 MINUTES

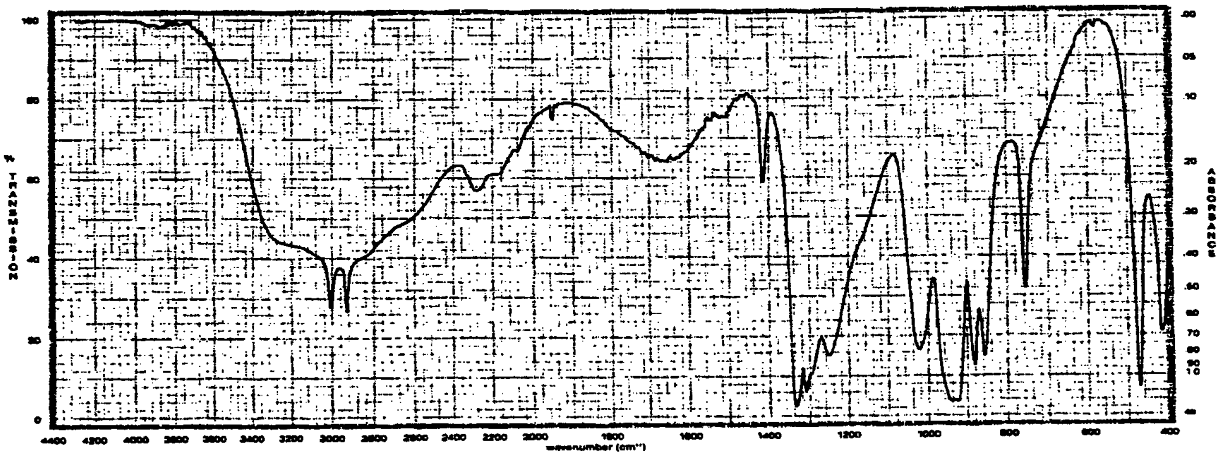


Figure 52C DIFLUOR, LIQUID, CF/KBr, AFTER 120 MINUTES

mainly the presence of methylphosphonofluoridic acid (**Fluoro Acid**). The infrared spectrum for an

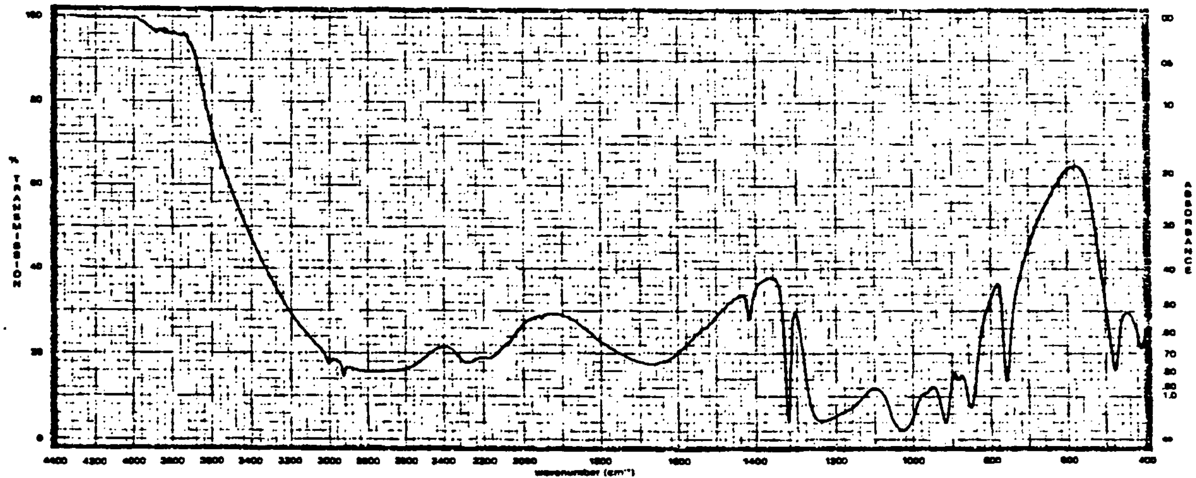


Figure 52D DIFLUOR, LIQUID, CF/KBr, AFTER 330 MINUTES

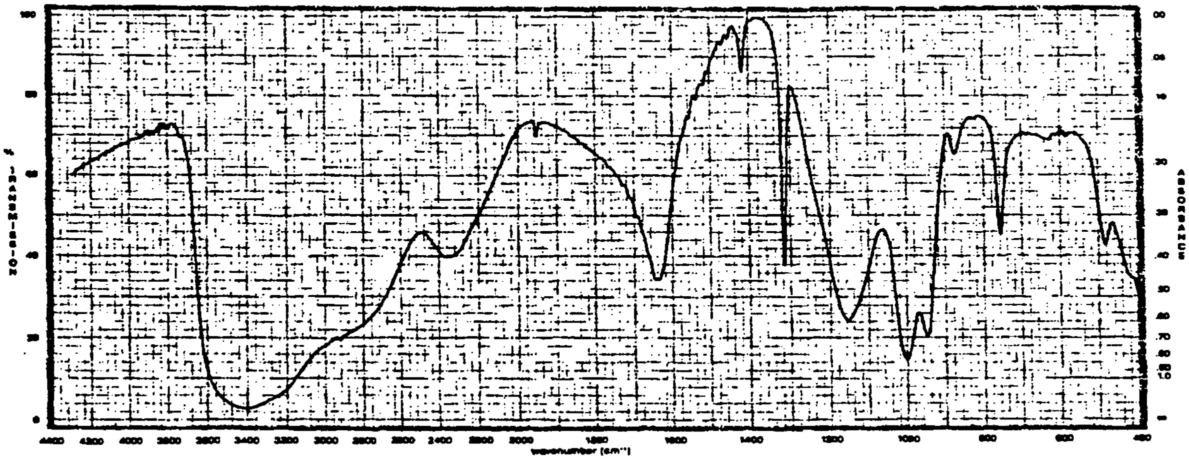


Figure 52E DIFLUOR, LIQUID, CF/KBr, AFTER 71 HOURS

authentic sample of the **Fluoro Acid** is given in ***Figure 53***. The infrared spectrum for the sample of **Difluor**, after 71 hours of atmospheric exposure, is reproduced as ***Figure 52E***. Here the sample of methylphosphonic difluoride has been hydrolyzed to a very wet methylphosphonic acid (**MPA**), $CH_3P{=}O(OH)_2$. An authentic spectrum of *wet* **MPA** is given in ***Figure 54***. Thus, the hydrolysis of **Difluor** may be summarized as follows:

$CH_3P{=}O(F)_2 \text{ -HOH}\rightarrow CH_3P{=}O(OH)(F) \text{ -HOH}\rightarrow CH_3P{=}O(OH)_2$.

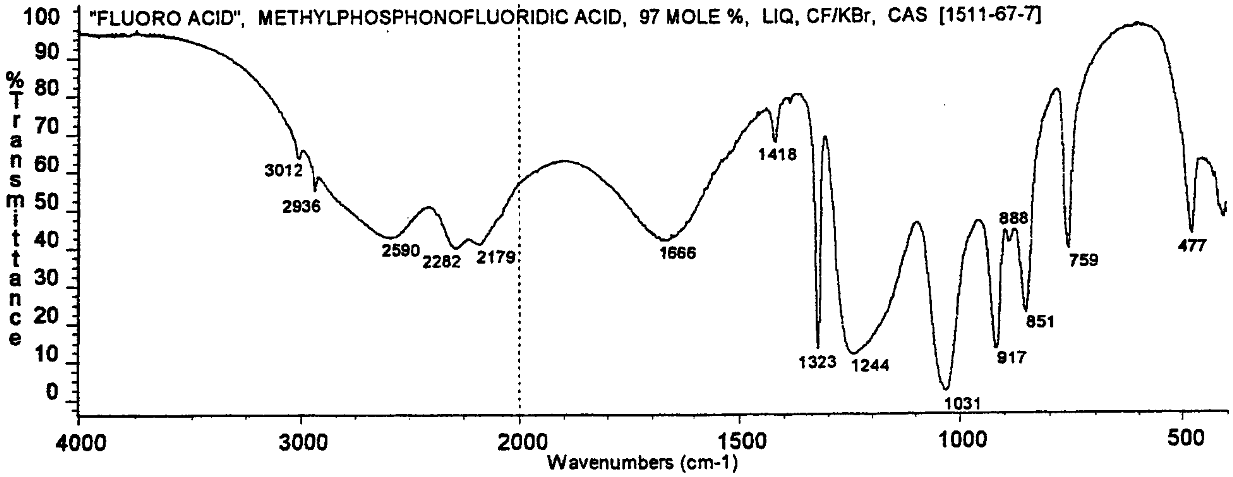


Figure 53 METHYLPHOSPHONOFLUORIDIC ACID (FLUORO ACID), LIQUID, CF/KBr

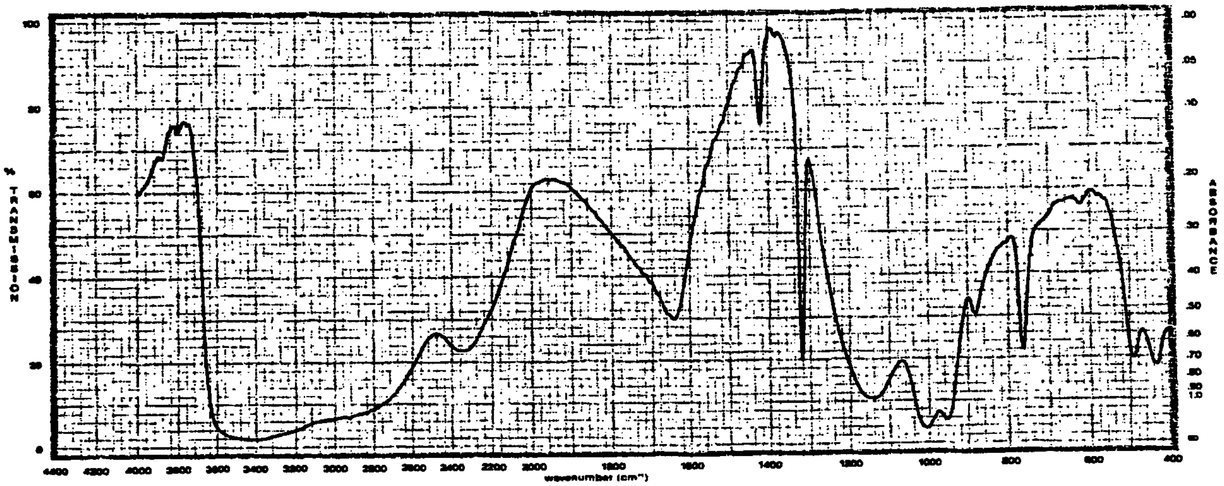


Figure 54 MIX OF A DROP OF WATER AND METHYLPHOSPHONIC ACID (MPA), CF/KBr

3.3.5 Methylphosphonofluoridic Acid (Fluoro Acid) $CH_3P{=}O(OH)(F)$

The infrared spectrum of methylphosphonofluoridic acid (**Fluoro acid**) is given in ***Figure 53***. Band assignments are as follows: 3012 cm^{-1} vw and 2936 vw cm^{-1} (ν_{as} and ν_{sy} CH_3), 2590 cm^{-1}, 2282 cm^{-1}, 2179 cm^{-1} and 1666 cm^{-1} (all w-m and broad, POH), 1418 cm^{-1} vw (δ_{as} P-CH_3), 1384 cm^{-1} vvw (KNO_3 from the KBr windows), 1323 cm^{-1} ms (δ_{sy} P-CH_3), 1244 cm^{-1} ms, somewhat broadened (ν P=O), 1031 cm^{-1} s (ν P-OH), 917 cm^{-1} ms (P-CH_3 rock), 851 cm^{-1} m (ν P-F), 759 cm^{-1} w (ν P-C), 477 cm^{-1} w (P=O deformation ?).

The effect of atmospheric moisture on **Fluoro acid**, after 18 hours of exposure to atmospheric moisture, is shown in ***Figure 55***. The P-F stretching band that was at 851 cm^{-1}, has been almost completely hydrolyzed off leaving a OH group in its place. The resultant compound is methylphosphonic acid, **MPA**, $CH_3P{=}O(OH)_2$. Compare this spectrum with that for MPA (***Figure 54***).

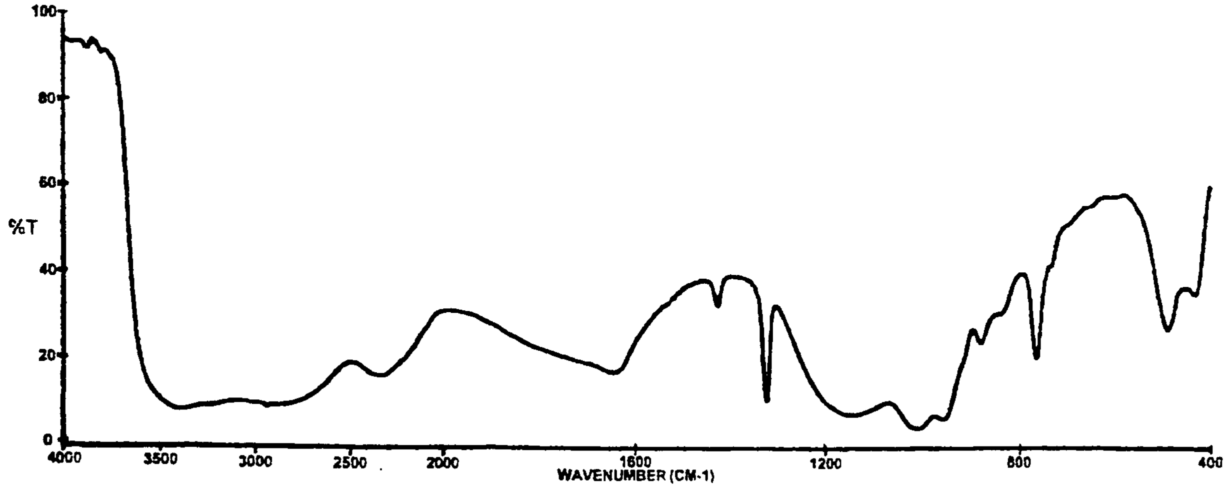


Figure 55 FLUORO ACID, LIQ, CF/KBr, AFTER 18 HOURS EXPOSED TO ATMOSPHERIC MOISTURE

3.3.6 Diisopropyl Methylphosphonate (DIMP) $CH_3P{=}O[O\text{-}CH(CH_3)_2]_2$

The infrared spectrum of diisopropyl methylphosphonate (**DIMP**) is presented in ***Figure 56***. The band assignments are as follows: 2979 cm^{-1} m, 2934 cm^{-1} w and 2877 cm^{-1} vw (ν CH_3), 1468 cm^{-1} and

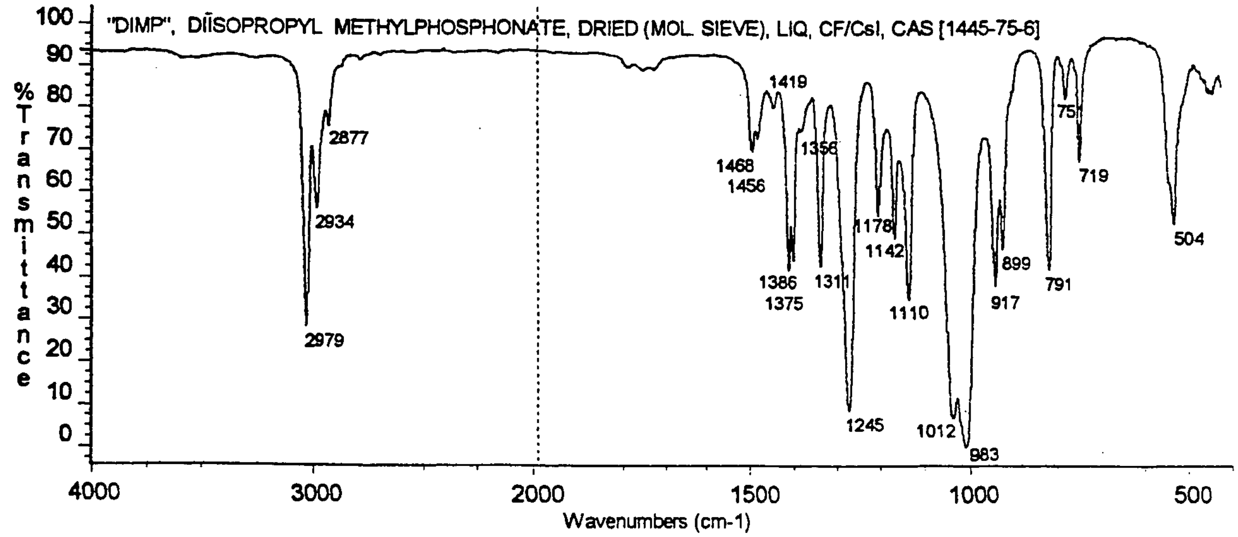
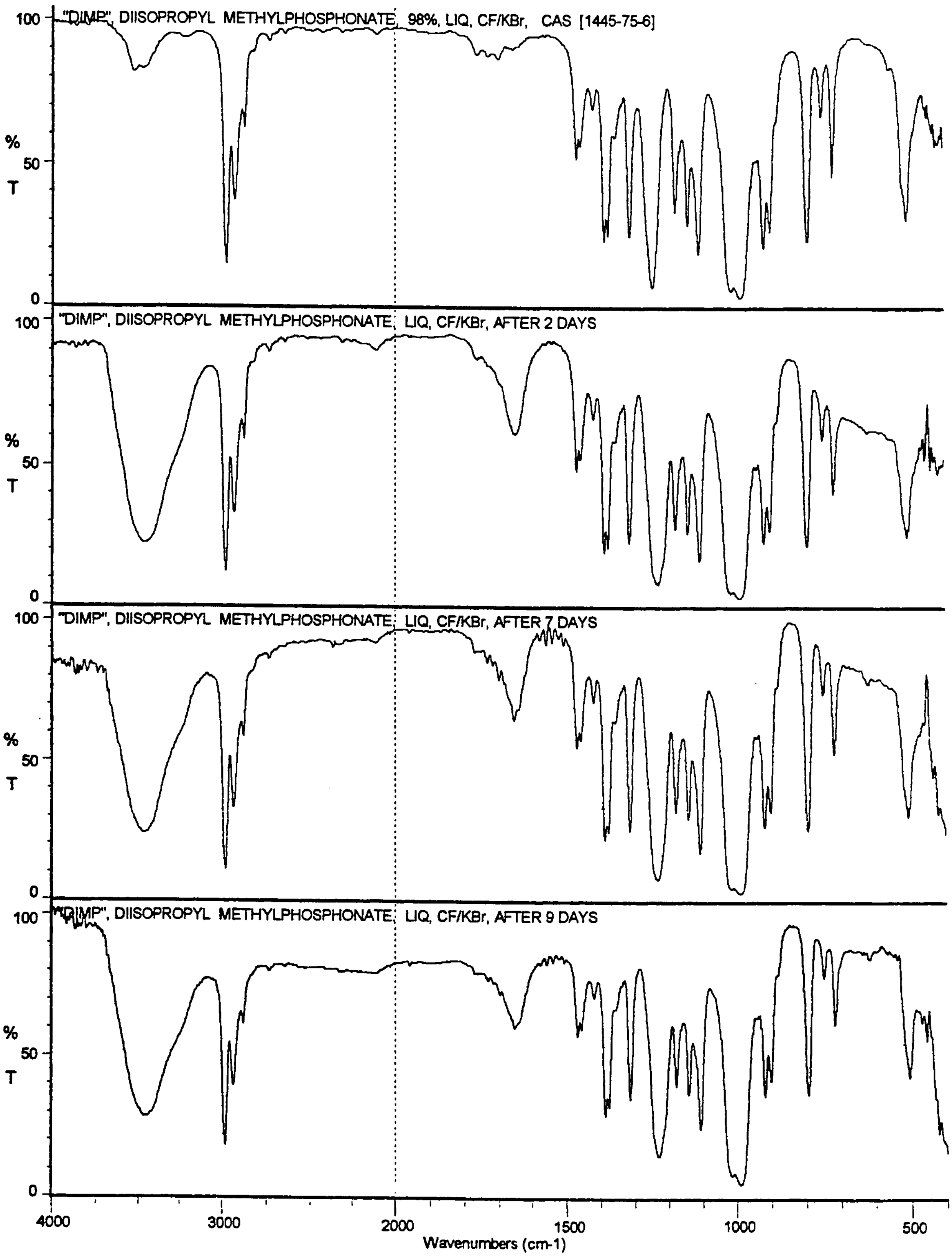


Figure 56 DIISOPROPYL METHYLPHOSPHONATE (DIMP), DRIED, CF/CsI

1458 cm^{-1} vw (δ_{as} CH_3), 1419 cm^{-1} vw (δ_{as} P-CH_3), 1386 and 1375 cm^{-1} medium (doublet, δ_{sy} CH_3 isopropyl group), 1356 cm^{-1} sh (δ -CH), 1311 cm^{-1} m (δ_{sy} P-CH_3), 1245 cm^{-1} ms (ν P=O), 1178 cm^{-1} w, 1142 cm^{-1} w and 1110 cm^{-1} m (triplet of bands characteristic of P-O-isopropyl), 1012 cm^{-1} sh and 983 cm^{-1} s (ν P-O-C), 917 cm^{-1} m and 899 cm^{-1} w (CH_3 rock of P-CH_3 and isopropyl groups), 791 cm^{-1} m (POC), 719 cm^{-1} w (ν P-C), 504 cm^{-1} m (P=O deformation ?).

The effect of atmospheric moisture on the infrared spectrum of diisopropyl methylphosphonate (**DIMP**) is illustrated by ***Figure 57***. As the amount of water increases, as indicated by the bands near 3465 cm^{-1} and 1650 cm^{-1}, the P=O stretching band at 1245 cm^{-1} decreases in value to 1230 cm^{-1} by the 9th day. This lowering of the phosphoryl stretching band by water is due to hydrogen bonding.


"DIMP", DIISOPROPYL METHYLPHOSPHONATE, 98%, LIQ, CF/KBr, CAS [1445-75-6]

"DIMP", DIISOPROPYL METHYLPHOSPHONATE, LIQ, CF/KBr, AFTER 2 DAYS

"DIMP", DIISOPROPYL METHYLPHOSPHONATE, LIQ, CF/KBr, AFTER 7 DAYS

"DIMP", DIISOPROPYL METHYLPHOSPHONATE, LIQ, CF/KBr, AFTER 9 DAYS

Figure 57 **EFFECT OF ATMOSPHERIC MOISTURE ON DIISOPROPYL METHYLPHOSPHONATE (DIMP), LIQUID, CF/KBr**

3.3.7 2-Propanol (Isopropyl Alcohol, Isopropanol) $HO\text{-}CH(CH_3)_2$

The infrared spectrum of 2-propanol (isopropyl alcohol) is reproduced in ***Figure 58***. The band assignments are as follows: 3350 cm^{-1} ms (ν OH bonded), 2972 cm^{-1} s, 2932 cm^{-1} m and 2884 cm^{-1} m (ν CH_3), 1468 cm^{-1} m (δ_{as} CH_3), 1409 cm^{-1} w (β OH), 1380 cm^{-1} m and 1368 cm^{-1} sh (δ_{sy} CH_3), 1341 cm^{-1} w (δ -CH), 1310 cm^{-1} m (CH wag), 1162 cm^{-1} m, 1130 cm^{-1} m and 1111 cm^{-1} sh (isopropyl skeletal and $\nu_{out\text{-}of\text{-}phase}$ C-C-O), 953 cm^{-1} s (isopropyl moiety, CH_3 rock), 817 cm^{-1} m ($\nu_{in\text{-}phase}$ C-C-O), 669 cm^{-1} w broad (γ OH).

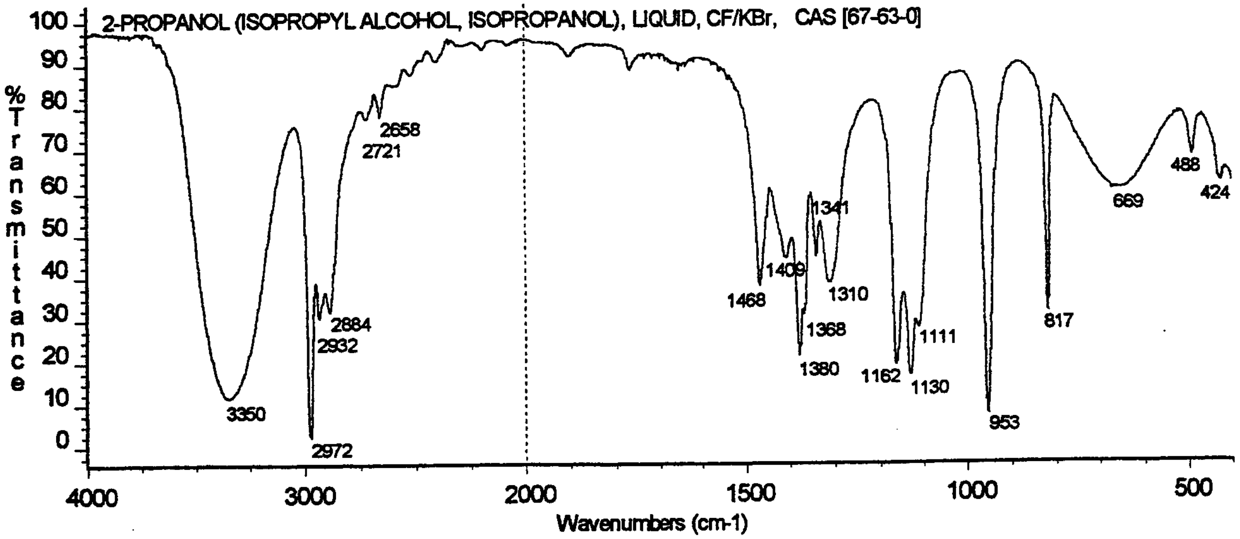


Figure 58 2-PROPANOL (ISOPROPYL ALCOHOL), LIQUID, CF/KBr

3.3.8 Cyclohexyl Methylphosphonic Acid (GF Acid) $CH_3P{=}O(OH)(O\text{-}C_6H_{11})$

The infrared spectrum of **GF acid**, cyclohexyl methylphosphonic acid (or cyclohexyl hydrogen methylphosphonate) is given in ***Figure 59***. The band assignments are as follows: 2937 cm^{-1} ms (ν_{as} CH_2), 2860 cm^{-1} m (ν_{sy} CH_2), 2661, 2292 and 1670 cm^{-1} all weak and broad (POH), 1452 cm^{-1} w (ring δ CH_2), 1419 cm^{-1} vw (δ_{as} P-CH_3), 1313 cm^{-1} w (δ_{sy} P-CH_3), 1202 cm^{-1} ms (ν P=O), 1042 cm^{-1} sh and 1007 cm^{-1} s (ν P-O-C), 909 cm^{-1} w (P-CH_3 rock), 762 cm^{-1} w (POC).

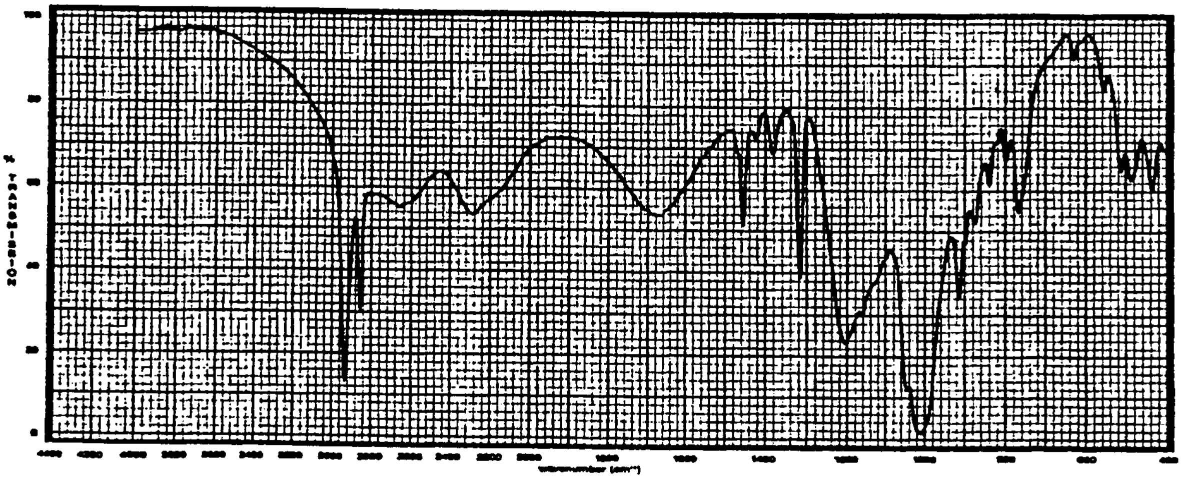


Figure 59 CYCLOHEXYL METHYLPHOSPHONIC ACID (GF ACID), LIQUID, CF/KBr

3.3.9 Pinacolyl Methylphosphonic Acid (GD Acid) $CH_3P{=}O(OH)[O\text{-}CH(CH_3)\text{-}C(CH_3)_3]$

The infrared spectrum of **GD acid**, pinacolyl methylphosphonic acid (pinacolyl hydrogen methylphosphonate or 1,2,2-trimethylpropyl hydrogen methylphosphonate is given in ***Figure 60***.

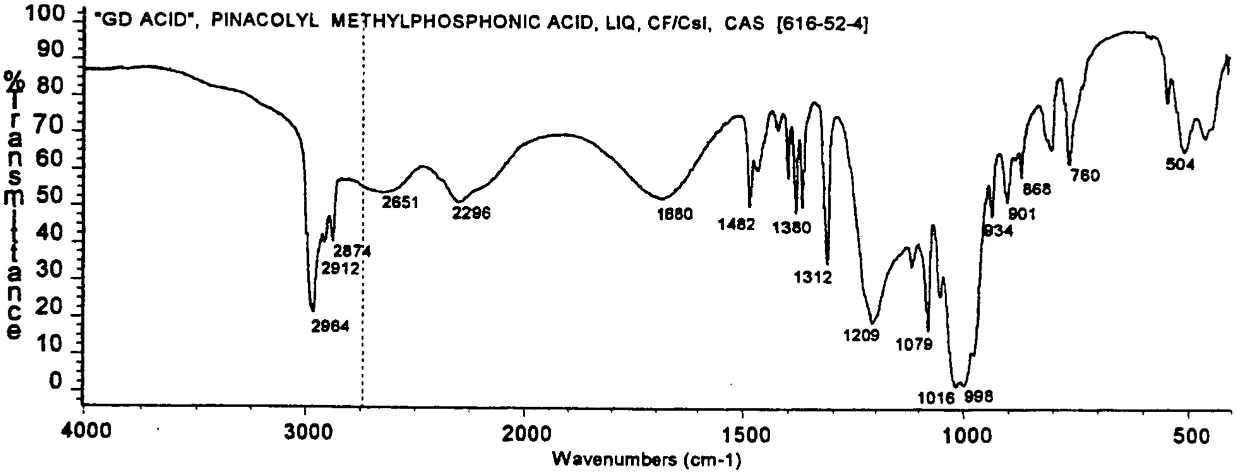


Figure 60 PINACOLYL METHYLPHOSPHONIC ACID (GD ACID), LIQUID, CF/CsI

The band assignments for **GD acid** are as follows: 2964 cm^{-1} ms, 2912 cm^{-1} w and 2874 cm^{-1} w (ν CH_3), 2651, 2296 and 1680 cm^{-1} all weak and broad (POH), 1482 cm^{-1} w and 1464 cm^{-1} vw (δ_{as} CH_3), 1418 cm^{-1} vvw (δ_{as} P-CH_3), 1397 cm^{-1} vw and 1380 cm^{-1} w [δ_{as} CH_3 from $C(CH_3)_3$], 1366 cm^{-1} w (δ_{sy} CH_3 from C-CH_3), 1312 cm^{-1} m (δ_{sy} P-CH_3), 1209 cm^{-1} ms (ν P=O), 1115 vvw, 1079 w and 1051 w cm^{-1} (pinacolyl moiety), 1016 and 998 cm^{-1} s (ν P-O-C), 976 cm^{-1} (ν P-OH), 934, 868 and 760 cm^{-1} all weak (pinacolyl moiety), 901 cm^{-1} w (P-CH_3 rock), 801 cm^{-1} w (POC ?), 504 cm^{-1} w (P=O deformation ?).

3.3.10 Dipinacolyl Methylphosphonate [bis(1,2,2-Trimethylpropyl) Methylphosphonate]

The infrared spectrum for dipinacolyl methylphosphonate, [bis(1,2,2-trimethylpropyl) methylphosphonate], $CH_3P{=}O[O\text{-}CH(CH_3)\text{-}C(CH_3)_3]_2$, is reproduced in ***Figure 61***. The band assignments are as follows: ca 3530 and 3470 cm^{-1} vw (H_2O), 2962 cm^{-1} ms, 2812 cm^{-1} m and 2874 cm^{-1} m (ν CH_3), 1481 cm^{-1} m and 1464 cm^{-1} w (δ_{as} CH_3), 1417 cm^{-1} vw (δ_{as} P-CH_3), 1396 cm^{-1} w, 1378 cm^{-1} m and 1365 cm^{-1} m [δ_{sy} $C(CH_3)_3$ and δ_{sy} C-CH_3)], 1307 cm^{-1} m (δ_{sy} P-CH_3), 1248 cm^{-1} ms (ν P=O), 1211 cm^{-1} w [$C(CH_3)_3$?], 1115 cm^{-1} w, 1081 cm^{-1} m, 1052 cm^{-1} m, 1021 cm^{-1} ms and 1006 cm^{-1} ms (pinacolyl moiety), 971 cm^{-1} s (ν P-O-C), 934 cm^{-1} m (pinacolyl moiety), 907 cm^{-1} w and 894 cm^{-1} w [P-CH_3 rock and CH_3 rock of $C(CH_3)_3$], 867 cm^{-1} w, 811 cm^{-1} m, 750 cm^{-1} w, 723 cm^{-1} vw and 548 cm^{-1} w (pinacolyl moiety).

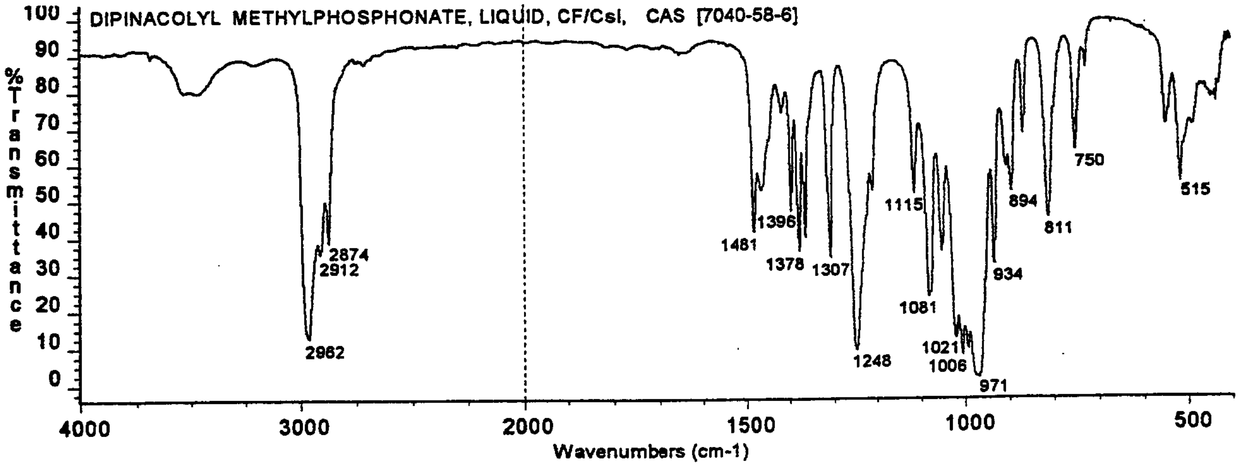


Figure 61 DIPINACOLYL METHYLPHOSPHONATE, LIQUID, CF/CsI

3.3.11 Pinacolyl Alcohol (1,2,2-Trimethyl-1-Propanol) HO-$CH(CH_3)$-$C(CH_3)_3$

The infrared spectrum for pinacolyl alcohol (1,2,2-trimethyl-1-propanol or 3,3-dimethyl-2-butanol) is given in ***Figure 62***. The band assignments are as follows: 3393 cm^{-1} ms (ν OH bonded), 2961 cm^{-1} s, 2909 cm^{-1} m and 2872 cm^{-1} ms (ν CH_3), 1480 cm^{-1} m and 1459 cm^{-1} m (δ_{as} CH_3), 1391 w and

1373 cm^{-1} m [δ_{sy} CH_3 of C(CH3)3], 1364 cm^{-1} m (δ_{sy} C-CH_3), 1299 cm^{-1} vw (β OH), 1098 and 1084 cm^{-1} ms (ν C-O), 1201 cm^{-1} w, 1051 cm^{-1} m, 1008 cm^{-1} ms (pinacolyl moiety), 913 cm^{-1} ms (CH_3 rock ?), 618 cm^{-1} w and broad (γ OH).

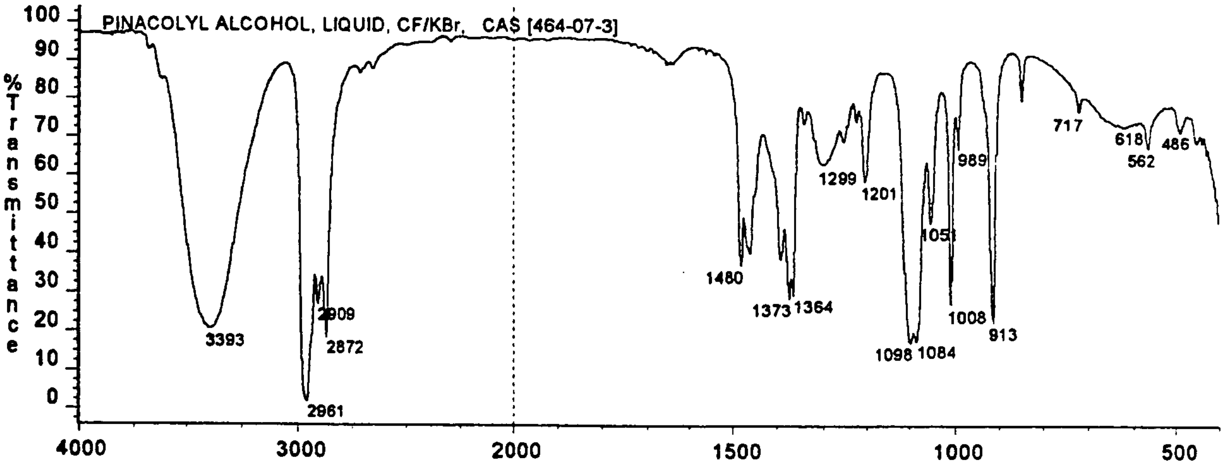


Figure 62 **PINACOLYL ALCOHOL (1,2,2-TRIMETHYL-1-PROPANOL), LIQUID, CF/KBr**

3.3.12 2-Methylcyclohexyl Methylphosphonic Acid (EA 1356 Acid)

$CH_3P{=}O(OH)[O\text{-}(2\text{-}CH_3\text{-}C_6H_{10})]$

The infrared spectrum of 2-methylcyclohexyl methylphosphonic acid (2-methyl-cyclohexyl hydrogen methylphosphonate), **EA 1356 Acid**, is reproduced in ***Figure 63***. The band assignments are as follows: 2931 cm^{-1} s and 2858 cm^{-1} ms (ν_{as} and ν_{sy} CH_3 and CH_2), 2660 cm^{-1}, 2296 cm^{-1} and 1684 cm^{-1} all weak and broad (POH), 1453 cm^{-1} w (δ_{as} CH_3 and δ CH_2), 1419 cm^{-1} vw (δ_{as} P-CH_3), 1380 cm^{-1} vw (δ_{sy} CH_3), 1311 cm^{-1} m (δ_{sy} P-CH_3), 1053 cm^{-1} sh and 954 cm^{-1} sh (cyclohexyl ring ?), 1001 cm^{-1} s (ν P-O-C and also ν P-OH, possible shoulder at 987 cm^{-1} ?), 904 cm^{-1} m (P-CH_3 rock), 760 cm^{-1} m (POC), 496 cm^{-1} w (P=O deformation ?).

3.3.13 Monosodium Salt of Methylphosphonic Acid (NAMPA) $CH_3P{=}O(ONa)(OH)$

The infrared spectrum of the monosodium salt of methylphosphonic acid (**NAMPA**) is given in ***Figure 64***. The band assignments for the dried sample are as follows: 3378 cm^{-1} w, 3283 cm^{-1} vw and

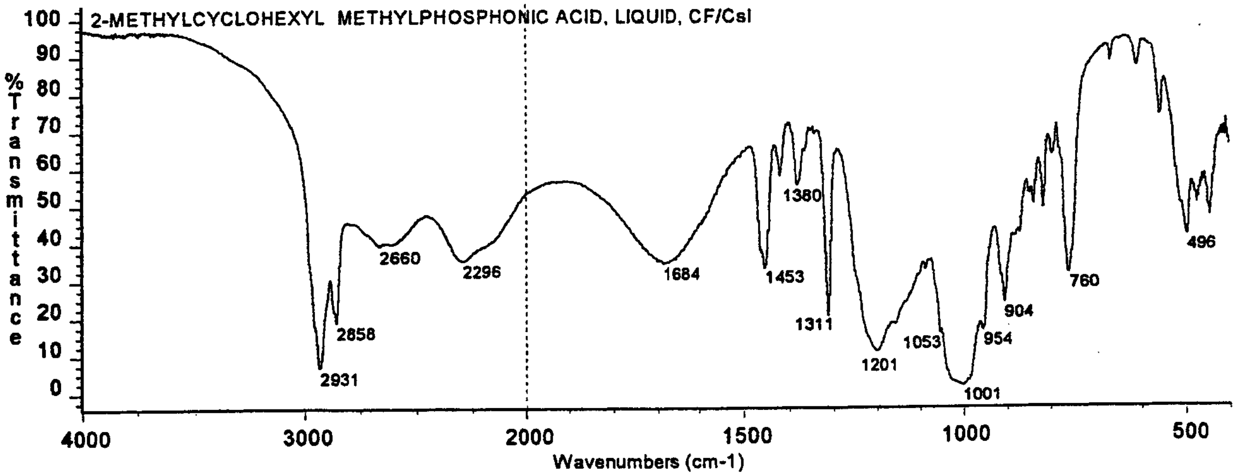


Figure 63 2-METHYLCYCLOHEXYL METHYLPHOSPHONIC ACID (EA 1356 ACID), LIQUID, CF/CsI

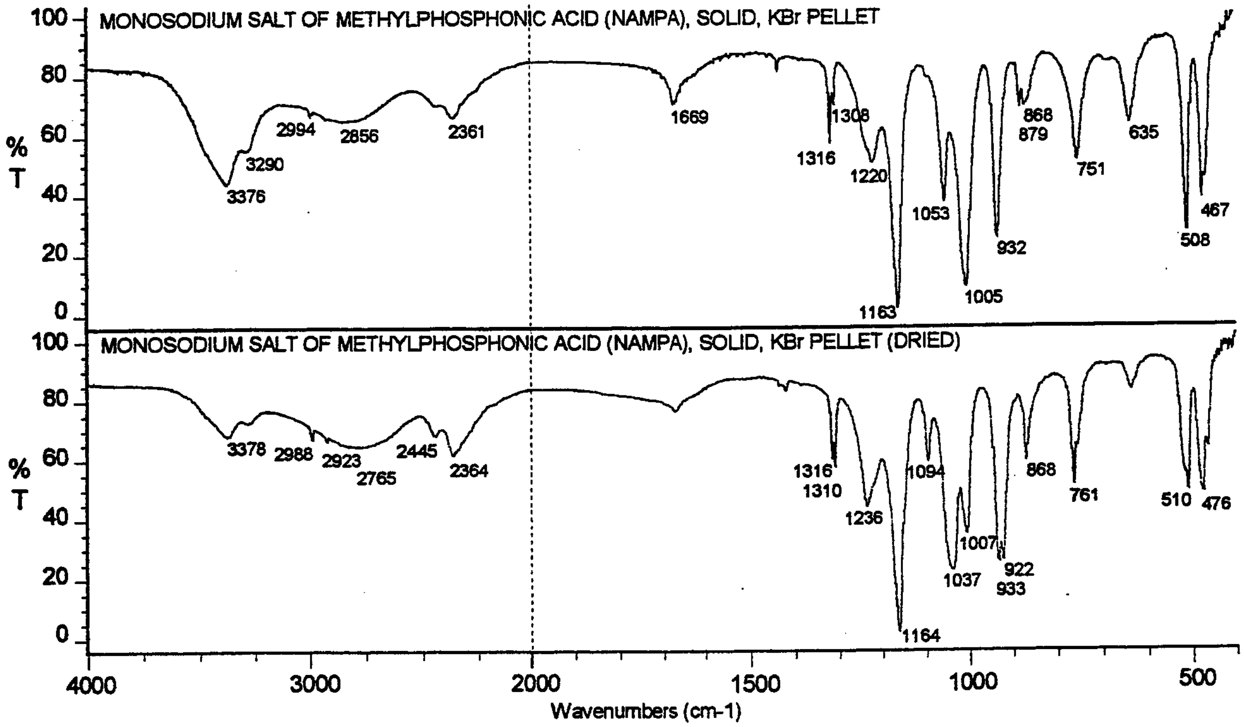


Figure 64 MONOSODIUM SALT OF METHYLPHOSPHONIC ACID (NAMPA), SOLID, KBr PELLET
Upper Spectrum WET SAMPLE
Lower Spectrum DRIER SAMPLE

1669 cm^{-1} vw (H_2O), 2988 cm^{-1} vw and 2923 cm^{-1} vw (ν_{as} and ν_{sy} CH_3), 2765 cm^{-1} w, 2445 cm^{-1} vw, 2364 cm^{-1} w, and ca 1700 cm^{-1} vw (POH), 1419 cm^{-1} vvw (δ_{as} P-CH_3), 1316 and 1310 cm^{-1} w (δ_{sy} P-CH_3), 1164 cm^{-1} s (ν_{as} PO_2^-), 1037 cm^{-1} m (ν_{sy} PO_2^-), 1007 cm^{-1} m (ν P-OH), 933 cm^{-1} and 922 cm^{-1} m

($P\text{-}CH_3$ rock), 761 cm^{-1} w (ν P-C), 510 and 476 cm^{-1} m (PO_2^-) deformation). Notice the difference in band intensities and band positions between the wet and dried samples. The only difference between these two samples was the KBr pellet from the upper spectrum in ***Figure 64*** was allowed to remain in the dry instrument purge for 15 days. The pellet was re-scanned and thus became the lower spectrum labeled '*drier*'.

3.3.14 Disodium Methylphosphonate (NA_2MP)[c] $CH_3P{=}O(O^-Na^+)_2$

The infrared spectrum of disodium methylphosphonate, **Na_2MP**, is given in ***Figure 65***. This figure shows the compound, as a KBr pellet, after various levels of drying time. Band assignments for the KBr pellet as originally prepared are as follows: 3285 ms, 3147 ms, 2333 w and 1701 vw cm^{-1} (H_2O), 2998 cm^{-1} vvw (ν CH_3), 1426 cm^{-1} vvw (δ_{as} CH_3), 1313 cm^{-1} w (δ_{sy} $P\text{-}CH_3$), 1058 s and 1035 sh cm^{-1} (ν_{as} $PO_3^=$), 976 and 967 cm^{-1} m (ν_{sy} $PO_3^=$), 837 cm^{-1} w ($P\text{-}CH_3$ rock ?), 762 cm^{-1} m (ν P-C), 526 and 489 w cm^{-1} ($PO_3^=$ deformation).

3.3.15 Sodium Isopropyl Methylphosphonate (NAIMP)[c] $CH_3P{=}O(O^- Na^+)[O\text{-}CH(CH_3)_2]$

The infrared spectrum of sodium isopropylmethylphosphonate (**NAIMP**) is given in ***Figure 66***. The band assignments are as follows: 2972 cm^{-1} w, 2922 cm^{-1} vw and 2871 cm^{-1} vvw (ν CH_3), 1467 cm^{-1} vw (δ_{as} CH_3), 1420 cm^{-1} vvw (δ_{as} $P\text{-}CH_3$), 1385 and 1370 cm^{-1} w (δ_{sy} CH_3), 1297 cm^{-1} w (δ_{sy} $P\text{-}CH_3$), 1220 cm^{-1} s (ν_{as} PO_2^-), 1177 cm^{-1} vw, 1139 cm^{-1} vw and 1097 cm^{-1} m (characteristic of P-O-isopropyl), 1073 cm^{-1} ms (ν_{sy} PO_2^-), 1009 cm^{-1} ms (ν P-O-C), 893 cm^{-1} m ($P\text{-}CH_3$ rock), 776 cm^{-1} m (POC), 720 cm^{-1} w (ν P-C), 523 and 500 cm^{-1} m (PO_2^- deformation). The two spectra that make up ***Figure 66*** again illustrate how moisture effects the resultant spectrum.

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[c] These compounds have been discussed previously in Edgewood Arsenal Technical Report EC-TR-76060, "Application of Infrared and Raman Spectroscopy to the Analysis of Phosphonic Acids and Their Salts (GB-Related Compounds), by Piffath, R. J. and Sass, S., June 1976. Approved for public release.

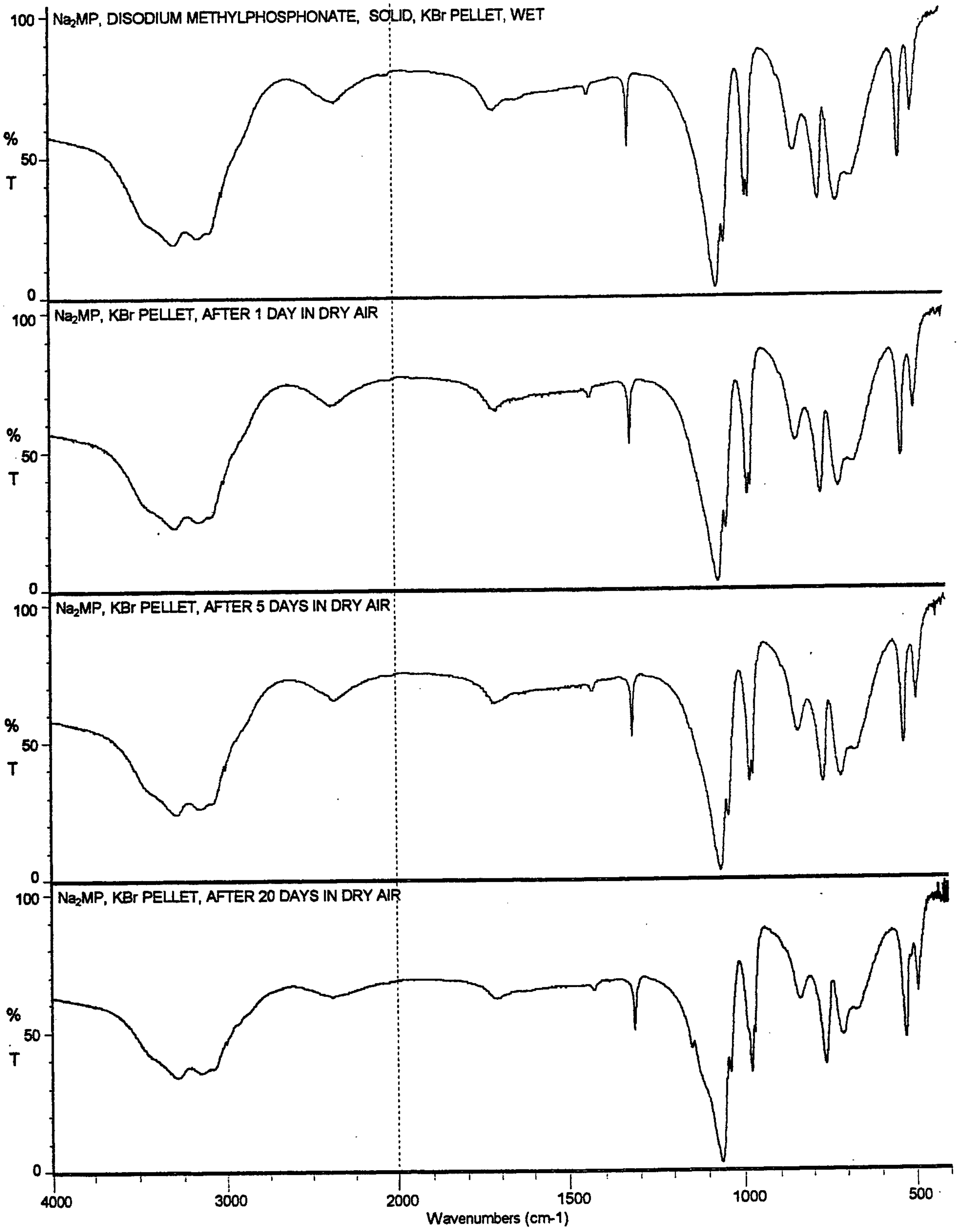

Figure 65 **DISODIUM METHYLPHOSPHONATE (NA$_2$MP), SOLID, KBr PELLET, AT VARYING DEGREES OF DRYNESS**

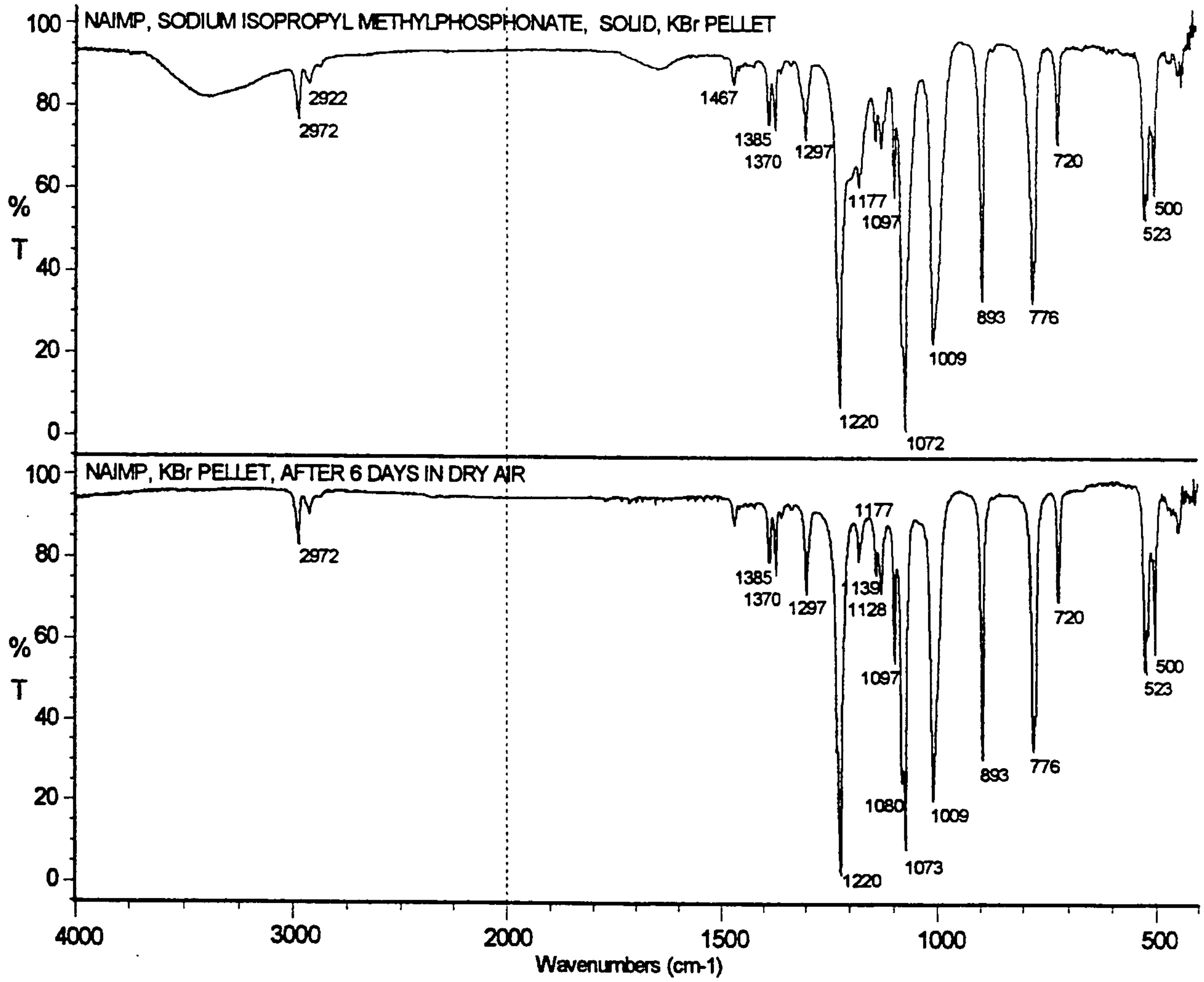

Figure 66 **SODIUM ISOPROPYL METHYLPHOSPHONATE (NAIMP), SOLID KBr PELLET**
UPPER SPECTRUM **KBr PELLET AS PREPARED**
LOWER SPECTRUM **KBr PELLET DRIED FOR 6 DAYS**

3.3.16 Disodium Dimethylpyrophosphonate (NA$_2$PYRO)

$(NaO)CH_3P(=O)\text{-}O\text{-}P(=O)CH_3(ONa)$

The infrared spectrum of disodium dimethylpyrophosphonate (**NA$_2$PYRO**) is reproduced in ***Figure 67***. The band assignments are as follows: 3432 cm^{-1} w and 1632 cm^{-1} vw (H_2O), 2998 cm^{-1} vw and 2933 cm^{-1} vw (ν_{as} and ν_{sy} CH_3), 1413 cm^{-1} vw (δ_{as} P-CH_3), 1304 cm^{-1} m (δ_{sy} P-CH_3), 1205 cm^{-1} s and 1195 cm^{-1} sh (ν_{as} PO_2^-), 1118 cm^{-1} ms (ν_{sy} PO_2^-), 968 cm^{-1} ms and 942 cm^{-1} ms (ν P-O-P), 874 cm^{-1} ms (P-CH_3 rock), 785 cm^{-1} m and 753 cm^{-1} ms (ν P-C), 452 cm^{-1} m (PO_2^- deformation).

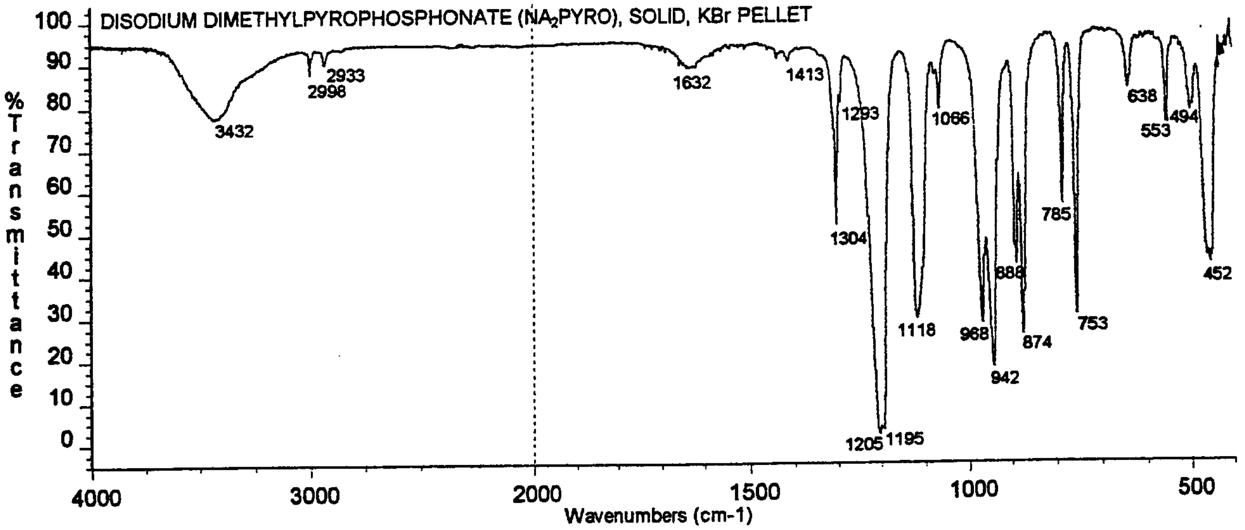

Figure 67 **DISODIUM DIMETHYLPYROPHOSPHONATE (NA$_2$PYRO), SOLID, KBr PELLET**

3.4 Precursors of Ethyl N,N-Dimethylphosphoramidocyanidate (GA, Tabun)

Dimethylamine hydrochloride

Phosphorus oxychloride

Dimethylphosphoramidic dichloride

Ethyl phosphorodichloridate

3.4.1 Dimethylamine Hydrochloride $(CH_3)_2N{\bullet}HCl$

The infrared spectrum of dimethylamine hydrochloride is given in ***Figure 68***. Band assignments for the compound are as follows: multiple bands near 3019 cm^{-1} and 2770 cm^{-1} are indicative of the ν_{as} NH_2^+ and the ν_{sy} NH_2^+, 2700-2300 cm^{-1} combination bands NH_2^+ group, 1600-1580 cm^{-1} w-m (δ NH_2^+), 1480-1460 cm^{-1} ms (δ_{as} N-CH_3), near 1420 cm^{-1} m (δ_{sy} N-CH_3), near 1020 cm^{-1} m-s (ν C-N).

3.4.2 Phosphorus Oxychloride (THO) $POCl_3$

The infrared spectrum for phosphorus oxychloride (phosphoryl chloride), **THO**, $POCl_3$, is given in ***Figure 69.*** Band assignments are as follows: 2585 cm^{-1} vvw (2 x 1298 = 2596 cm^{-1}), 1384 cm^{-1} vvw (KNO_3 from the KBr windows), 1298 cm^{-1} ms (ν P=O), 1180 cm^{-1} vw (ν P=O from the hydrolysis of $POCl_3$), 588 cm^{-1} s (ν_{as} PCl_3), 484 cm^{-1} m (ν_{sy} PCl_3).

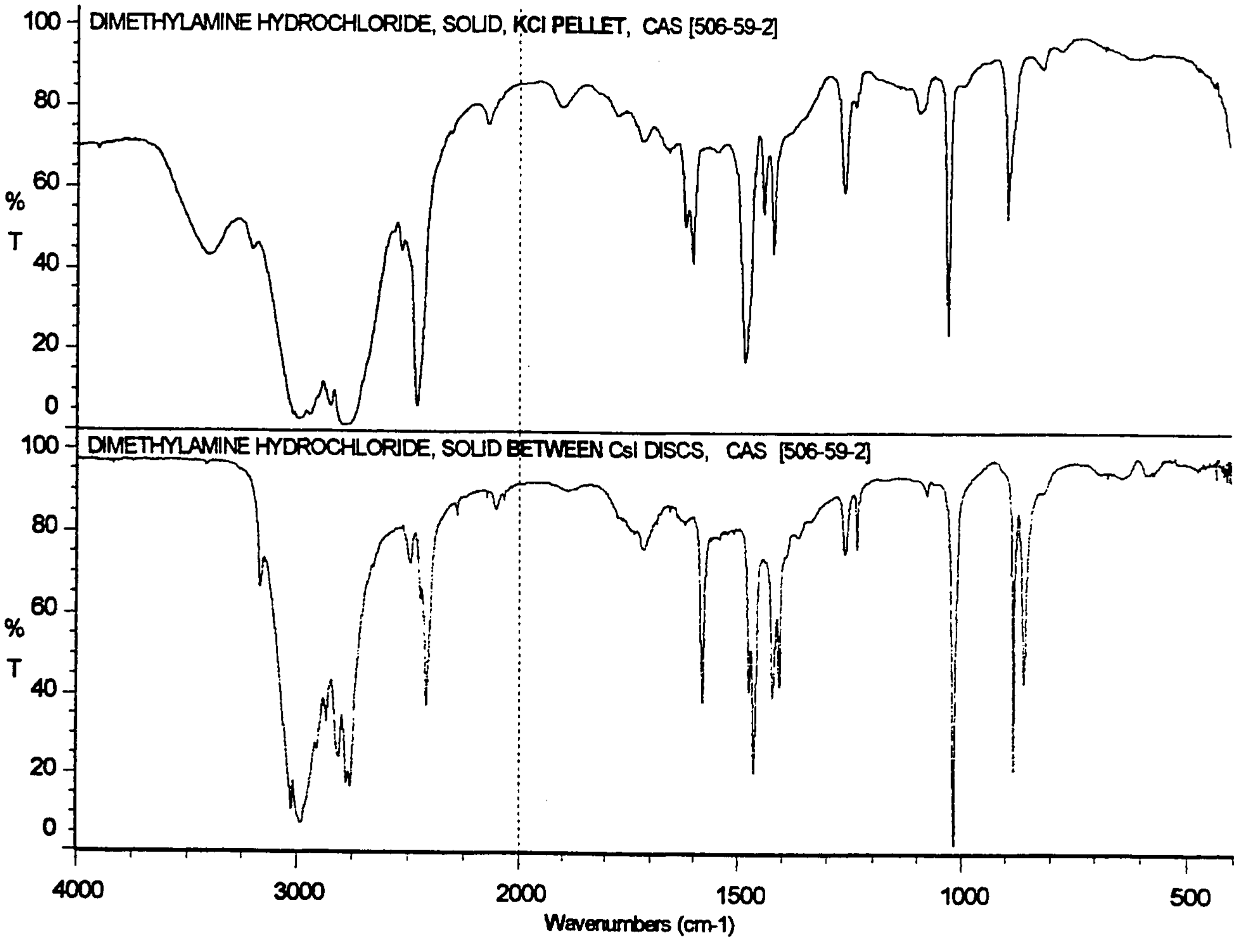

Figure 68 DIMETHYL HYDROCHLORIDE SOLID AS A KCl PELLET (upper spectrum) AND AS A SOLID BETWEEN CsI WINDOWS (lower spectrum)

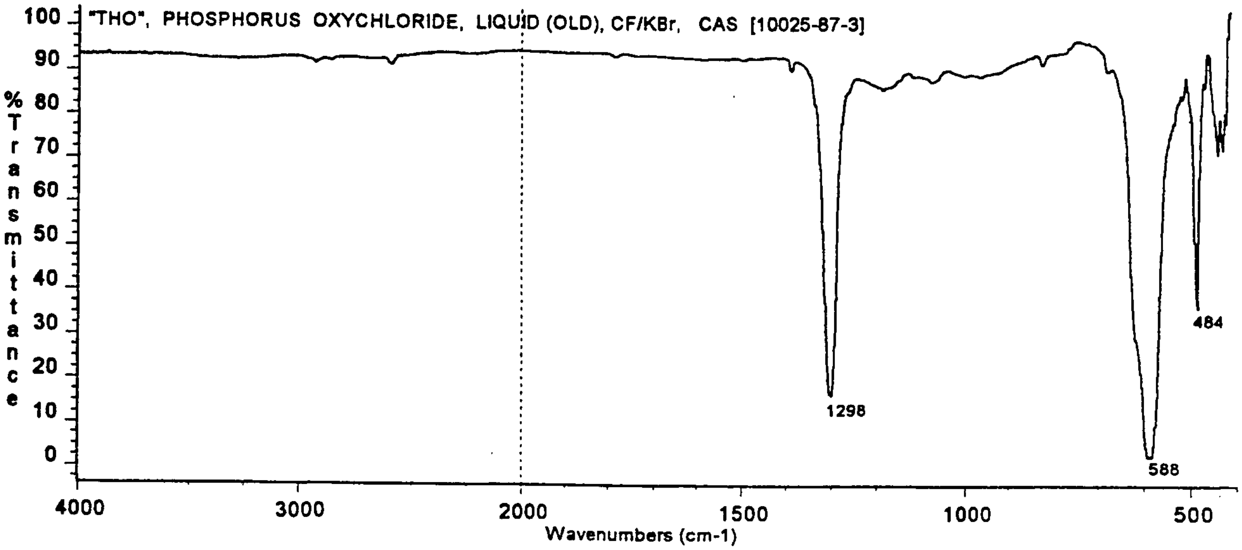

Figure 69 PHOSPHORUS OXYCHLORIDE (THO), LIQUID (OLD), CF/KBr

3.4.3 N,N-Dimethylphosphoramidic Dichloride $(CH_3)_2NP{=}OCl_2$

The infrared spectrum of N,N-dimethylphosphoramidic dichloride (dimethylamidophosphoric dichloride) is given in ***Figure 70***. The band assignments are as follows: 3007 cm^{-1} vw, 2938 cm^{-1} w, 2860 cm^{-1} vw and 2825 cm^{-1} vw (ν CH_3), 1715 cm^{-1} vvw (992 + 724 =1716 cm^{-1}), 1480 cm^{-1} w and 1457 cm^{-1} m (δ CH_3), 1309 cm^{-1} ms [$PN(CH_3)_2$], 1267 cm^{-1} s (ν P=O), 1171 cm^{-1} m and 1066 cm^{-1} w [$PN(CH_3)_2$], 992 cm^{-1} s (ν_{as} P-N-C), 724 cm^{-1} ms (ν_{sy} P-N-C), 561 cm^{-1} ms and 518 cm^{-1} ms (ν_{as} and ν_{sy} PCl_2).

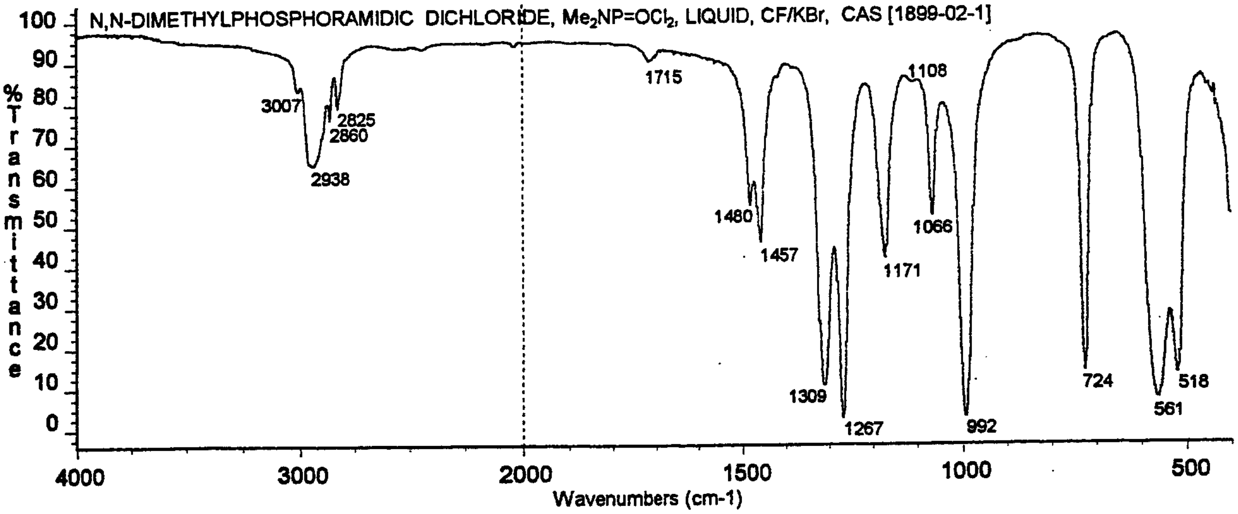

Figure 70 N,N-DIMETHYLPHOSPHORAMIDIC DICHLORIDE, LIQUID, CF/KBr

The effect of atmospheric moisture on N,N-dimethylphosphoramidic dichloride is shown in ***Figure 71***. The compound seems to remain pretty much intact until 5 hours had elapsed. Between the 5 and 23 hour periods the compound hydrolyzes as evidenced by the appearance of strong bands near 3020 and 2780 cm^{-1} and a weak band near 2439 cm^{-1} indicative of a NH_2^+ moiety. The bands due to the PCl_2 group at 561 and 518 cm^{-1} are almost gone from the spectrum as are the bands due to the $PN(CH_3)_2$ group (1480, 1457,1309, 1171, 1066, 992 and 724 cm^{-1} . By day two the remaining material may be a mix of $HOP{=}O(OH)_2$ and $(CH_3)_2NH$, perhaps best represented as $[(HO)_2\text{-}PO_2^-]H_2N^+(CH_3)_2$.

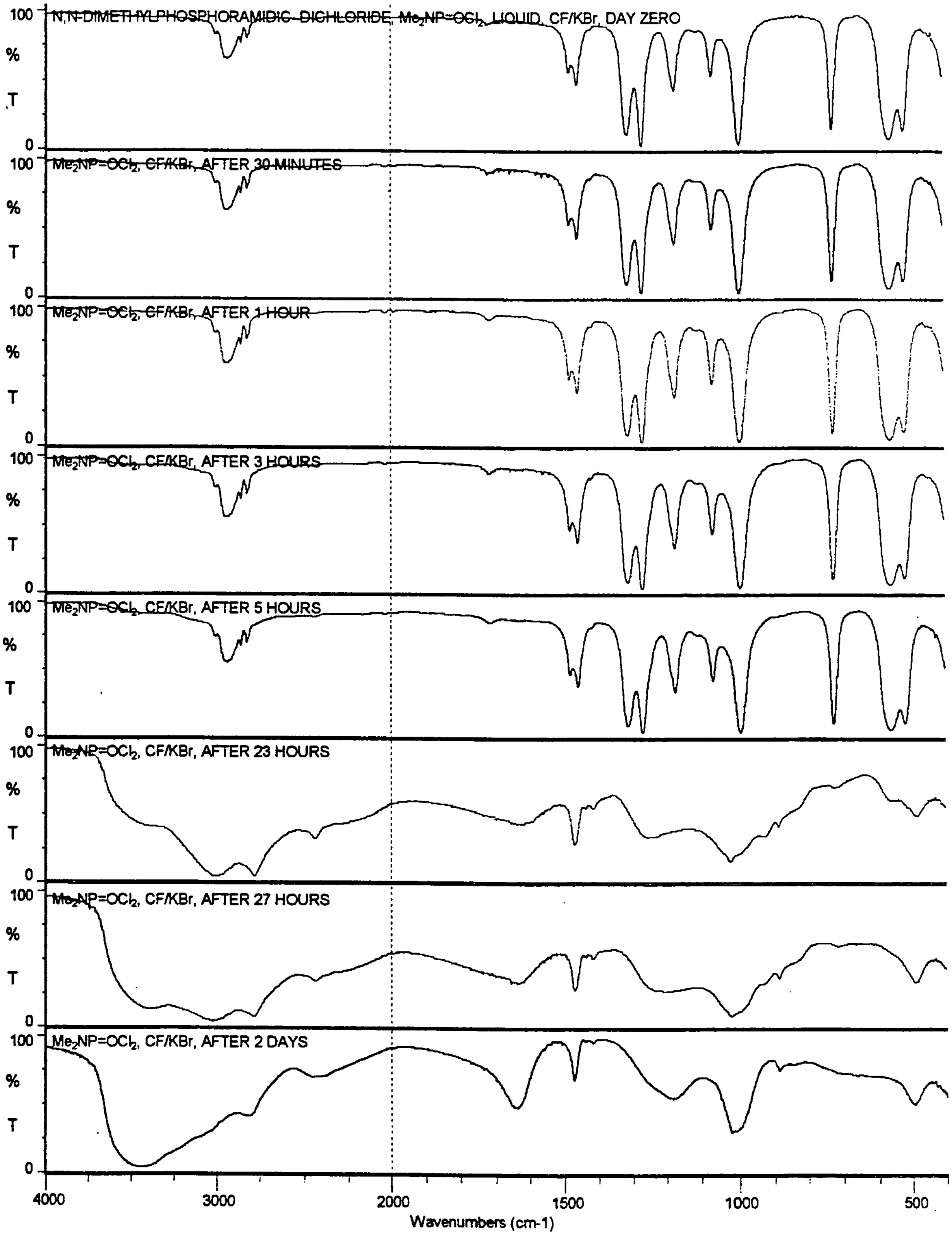

Figure 71 **EFFECT OF ATMOSPHERIC MOISTURE ON N,N-DIMETHYLPHOSPHORAMIDIC DICHLORIDE, LIQUID, CF/KBr**

3.4.4 Ethyl Phosphorodichloridate CH_3-CH_2-O-P=OCl_2

The infrared spectrum of ethyl phosphorodichloridate (ethyl dichlorophosphate) is reproduced as ***Figure*** *72*. Band assignments are as follows: 2990 cm^{-1} m (ν_{as} CH_3), 2942 cm^{-1} w (ν_{as} CH_2), 2912 cm^{-1} w (ν_{sy} CH_3) and 2872 cm^{-1} vw (ν_{sy} CH_2), 2594 cm^{-1} vw (1310 + 1295 = 2605 cm^{-1}), 1799 cm^{-1} w (1036 + 776 = 1816 , 1013 + 776 = 1789 cm^{-1}), 1476 cm^{-1} m (δ OCH_2), 1445 cm^{-1} m (δ_{as} CH_3), 1393 cm^{-1} m (ω OCH_2), 1371 cm^{-1} m (δ_{sy} CH_3), 1310 and 1295 cm^{-1} s (ν P=O doublet, isomers ?), 1161 cm^{-1} m and 1101 cm^{-1} w (CH_3 rock, characteristic of P-O-ethyl), 1036 and 1013 cm^{-1} s (ν P-O-C), 980 cm^{-1} ms (ν C-C of P-O-ethyl), 776 cm^{-1} ms (POC), 605 cm^{-1} sh and 579 cm^{-1} s (ν_{as} PCl_2 doublet possibly due to isomers), 552 cm^{-1} sh and 517 cm^{-1} ms (ν_{sy} PCl_2 doublet possibly due to isomers).

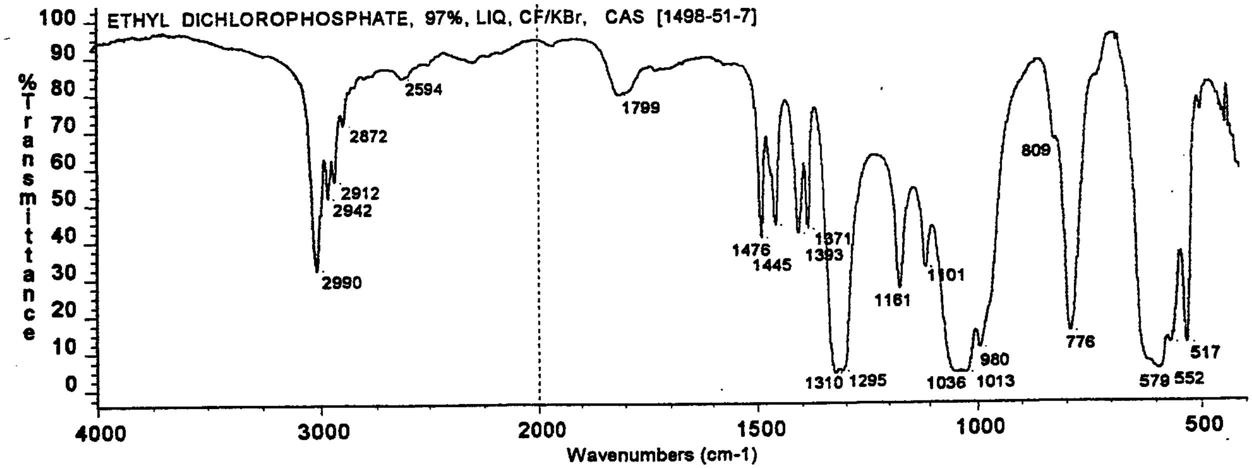

Figure 72 ETHYL PHOSPHORODICHLORIDATE (ETHYL DICHLOROPHOSPHATE), LIQUID, CF/KBr

The effect of atmospheric moisture on the infrared spectrum of ethyl phosphorodichloridate is given is ***Figure*** *73*. The infrared spectrum after 1 day shows the presence of the POH group as indicated by the broad bands near 2770, 2280 and 1670 cm^{-1}. Some PCl is probably still present as indicated by the band near 579 cm^{-1}. The P=O stretching band has dropped from near 1300 cm^{-1} to 1224 cm^{-1}. The P-O-Ethyl group is still present as indicated by the bands at 2990, 1479, 1445,1396, 1373, 1167, 1041 and 779 cm^{-1}. By the second day of exposure to atmospheric moisture the spectrum shows a decrease in the P=O stretching frequency to 1205 cm^{-1}. The POH and POEthyl moieties are still present. The band near 578 cm^{-1} has greatly diminished in intensity and may now be due to the P-acid moiety and not to PCl. The resultant compound may now be represented as $H_5C_2\text{-O-P=O(OH)}_2$, ethyl phosphoric acid (ethyl dihydrogen phosphate). The compound may undergo further hydrolysis to form phosphoric acid, HO-P=O(OH)_2. The hydrolysis may be represented as follows:

EtO-P=OCl_2 -HOH-> EtO-P=O(OH)(Cl) -HOH->Et-P=O(OH)_2 ~HOH~> HOP=O(OH)_2 .

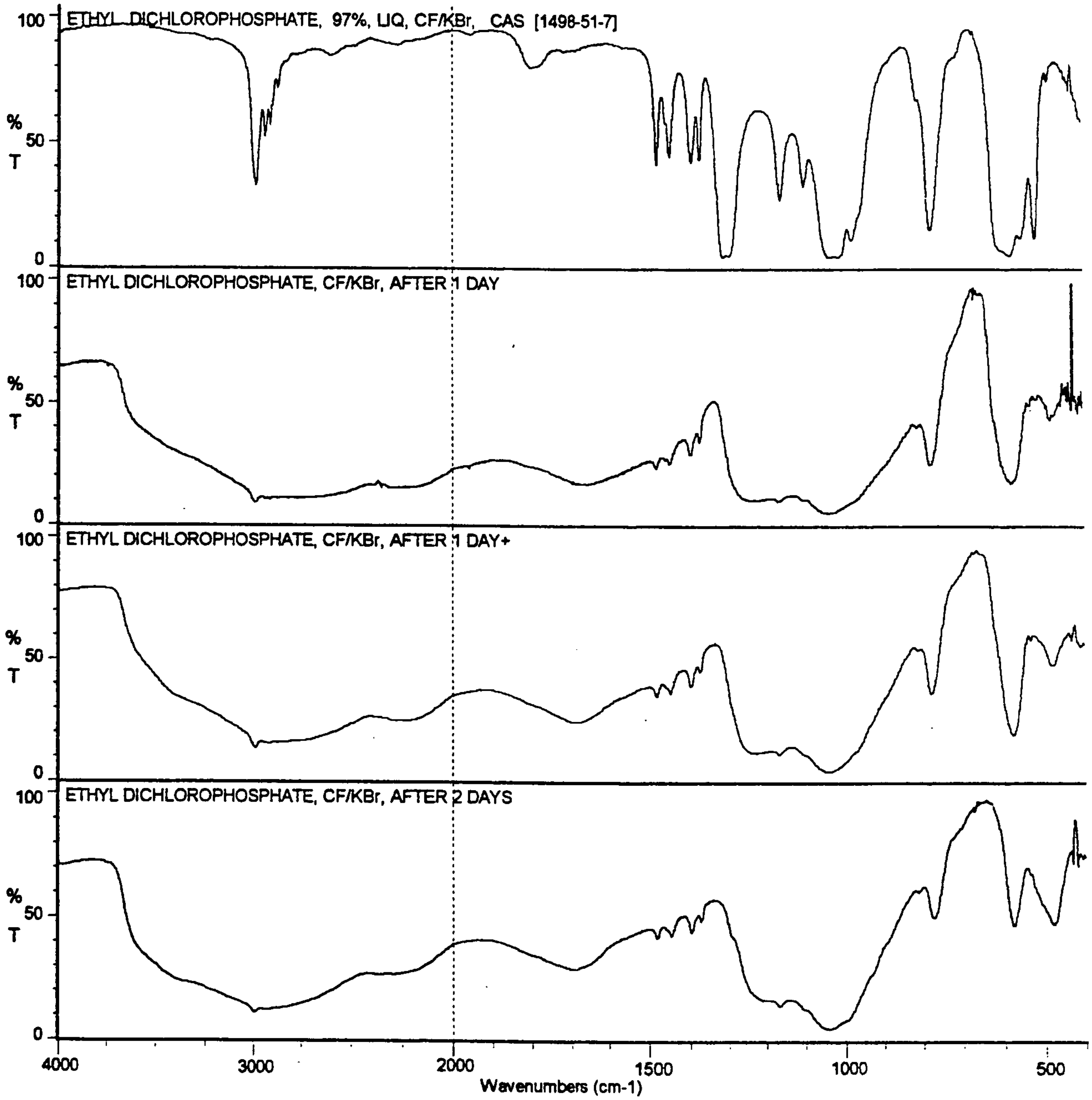

Figure 73 EFFECT OF ATMOSPHERIC MOISTURE ON ETHYL PHOSPHORODICHLORIDATE, (ETHYL DICHLOROPHOPHATE), LIQUID, CF/KBr

3.5 Impurities of Ethyl N,N-Dimethylphosphoramidocyanidate (GA, Tabun)

Triethyl phosphate (**TEPO**)

Triethyl Phosphate (TEPO) $O{=}P(O\text{-}CH_2\text{-}CH_3)_3$

The infrared spectrum of triethyl phosphate (TEPO) is reproduced as ***Figure 74***. The band assignments are as follows: 3545 cm^{-1} and 3489 cm^{-1} vw (H_2O), 2985 cm^{-1} m (ν_{as} CH_3), 2935 cm^{-1} w (ν_{as} CH_2), 2910 cm^{-1} w (ν_{sy} CH_3), and 2873 cm^{-1} vw (ν_{sy} CH_2), 1480 cm^{-1} vw (δ OCH_2), 1445 cm^{-1} vw (δ_{as} CH_3), 1394 cm^{-1} w (ω OCH_2), 1369 cm^{-1} vw (δ_{sy} CH_3), 1275 cm^{-1} ms and 1264 cm^{-1} sh (ν P=O), 1167 cm^{-1} and 1100 cm^{-1} w (CH_3 rock, characteristic of POEthyl), 1031 cm^{-1} s (ν P-O-C), 976 cm^{-1} ms (ν C-C of POEthyl), 823 and 800 cm^{-1} w and 744 cm^{-1} (POC), 542 and 523 cm^{-1} vw (P=O deformation).

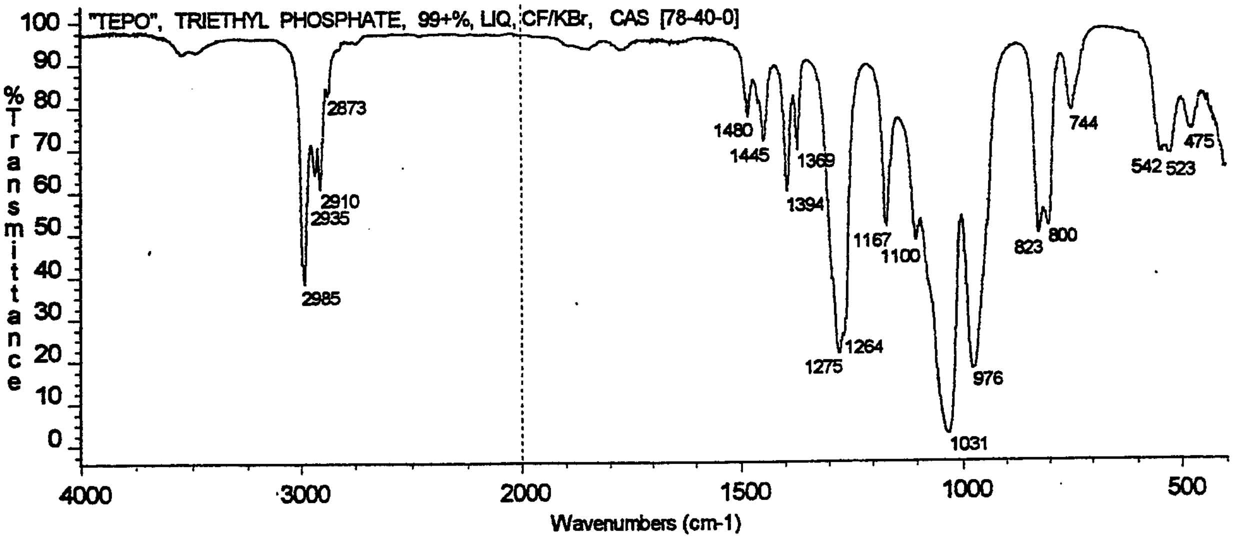

Figure 74 TRIETHYL PHOSPHATE (TEPO), 99$^+$%, LIQUID, CF/KBr

The only atmospheric effect on triethyl phosphate was a slight pick-up of water by the compound on standing. This is shown in ***Figure 75*** by the increase in intensity of the water bands near 3500 cm^{-1} with time. Also, at the 16 day period a lot of the compound has apparently evaporated as indicated by the relative intensities of the bands. Ordinate scale expansion was used to produce a full scale spectrum. This is indicated by the more than usual amount of noise in the spectrum.

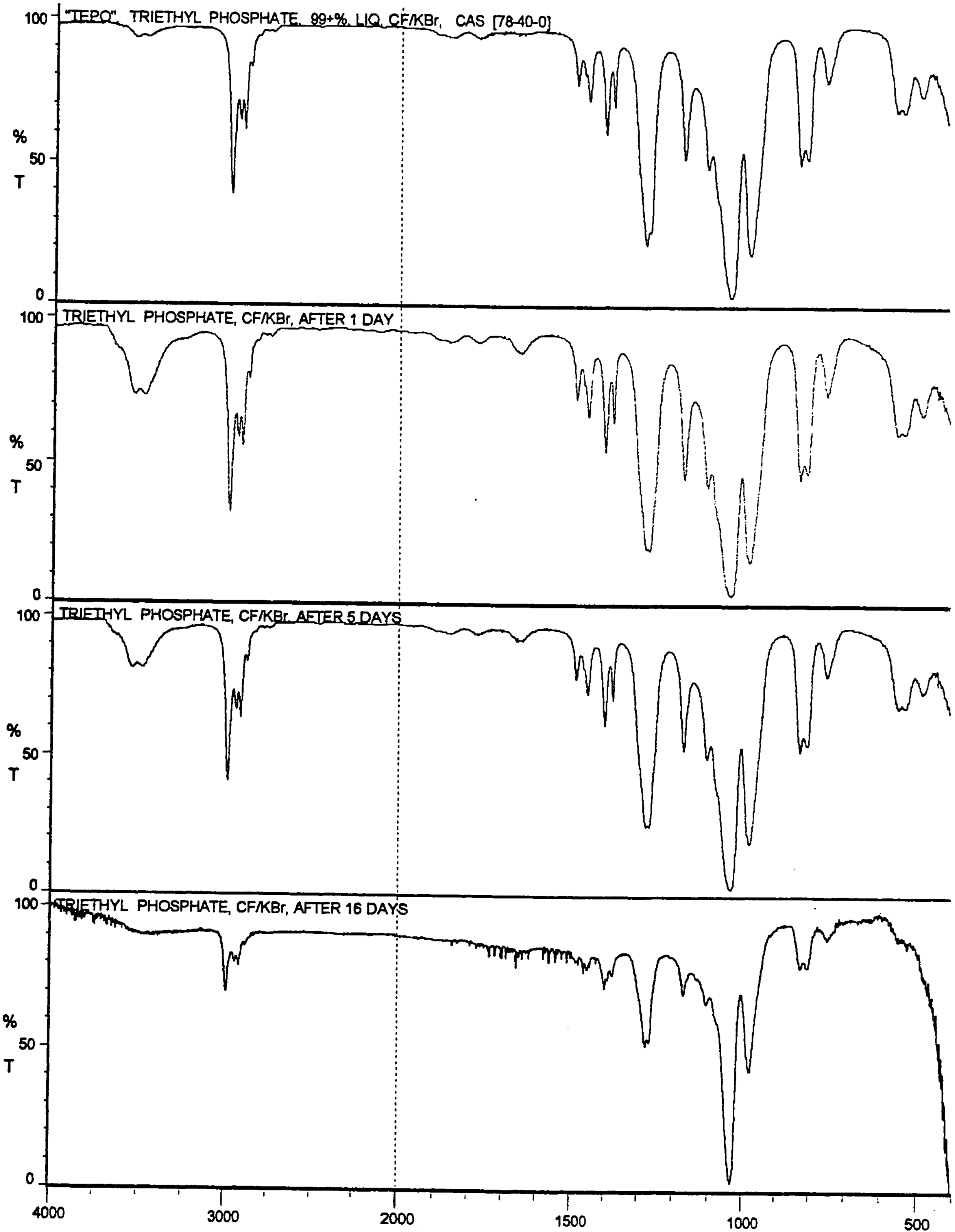

Figure 75 EFFECT OF ATMOSPHERIC MOISTURE ON TRIETHYL PHOSPHATE (TEPO), 99^{+}%, LIQUID, CF/KBr

3.6 Decomposition Products of Ethyl N,N-Dimethylphosphoramidocyanidate **(GA,Tabun)**

Hydroxylamine hydrochloride

Phosphoric acid

Ethyl alcohol (Ethanol)

sym-Bis(dimethylamido)-diethyl pyrophosphate **(GA Pyro)**

Ethyl N,N-dimethylamidophosphoric acid, sodium salt, **(sodium salt of GA Acid)**

3.6.1 Hydroxylamine Hydrochloride $HONH_2 \cdot HCl$

The infrared spectrum of hydroxylamine hydrochloride is given in ***Figure 76***. Band assignments are as follows: a series of bands between 3200 and 2800 cm^{-1} are due to the ν_{as} and ν_{sy} NH_3^+ (the ν O-H probably absorbs under these bands also), bands near 2660 cm^{-1} are combination bands enhanced by Fermi resonance, 1567 cm^{-1} m (δ_{as} NH_3^+), 1491 cm^{-1} w (δ_{sy} NH_3^+), 1401 cm^{-1} w (β OH ?), 1189 and 1152 cm^{-1} ms (ν C-O), 994 cm^{-1} ms (ν N-O), 542 cm^{-1} m (NH_3^+ torsion ?).

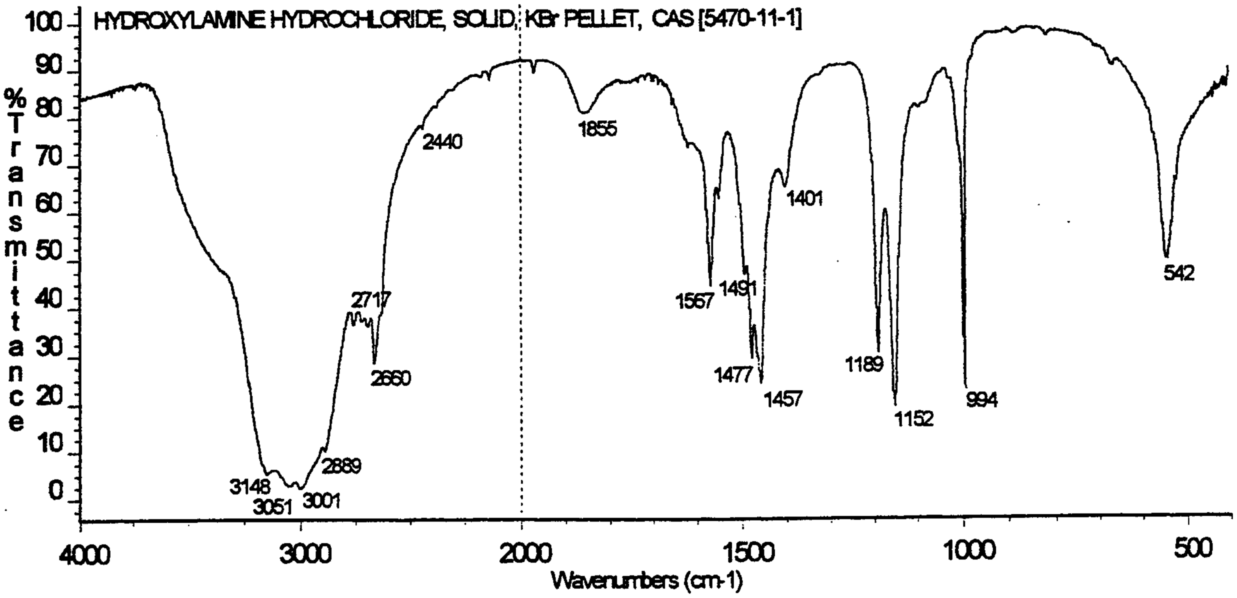

Figure 76 HYDROXYLAMINE HYDROCHLORIDE, SOLID, KBr PELLET

3.6.2 Phosphoric Acid H_3PO_4 , $(OH)_3P=O$

The infrared spectrum of phosphoric acid is given in ***Figure** 77*. The band assignments are as follows: 2883 cm^{-1}, 2342 cm^{-1}, 1654 cm^{-1} all m and broad (POH), 1144 cm^{-1} ms (ν P=O), 1013 cm^{-1} s and 889 cm^{-1} w (ν P-OH), 490 cm^{-1} m (P=O deformation).

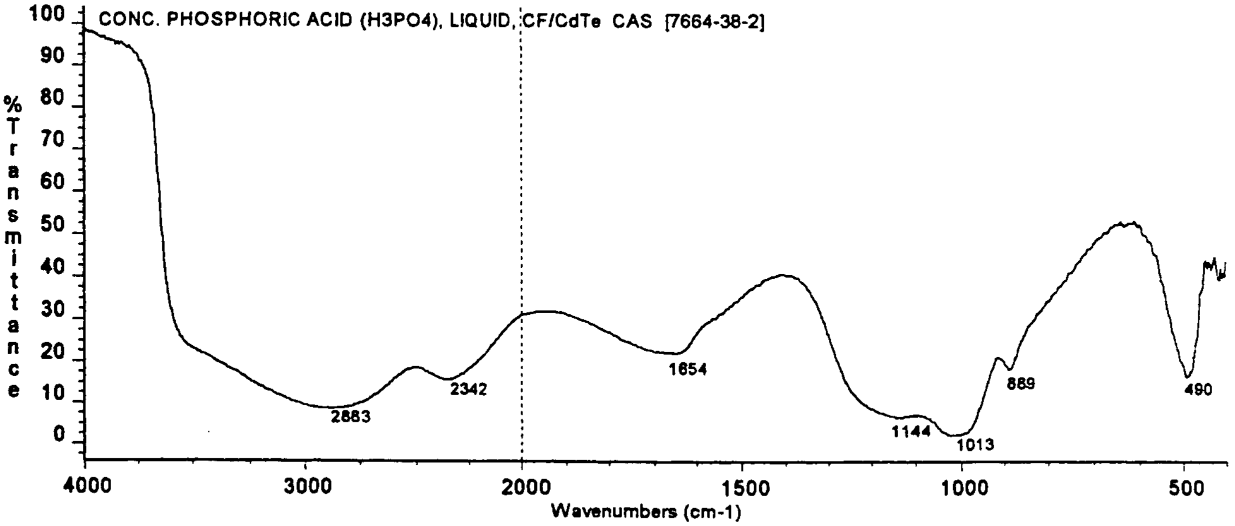

Figure 77 CONCENTRATED PHOSPHORIC ACID (H_3PO_4), LIQUID, CF/CdTe

3.6.3 Ethyl Alcohol (Ethanol) CH_3-CH_2-OH

The infrared spectrum of ethyl alcohol (ethanol) is given in ***Figure 78***. The band assignments are as follows: 3357 cm^{-1} s (ν OH bonded), 2975 cm^{-1} s, 2928 cm^{-1} w and 2892 cm^{-1} m (ν CH_3 and CH_2), 1454 cm^{-1} w (δ_{as} CH_3 and δ CH_2), 1420 cm^{-1} w (β OH), 1381 cm^{-1} w (δ_{sy} CH_3), 1330 cm^{-1} w (ω CH_2), 1090 and 1050 cm^{-1} ms-s ($\nu_{o.o.p.}$ C-C-O), 881 cm^{-1} m ($\nu_{i.p.}$ C-C-O), 668 cm^{-1} w broad (γ C-OH).

3.6.4 *sym*-Bis(Dimethylamido)-diethyl Pyrophosphate (GA Pyro)

$(EtO)[N(CH_3)_2]P(=O)$-O-$P=O[N(CH_3)_2](OEt)$

The infrared spectrum of **GA Pyro**, *sym*-bis(dimethylamido)-diethyl pyrophosphate, [bis(ethyl N,N-dimethylphosphoramidic) anhydride], was presented previously as ***Figure 23*** in section 3.1.9 under the discussion of **GA**. The effect of atmospheric moisture on **GA Pyro** was also discussed in section 3.1.9, ***Figure 24***.

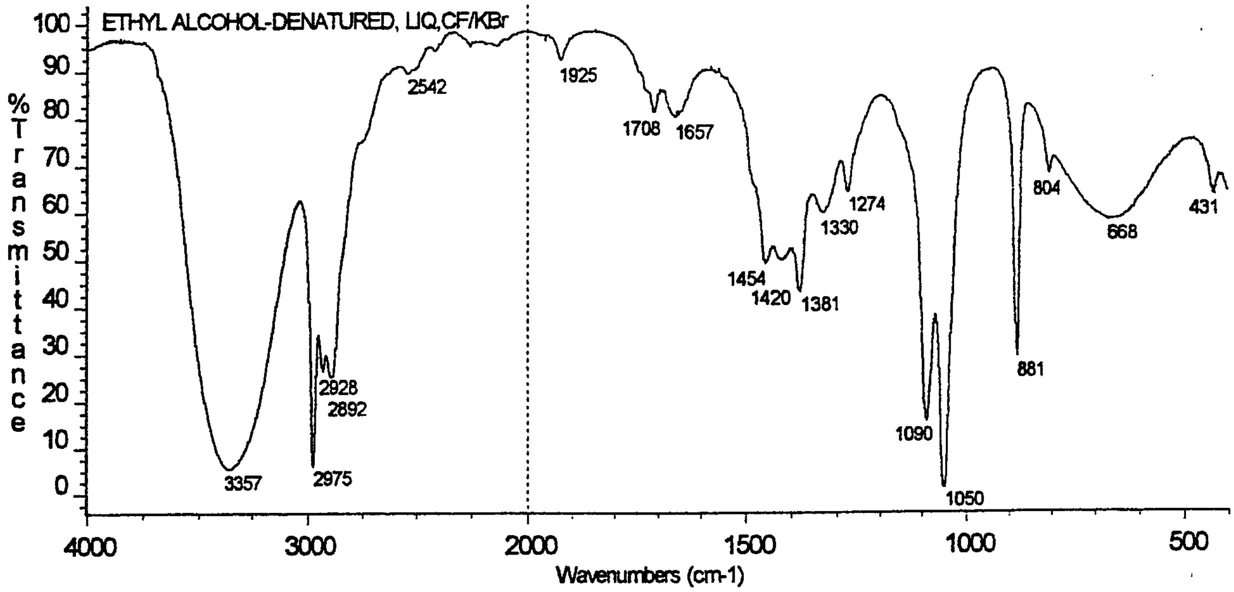

Figure 78 **ETHYL ALCOHOL (DENATURED), LIQUID, CF/KBr**

3.6.5 Ethyl N,N-Dimethylamidophosphoric Acid, Sodium Salt (Sodium Salt of GA Acid)

$(CH_3)_2N\text{-}P{=}O(ONa)(O\text{-}CH_2\text{-}CH_3)$

The infrared spectrum for the sodium salt of ethyl N,N-dimethylamidophosphoric acid (**sodium salt of GA Acid**), or the sodium salt of ethyl N,N-dimethylphosphoramidic acid, is given in ***Figure 79***. This compound results from the basic hydrolysis of **GA** (**Tabun**). The band assignments (for the dried sample) are as follows: 2971 cm^{-1} m, 2925 cm^{-1} sh, 2882 cm^{-1} and 2868 cm^{-1} m, 2837 cm^{-1} sh, 2794 cm^{-1} m (ν CH_3 and νCH_2), 1481 cm^{-1} w (δ OCH_2), 1458 m (δ CH_3), 1390 cm^{-1} w (ω OCH_2), 1365 cm^{-1} vw (δ_{sy} CH_3), 1296 cm^{-1} ms [$P\text{-}N(CH_3)_2$], 1251 cm^{-1} and 1237 cm^{-1} s (ν_{as} PO_2^-), 1200 cm^{-1} sh and 1110 cm^{-1} (?) w [$PN(CH_3)_2$], 1087 cm^{-1} sh (ν P-O-C ?), 1053 cm^{-1} s (ν_{sy} PO_2^-), 989 cm^{-1} ms (ν_{as} P-N-C), 943 cm^{-1} ms (ν C-C of POEthyl), 783 and 770 cm^{-1} ms (POC), 690 cm^{-1} ms (ν_{sy} PNC), 546 cm^{-1} ms, 526 cm^{-1} sh and 497 cm^{-1} ms (PO_2^- deformation).

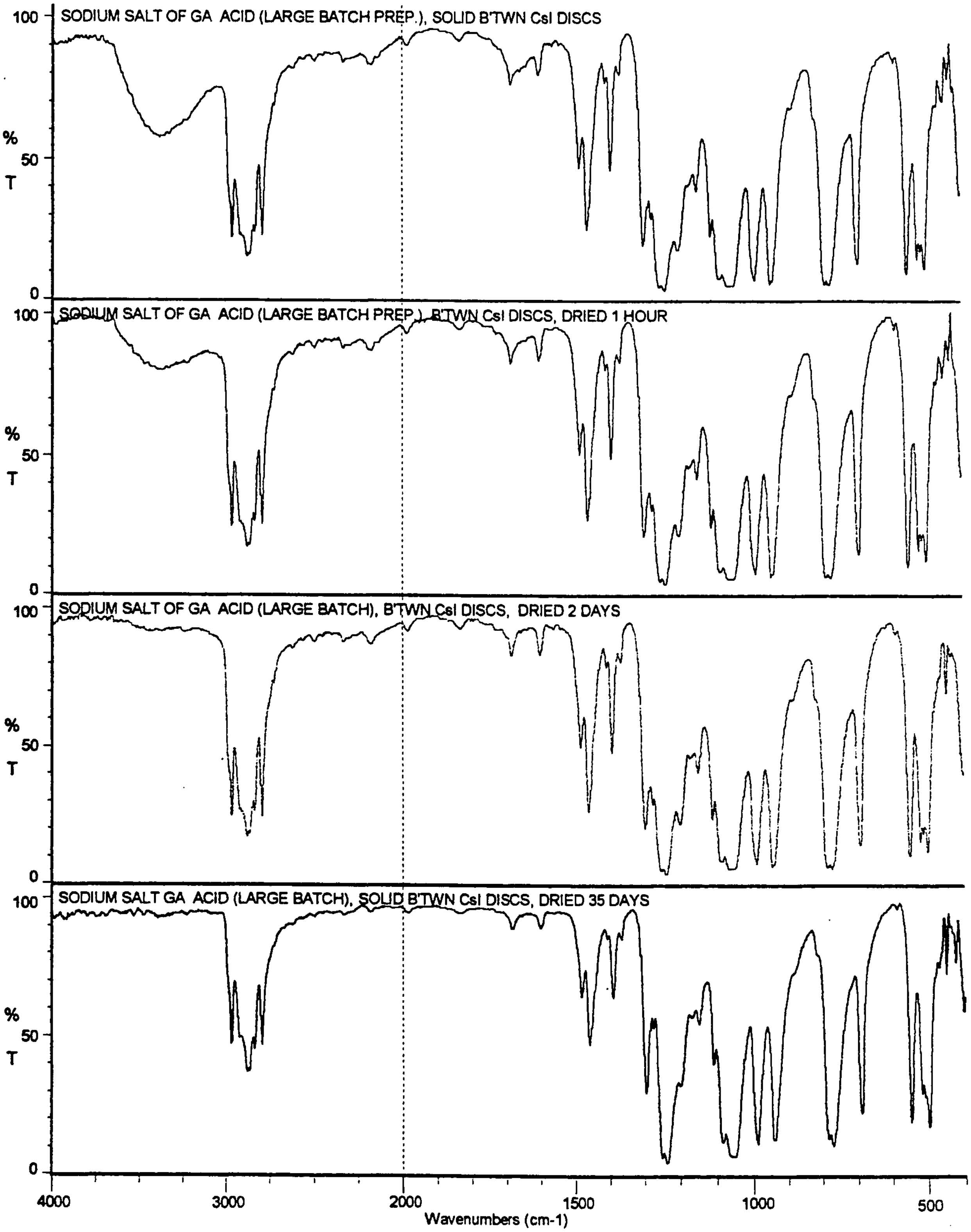

Figure 79 **INFRARED SPECTRUM OF THE SODIUM SALT OF ETHYL N,N-DIMETHYLAMIDOPHOSPHORIC ACID (SODIUM SALT OF GA ACID), SOLID BETWEEN CsI DISCS, AT VARYING DEGREES OF DRYNESS**

4. ADDITIONAL COMPOUNDS OF INTEREST

4.1 Methylphosphonocyanidic Fluoride $CH_3P{=}O(F)(C{\equiv}N)$

The infrared spectrum of methylphosphonocyanidic fluoride is reproduced as ***Figure 80A***. The band assignments are as follows: ca 3174 cm^{-1} vw (ν C-H of HCN), 3005 cm^{-1} w and 2924 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 2212 cm^{-1} ms (ν C≡N), 2090 cm^{-1} vw (ν C≡N of HCN, hydrolysis product), 1405 cm^{-1} w (δ_{as} P-CH_3), 1323 cm^{-1} s (δ_{sy} P-CH_3), 1293 cm^{-1} s (ν P=O), 1009 cm^{-1} w (ν P-OH ?, hydrolysis product), 925 cm^{-1} s and 897 cm^{-1} ms (P-CH_3 rock), 866 cm^{-1} ms (ν P-F), 776 cm^{-1} s (ν P-C), 587 cm^{-1} ms (P-C≡N ?), 471 cm^{-1} ms (δ P-F ?).

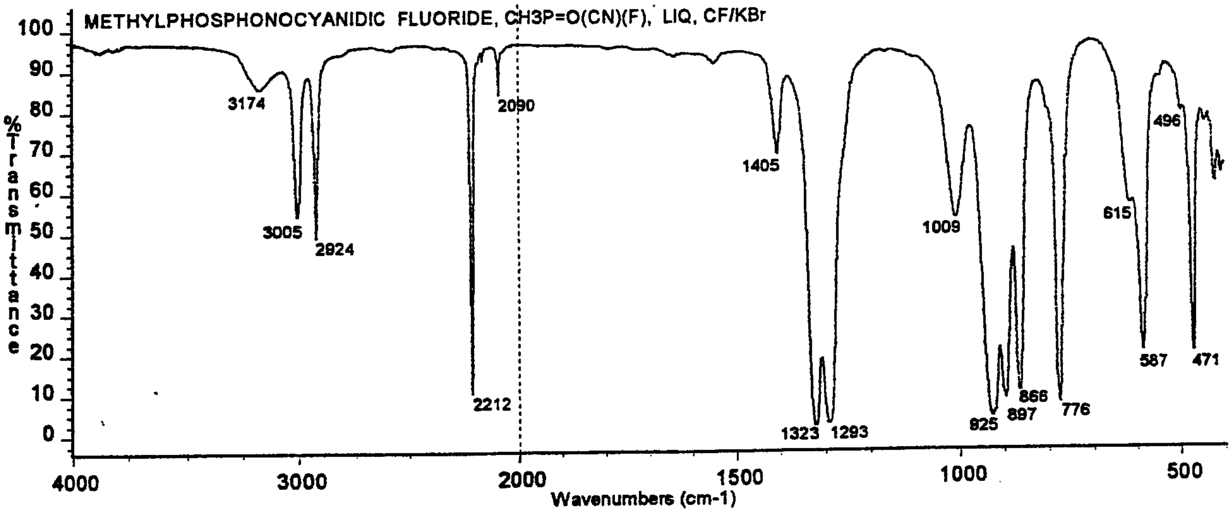

Figure 80A METHYLPHOSPHONOCYANIDIC FLUORIDE, LIQUID, CF/KBr

The exposure of methylphosphonocyanidic fluoride to atmospheric moisture is depicted by ***Figure 80B***. As time passes to the 135 minute mark, bands at 3174 and 2090 cm^{-1} (H-C≡N) have increased in intensity. Also increasing is the band at 1009 cm^{-1} (P-OH). After 21 hours of exposure to atmospheric moisture, the ν C≡N band from the compound (2212 cm^{-1}) has disappeared from the spectrum, having been replaced by the ν C≡N of HCN (2090 cm^{-1}). Other bands now visible in the spectrum are: 3012 and 2935 vw, 1416 vw, 1325 s and 900 cm^{-1} sh all due to the P-CH_3 group; ca 2634 and 2287 vw, 1653 w, 1017 s cm^{-1} due to P-OH; 867 cm^{-1} ms (ν P-F); 1298 cm^{-1} (ν P=O) a strong band but tailing off into broadness-indicating the possibility of more than one P=O containing species. The

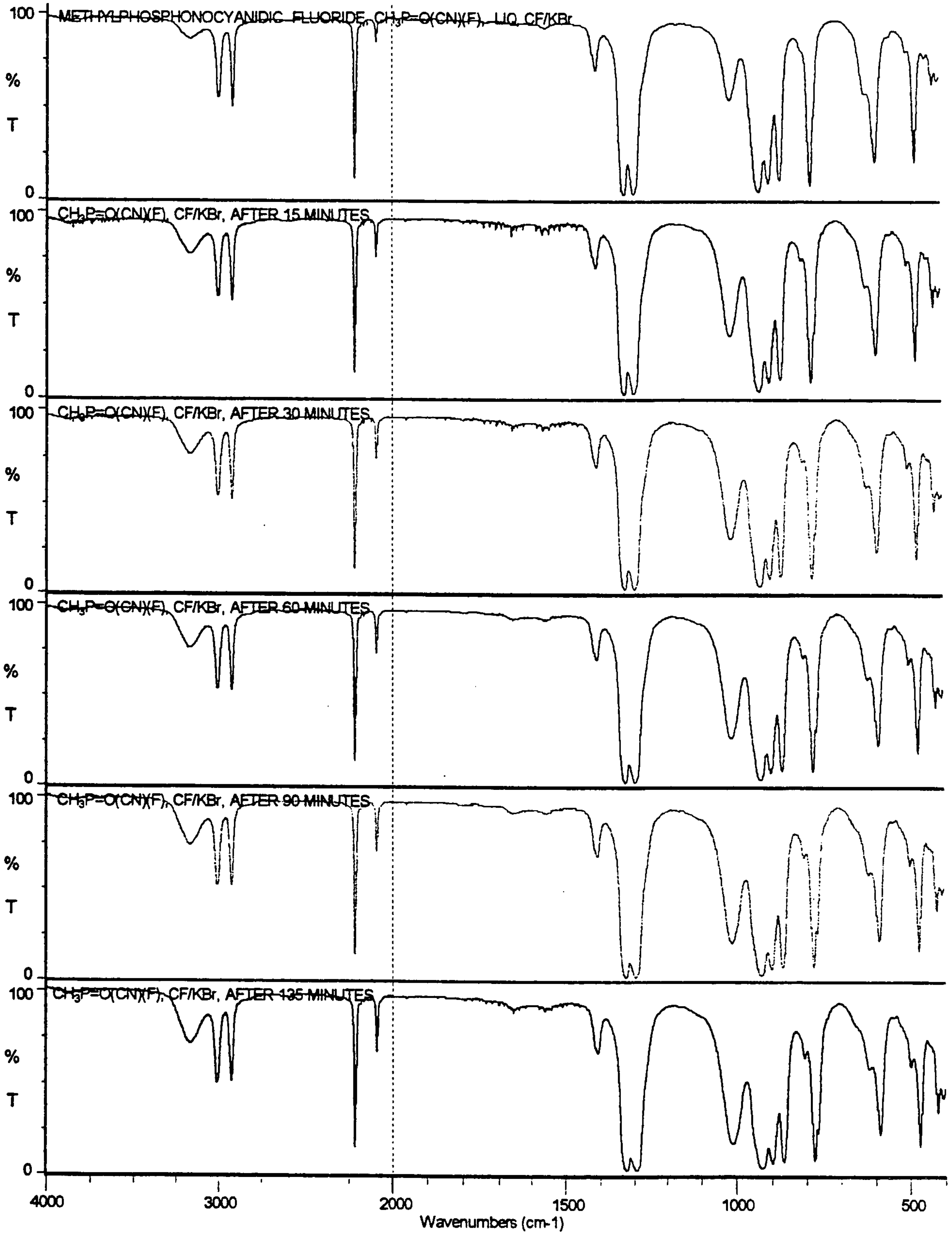

Figure 80B METHYLPHOSPHONOCYANIDIC FLUORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

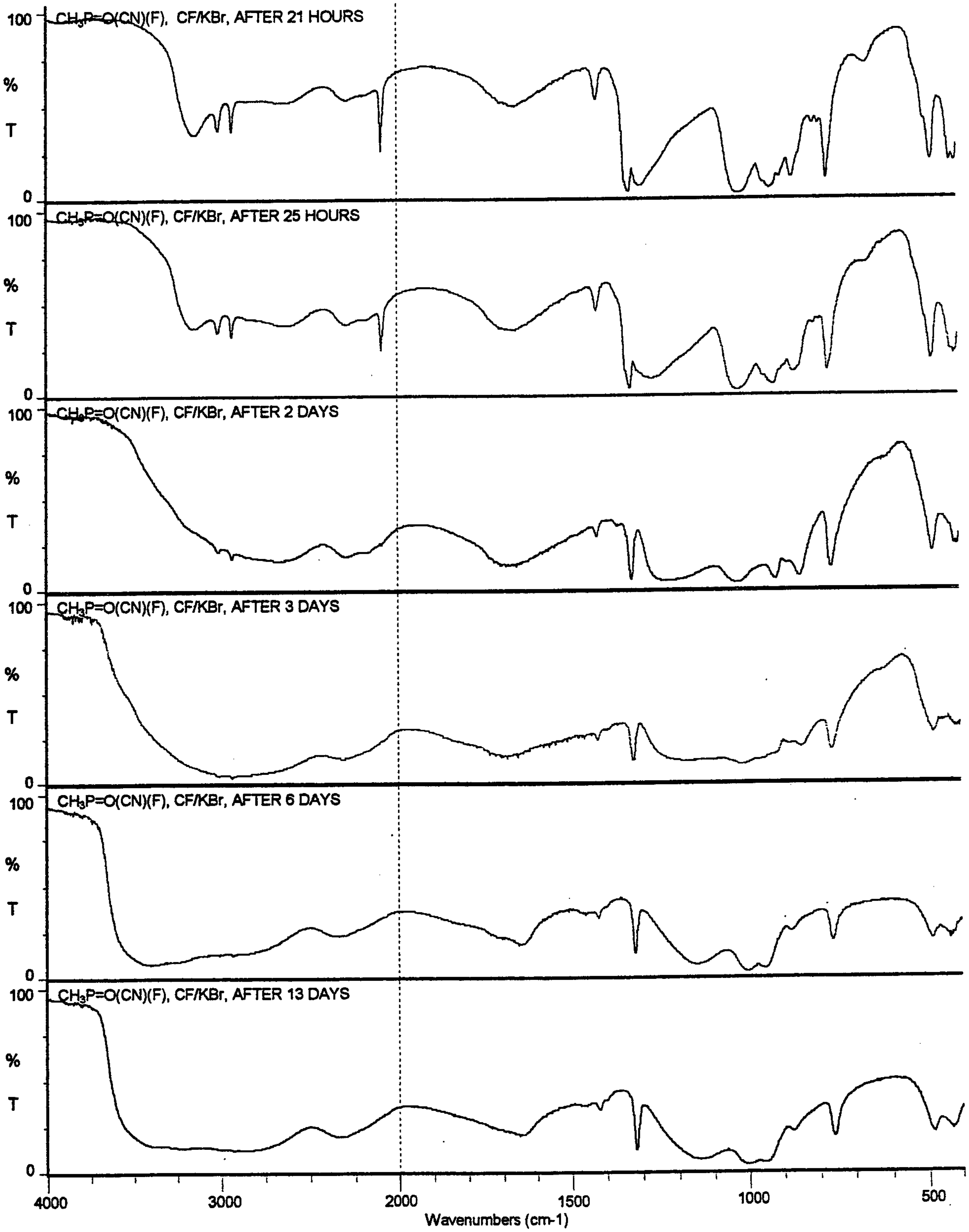

Figure 80B METHYLPHOSPHONOCYANIDIC FLUORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED) high value of this band could indicate the presence of a pyro compound, especially considering that there is a band near 950 cm^{-1} (ν P-O-P) and 650 cm^{-1} which could also corroborate the existence of a pyro group. A compound such as methylphosphonofluoridic anhydride, $CH_3(F)P(=O)-O-P(=O)(F)CH_3$, would have a ν P=O (calculated value) of 1302 cm^{-1}. Methylphosphonofluoridic acid (**Fluoro Acid**), $CH_3P=O(OH)(F)$, would absorb at 1244 cm^{-1} and could contribute to the observed broadness of the P=O band. However, let us move to the sample after an exposure to atmospheric moisture of 2 days. Note that the POH bands near 2678, 2294, 1650 and 1022 cm^{-1} are greatly enhanced from what they were previously. The band assigned to the P=O stretching region has decreased to 1222 cm^{-1} and is still quite broad. ***Figure 81*** shows a comparison of the coumpound after 2 days to that of a known sample of **Fluoro Acid**. Note the excellant agreement between the two spectra despite the fact that the hydrolyzed sample is somewhat heavier in concentration than the **Fluoro Acid**.

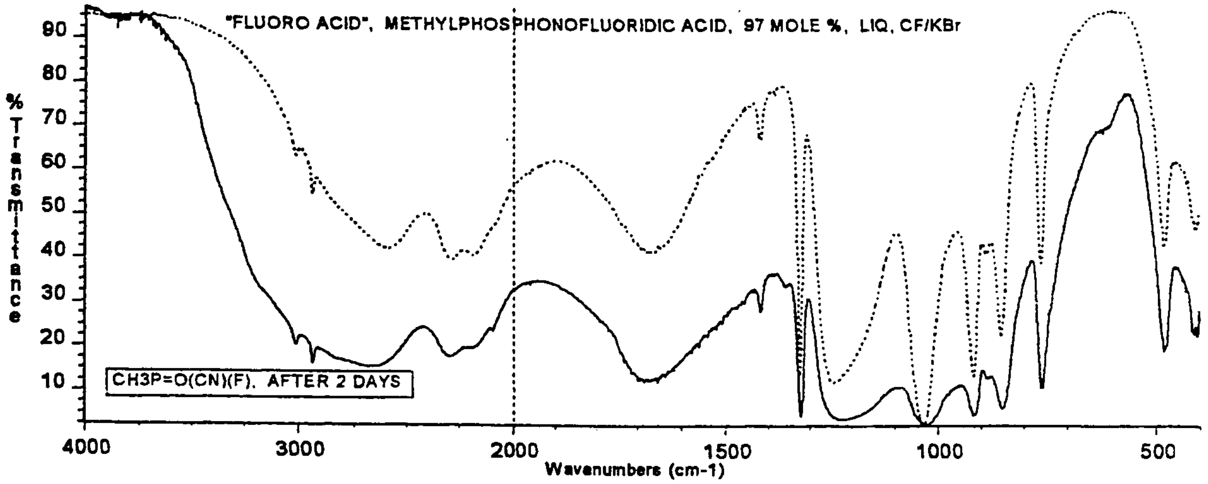

Figure 81 COMPARISON OF THE INFRARED SPECTRA OF FLUORO ACID (UPPER IR) AND THE PRODUCT FROM METHYLPHOSPHONOCYANIDIC FLUORIDE AFTER AN EXPOSURE TO ATMOSPHERIC MOISTURE FOR 2 DAYS (LOWER IR)

The infrared spectrum continues to change, so that by the 6th through 13th days the sample has taken on the appearance of a wet methylphosphonic acid (**MPA**), $CH_3P=O(OH)_2$ (see ***Figure 54*** for the spectrum of a wet **MPA**). Thus, the hydrolysis of methylphosphonocyanidic fluoride may be summarized as follows: $CH_3P=O(CN)(F)$ -HOH-> $(F)CH_3P(=O)-O-P(=O)CH_3(F)$ [?] + HCN ↑ -HOH-> $CH_3P=O(OH)(F)$ -HOH-> $CH_3P=O(OH)_2$—HF ↑.

4.2 Phenyl Methylphosphonofluoridate $CH_3P{=}O(F)(O\text{-}C6H5)$

The infrared spectrum of phenyl methylphosphonofluoridate is give in ***Figure 82***. Band assignments are as follows: 3064 cm^{-1} vw (ν C-H aromatic), 3004 cm^{-1} vw and 2930 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 1592 cm^{-1} m, 1493 cm^{-1} s and 1457 cm^{-1} w (aromatic ring), 1415 cm^{-1} vw (δ_{as} P-CH_3), 1323 cm^{-1} s (δ_{sy} P-CH_3), 1292 cm^{-1} s (ν P=O), 1202 cm^{-1} s (ν C-O), 1166 cm^{-1} m, 1072 cm^{-1} w 1026 cm^{-1} m and 1008 cm^{-1} m (β C-H phenyl ring), 958 cm^{-1} s (ν P-O), 918 ms (P-CH_3 rock), 848 cm^{-1} ms (ν P-F), 763 cm^{-1} m and 690 cm^{-1} m (mono substituted aromatic ring), 721 cm^{-1} w (ν P-C ?).

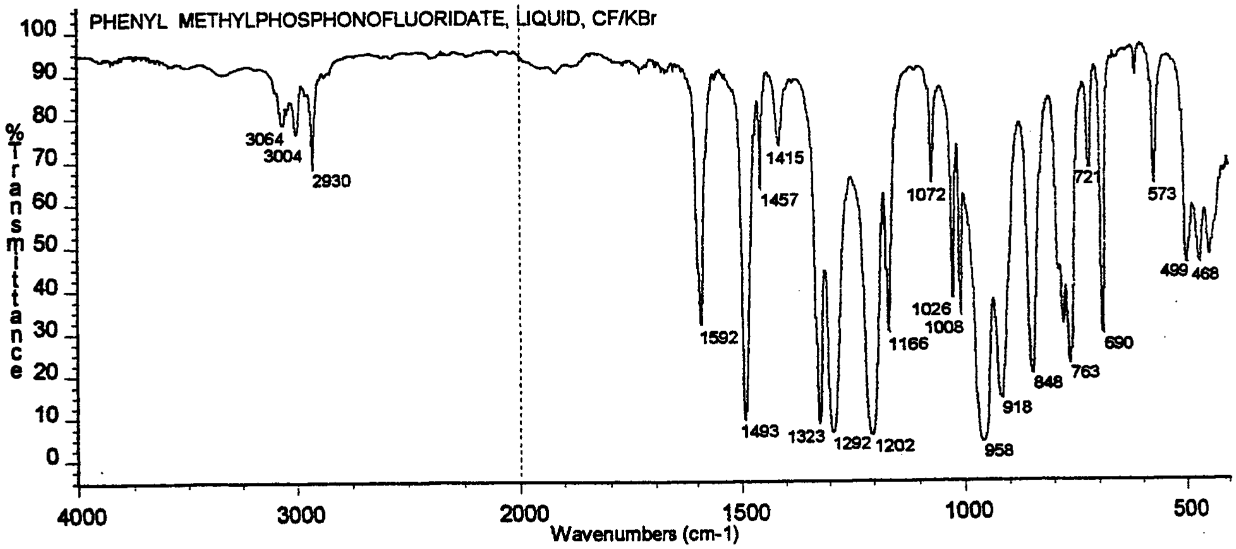

Figure 82 PHENYL METHYLPHOSPHONOFLUORIDATE, LIQUID, CF/KBr

The effect of atmospheric moisture on phenyl methylphosphonofluoridate is shown by the infrared spectra reproduced in ***Figure 83***. The infrared spectrum of the compound after 1 day of exposure to atmospheric moisture shows a strong band at 3348 cm^{-1} due to bonded OH. New bands also appear at 1606 cm^{-1}, 1501 cm^{-1}, 1474 cm^{-1}, 1367 cm^{-1}, and 1229 cm^{-1} and are believed to be due to the formation of phenol on hydrolysis. The P-F stretching band at 848 cm^{-1} has decreased greatly in intensity. A new band also appears at 1263 cm^{-1} which may be assigned to the P=O stretch from a pyro compound such as $CH_3\ (OC_6H_5)P({=}O)\text{-}O\text{-}P({=}O)(OC_6H_5)CH_3$, which would have a calculated P=O stretch

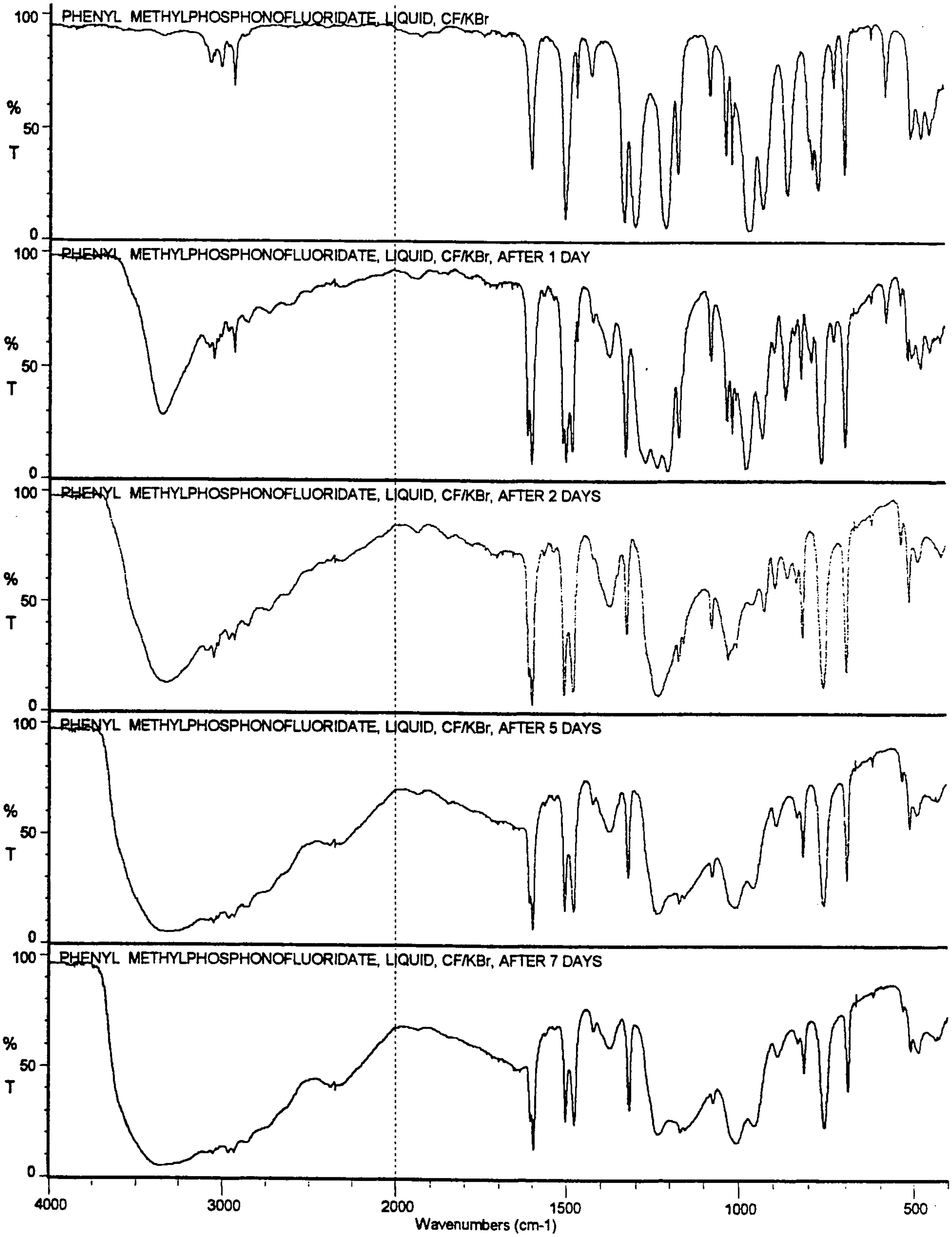

Figure 83 PHENYL METHYLPHOSPHONOFLUORIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

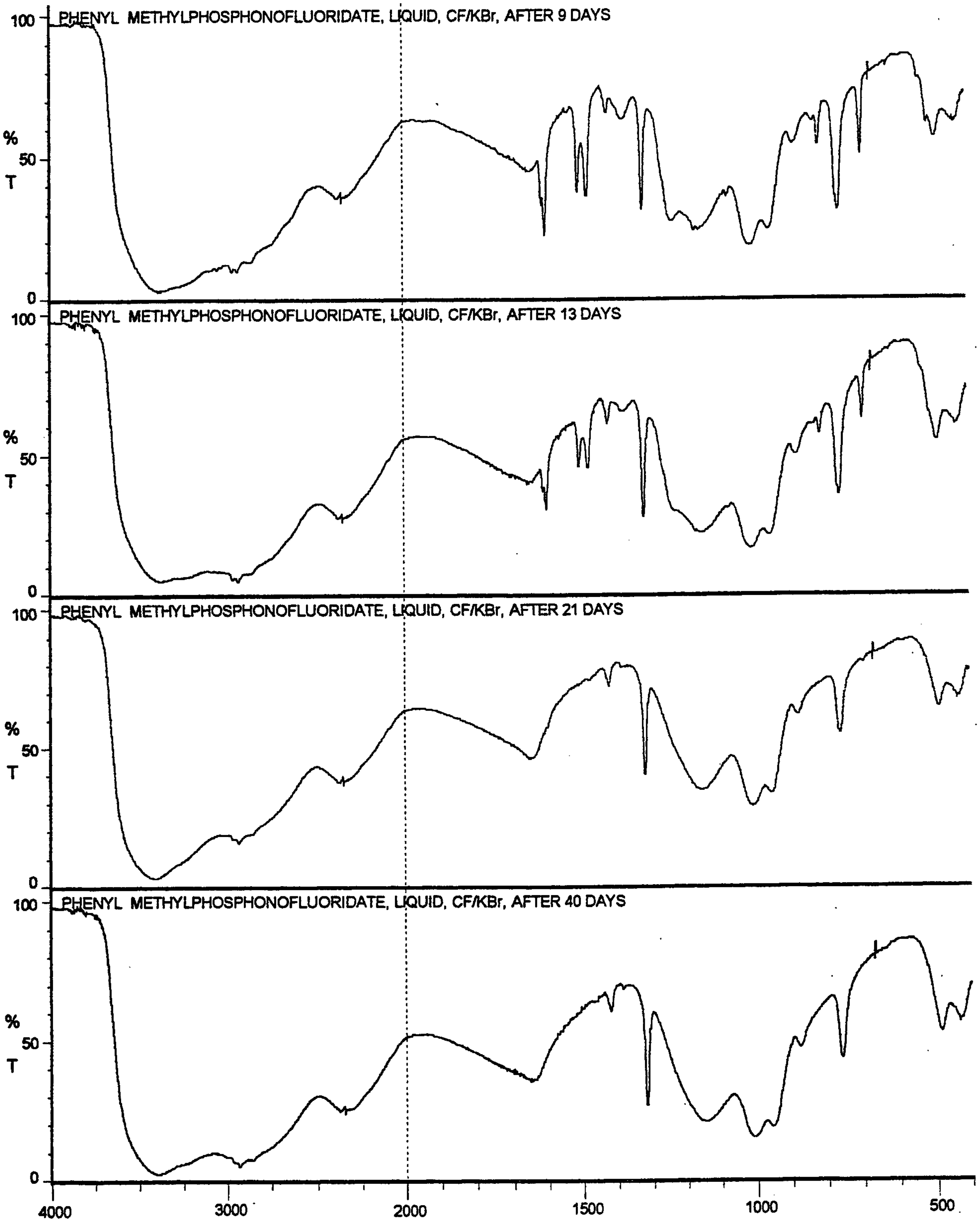

Figure 83 **PHENYL METHYLPHOSPHONOFLUORIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE** (CONTINED)

of 1266 cm^{-1}. By day 2 only a single strong band is left in the range between 1300-1200 cm^{-1} namely at 1229 cm^{-1}. This may be assigned to a C-O stretch of phenol. A weak band near 1368 cm^{-1} may be assigned to the OH deformation of phenol. The strong band that was at 3348 cm^{-1} (after 1 day) has now broadened and moved to 3323 cm^{-1} is assigned to the OH stretch of phenol (see ***Figure 84 UPPER IR*** for spectrum of phenol). As time progressed the infrared spectrum takes on the appearance of that for a mixture of phenol and methylphosphonic acid (see ***Figure 84 LOWER IR*** for the spectrum of a mix of phenol and methylphosphonic acid). By the 21st through 40th days the infrared spectrum becomes that of essentially a wet methylphosphonic acid, $CH_3P=O(OH)_2$.

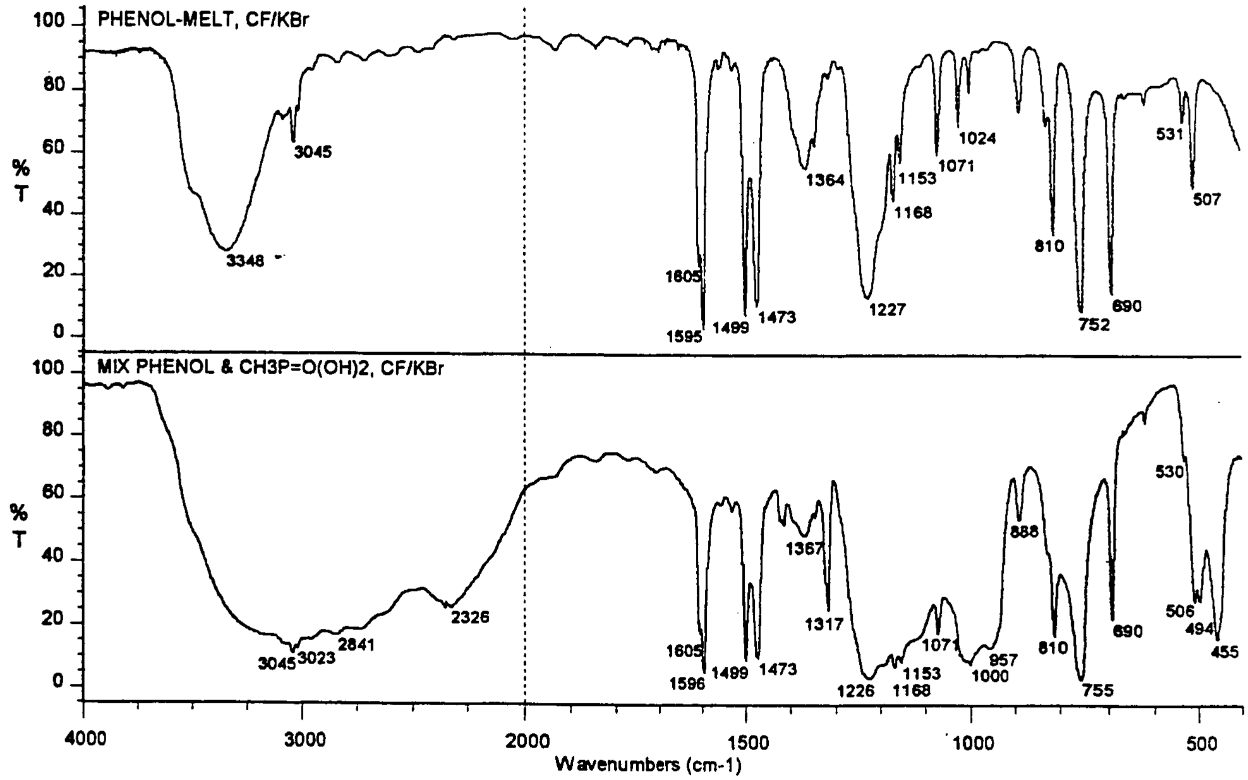

Figure 84 ***UPPER IR*** **PHENOL, MELTED BETWEEN KBr WINDOWS**
LOWER IR **MIX OF PHENOL AND METHYLPHOSPHONIC ACID, $CH_3P=O(OH)_2$, CF/KBr**

Thus, the hydrolysis of phenyl methylphosphonofluoridate may be summarized as follows:

$CH_3P=O(F)(O-C_6H_5)$ -HOH-> $CH_3(OC_6H_5)P(=O)-O-P(=O)(OC_6H_5)CH_3$ -HOH-> $CH_3P=O(OH)_2 + C_6H_5OH$.

Some phenyl methylphosphonic acid, $CH_3P=O(OH)(O-C_6H_5)$, may also have been formed.

4.3 Diethyl Cyanophosphonate $(C\equiv N)P{=}O(OCH_2CH_3)_2$

The infrared spectrum of diethyl cyanophosphonate is give in ***Figure 85***. The band assignments are as follows: 2990 cm^{-1} m (ν_{as} CH_3), 2941 cm^{-1} w (ν_{as} CH_2), 2914 cm^{-1} w (ν_{sy} CH_3), 2874 cm^{-1} vw (ν_{sy} CH_2), 2208 cm^{-1} m (ν C≡N), 2084 vvw (ν C≡N of HCN), 1830 cm^{-1} vw (1027 + 798 = 1825 cm^{-1}), 1792 cm^{-1} vw (1027 + 761 = 1788 cm^{-1}), 1479 cm^{-1} w (δ OCH_2), 1446 cm^{-1} m (δ_{as} CH_3), 1395 cm^{-1} m (ω OCH_2), 1373 cm^{-1} m (δ_{sy} CH_3), 1304 cm^{-1} ms (ν P=O), 1165 cm^{-1} and 1101 cm^{-1} w-m (CH_3 rock, characteristic of POEt), 1027 cm^{-1} s (ν P-O-C), 971 cm^{-1} sh (ν C-C of POEt), 798 cm^{-1} m and 761 cm^{-1} m (POC), 619 cm^{-1} m (ν P-C ?).

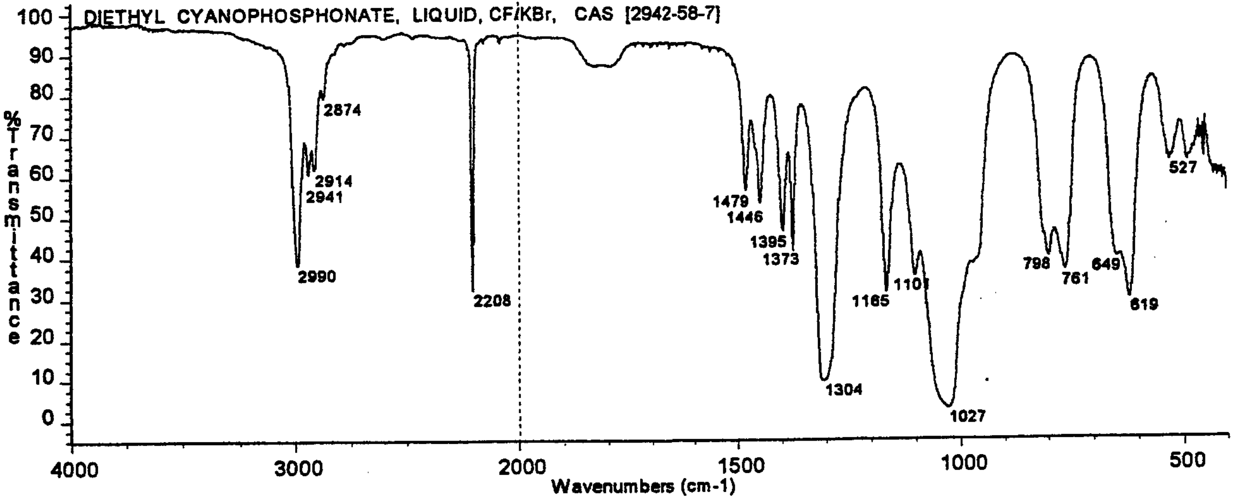

Figure 85 DIETHYL CYANOPHOSPHONATE, LIQUID, CF/KBr

The effect of atmospheric moisture on diethyl cyanophosphonate is illustrated by the infrared spectra in ***Figure 86***. After 1 hour exposure to atmospheric moisture the infrared spectrum for the compound shows a trace of HCN at ca 2085 and 3115 cm^{-1}. After 2 hours the 2208 cm^{-1} band (ν C≡N) shows a slight decrease in intensity with a corresponding small increase in the 2085 cm^{-1} (HCN) band. Bands due to the POH moiety begin to appear in the spectrum near 2600 and 1700 cm^{-1}, and a new band appears at 1235 cm^{-1} which could be due to the P=O stretching of an P-acid moiety. The formation of a P-acid continues as the C≡N band at 2208 decreases in intensity with time. The P=O stretching band

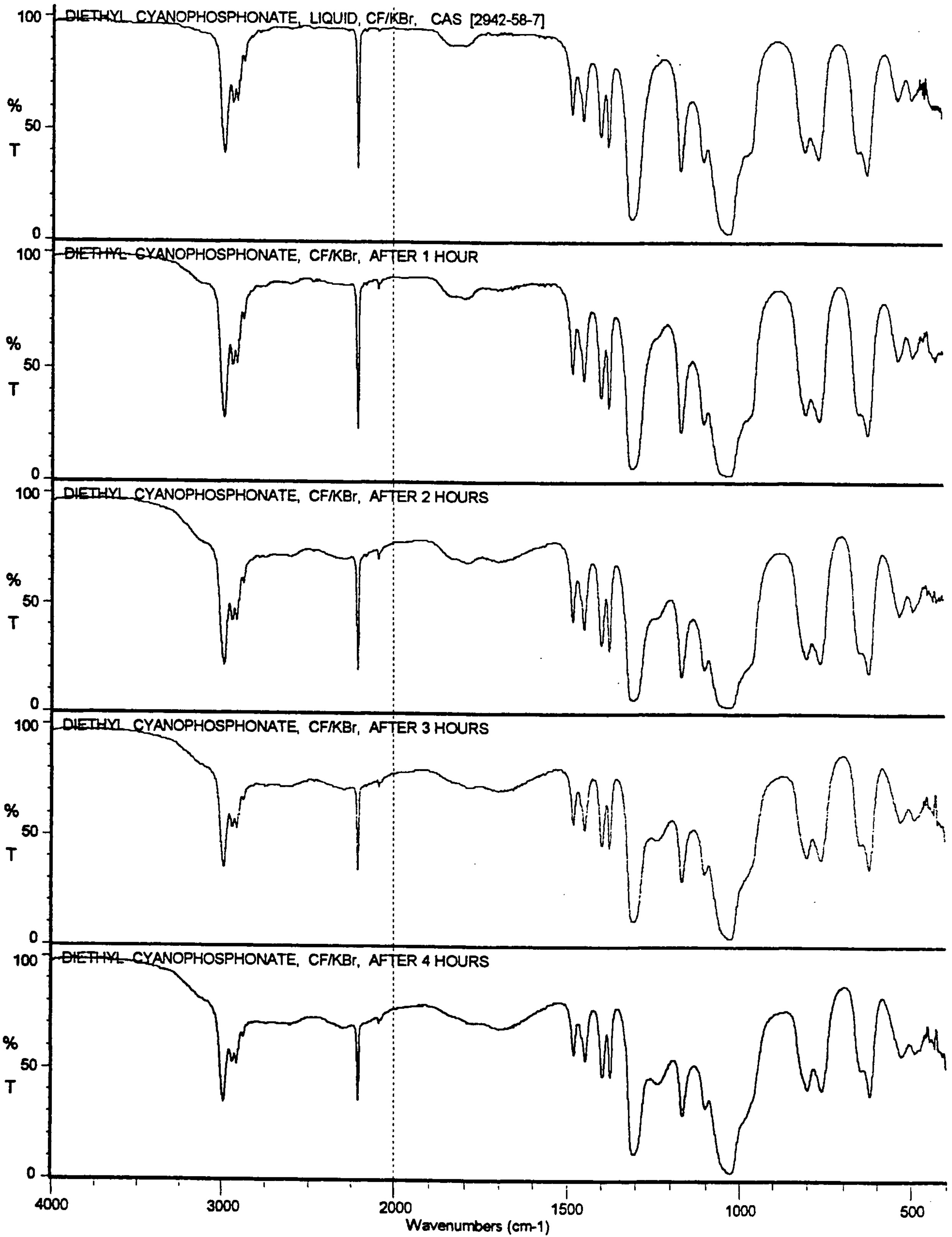

Figure 86 **DIETHYL CYANOPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE**

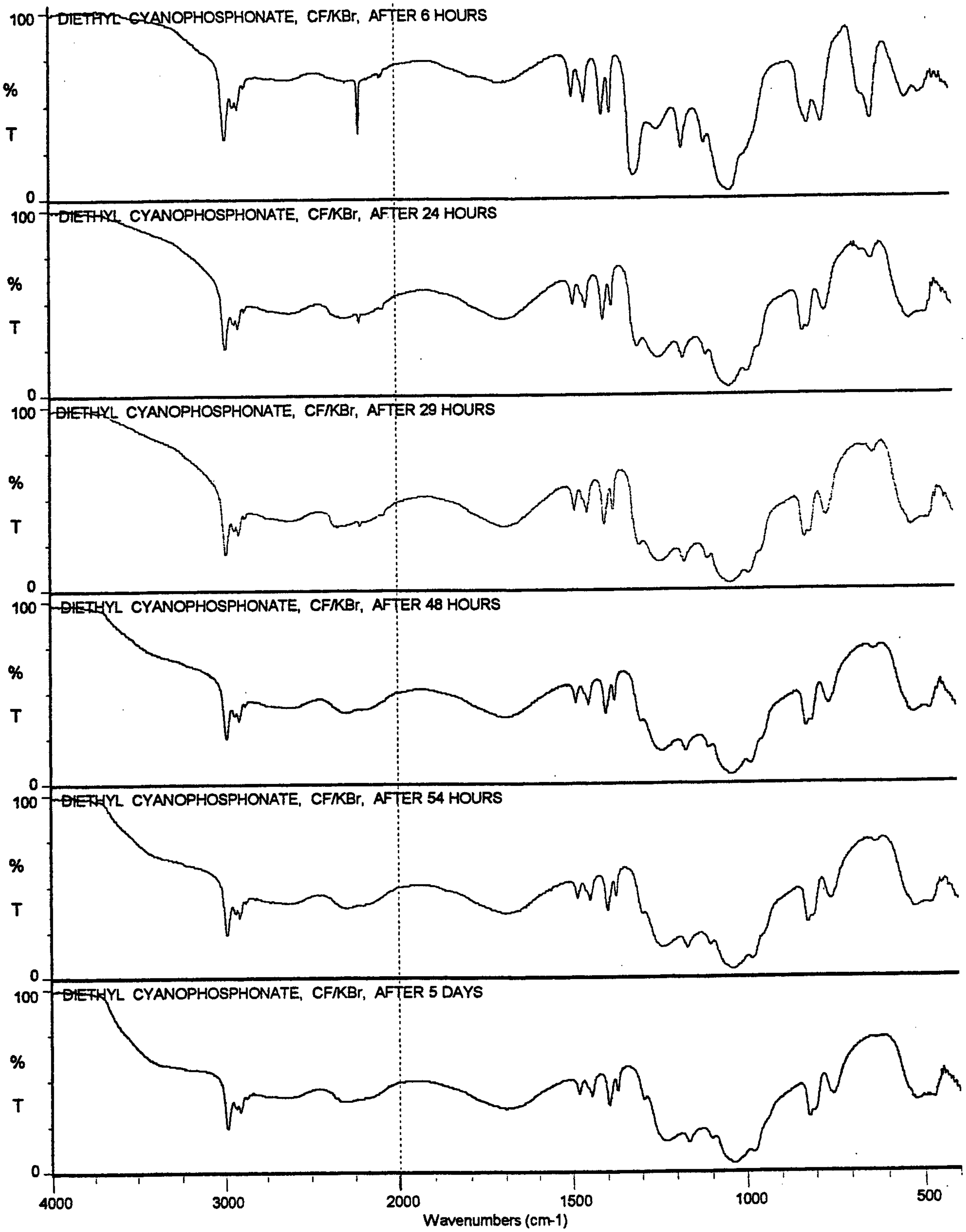

Figure 86 DIETHYL CYANOPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

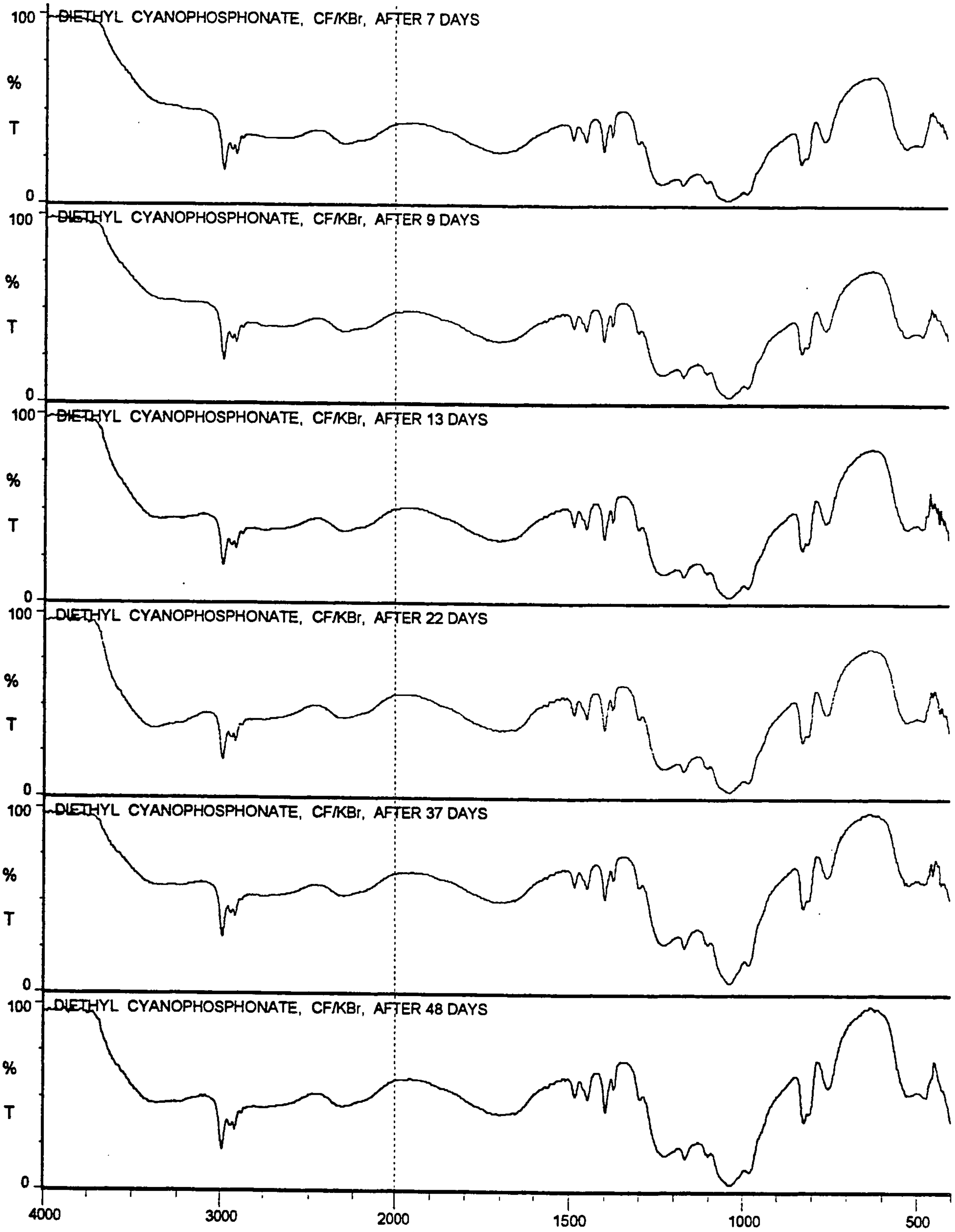

Figure 86 **DIETHYL CYANOPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE** (CONTINUED)

near 1300 cm^{-1} also decreases in intensity as hydrolysis occurs. By 48 hours of exposure to atmospheric moisture the infrared spectrum of the sample corresponds to that of a P-acid, mostly likely, diethyl hydrogen phosphate [HO-P=O(OEt)$_2$]. This result holds for the rest of the time of exposure that is, 48 days. Even after 48 days a weak band remains at 1294 cm^{-1}, could this be due to the presence of a pyro compound, namely tetraethyl pyrophosphate (**TEPP**) or diethyl phosphoric anhydride, (EtO)$_2$P(=O)-O-P(=O)(OEt)$_2$? The P=O stretch for this compound would occur near 1290 cm^{-1}.

4.4 *t*-Butylphosphonic Difluoride (CH$_3$)$_3$C-P=OF$_2$

The infrared spectrum of *t*-butylphosphonic difluoride is given in ***Figure 87***. The bands assignments are as follows: 3396 cm^{-1} vw (H$_2$O), 2980 cm^{-1} m (ν_{as} CH$_3$), 2946 cm^{-1} sh (1480 + 1468 = 2948 cm^{-1}), 2915 cm^{-1} w, 2883 cm^{-1} w (ν_{sy} CH$_3$), 1480 cm^{-1} m and 1468 cm^{-1} w (δ_{as} CH$_3$), 1406 cm^{-1} w and 1374 cm^{-1} w (δ_{sy} CH$_3$), 1326 cm^{-1} s (ν P=O), 1230 cm^{-1} w (*t*-butyl skeletal), 946 cm^{-1} vw (CH$_3$ rock), 895 cm^{-1} sh and 877 cm^{-1} s (ν PF$_2$), 642 cm^{-1} m (ν P-C ?), 483 cm^{-1} ms and 464 cm^{-1} w (P-F deformations ?).

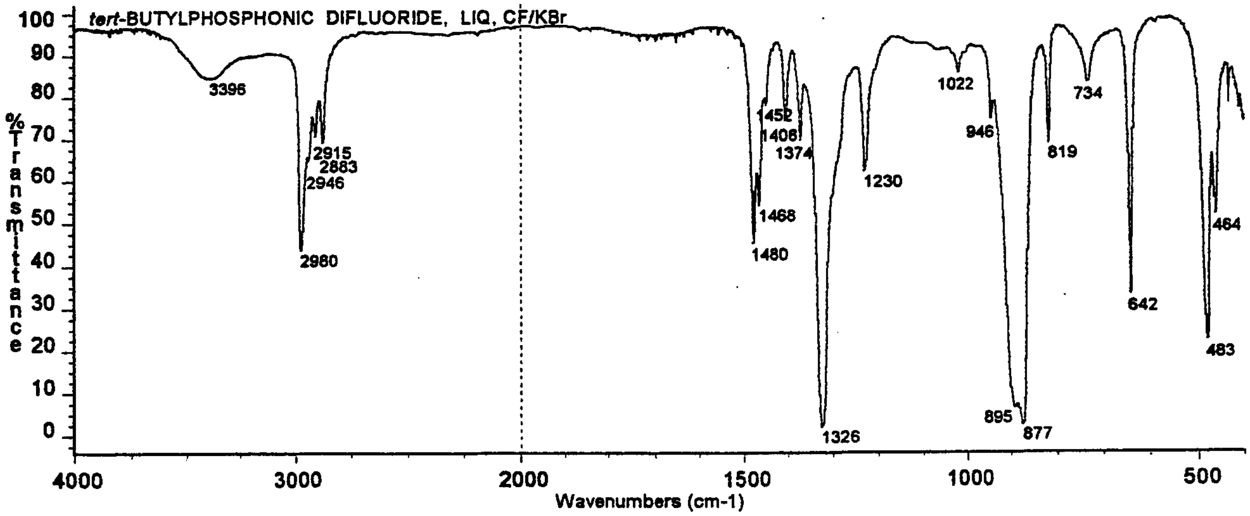

Figure 87 *t*-BUTYLPHOSPHONIC DIFLUORIDE, LIQUID, CF/KBr

4.5 *t*-Butylphosphonic Acid (CH$_3$)$_3$C-P=O(OH)$_2$

The infrared spectrum for *t*-butylphosphonic acid is given in ***Figure 88***. The band assignments are as follows: 2978 cm^{-1} w (ν_{as} CH$_3$), 2938 cm^{-1} vw (1470 x 2 = 2940 cm^{-1} ?), 2909 cm^{-1} vw, 2875 cm^{-1}

vw (ν_{sy} CH_3), 2754 cm^{-1} m and 2311 cm^{-1} m (POH), 1481 cm^{-1} m and 1470 cm^{-1} w (δ CH_3), 1397 cm^{-1} w and 1370 cm^{-1} w (δ_{sy} CH_3), 1243 cm^{-1} m and 1217 cm^{-1} m (*t*-butyl skeletal), 1192 cm^{-1} ms (ν P=O), 1005 cm^{-1} s and 921 cm^{-1} (ν P-OH), 828 cm^{-1} w (*t*-butyl CH_3 rock), 651 ms (ν P-C), 502 and 486 cm^{-1} ms (P=O deformation ?, *t*-butyl ?).

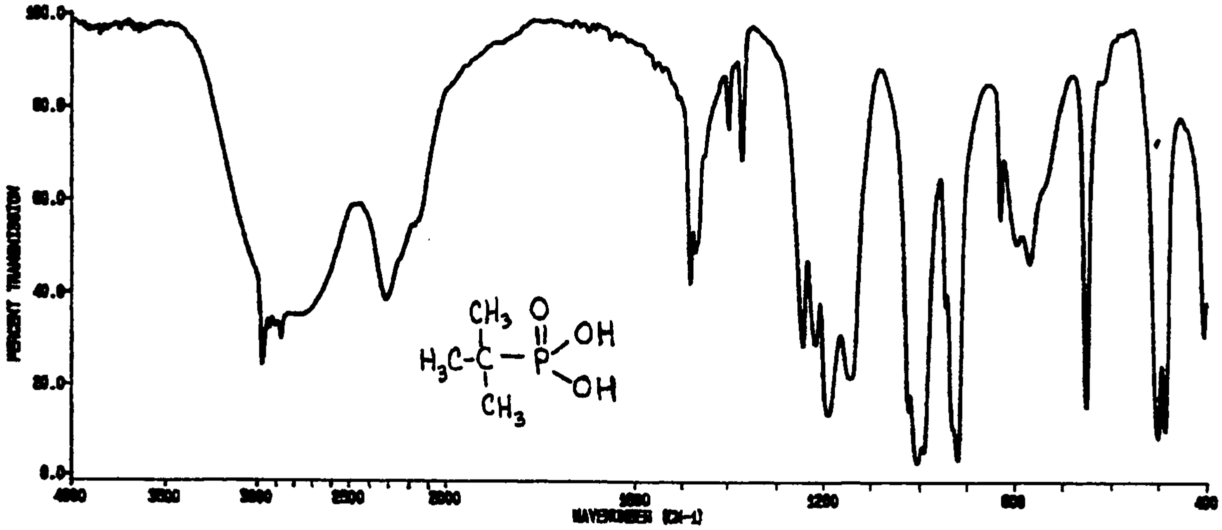

Figure 88 *t*-BUTYLPHOSPHONIC ACID, SOLID BETWEEN KBr DISCS

4.6 Isopropyl *t*-Butylphosphonofluoridate $(CH_3)_3C\text{-}P{=}O(F)[O\text{-}CH(CH_3)_2]$

The infrared spectrum of isopropyl *t*-butylphosphononofluoridate is reproduced in ***Figure 89***. The band assignments are as follows: 2980 cm^{-1} m (ν_{as} CH_3), 2939 cm^{-1} w (1481 + 1465 = 2946 cm^{-1} ?), 2877 cm^{-1} vw (ν_{sy} CH_3), 1481 cm^{-1} w and 1465 cm^{-1} vw (δ_{as} CH_3), 1399 cm^{-1} vw (δ_{sy} CH_3 *t*-butyl), 1388 cm^{-1} w and 1378 cm^{-1} w (δ_{sy} CH_3 isopropyl and *t*-butyl), 1354 cm^{-1} vvw (δ -CH isopropyl), 1283 cm^{-1} ms (ν P=O), 1228 cm^{-1} w (t-butyl skeletal), 1180 cm^{-1} vw and 1144 cm^{-1} vw and 1105 cm^{-1} w (a triplet of bands characteristic of P-O-isopropyl, involving C-C-C and C-C-O),[c] 1006 cm^{-1} s (ν P-O-C), 945 cm^{-1} vw and 897 cm^{-1} vw (CH_3 rock *t*-butyl and isopropyl), 849 cm^{-1} ms (ν P-F), 824 cm^{-1} m (POC), 659 m (ν P-C *t*-butyl), 520 cm^{-1} w (P=O deformation ?), 487 cm^{-1} vw (*t*-butyl ?).

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[c] See general reference 4, page 346.

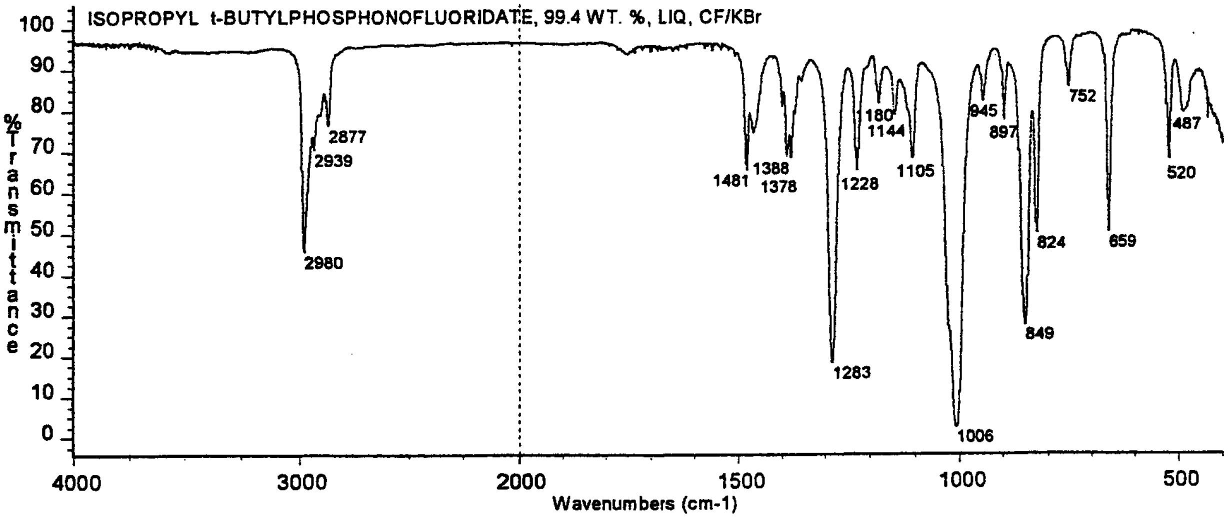

Figure 89 ISOPROPYL *t*-BUTYLPHOSPHONOFLUORIDATE, 99.4 wt %, LIQUID, CF/KBr

4.7 Isobutyl *t*- Butylphosphonofluoridate $(CH_3)_3C\text{-}P{=}O(F)[O\text{-}CH_2\text{-}CH(CH_3)_2$

The infrared spectrum of isobutyl *t*-butylphosphonofluoridate is given in ***Figure 90***. Band assignments are as follows: 2969 cm^{-1} ms (ν_{as} CH_3), ca 2940 cm^{-1} sh (ν_{as} CH_2), 2912 cm^{-1} vw (ν -CH ?), 2877 cm^{-1} m (ν_{sy} CH_3 and ν_{sy} CH_2), 1481 cm^{-1} m and 1473 cm^{-1} sh (δ_{as} CH_3 and δ CH_2), 1399 cm^{-1} and 1370 cm^{-1} w (δ_{sy} CH_3), 1285 cm^{-1} s (ν P=O), 1229 cm^{-1} m (*t*-butyl skeletal), 1182, 1167, 1130 and 1101 cm^{-1} all vw (characteristic of isobutyl moiety ?), 1036 cm^{-1} s (ν P-O-C), 945 cm^{-1} w (ν C-C of isobutyl ?), 914 cm^{-1} vw (CH_3 rock ?), 847 cm^{-1} ms (ν P-F), 811 cm^{-1} m (POC), 657 cm^{-1} m (*t*-butyl moiety), 511 cm^{-1} w (P=O deformation), 470 cm^{-1} w (*t*-butyl moiety).

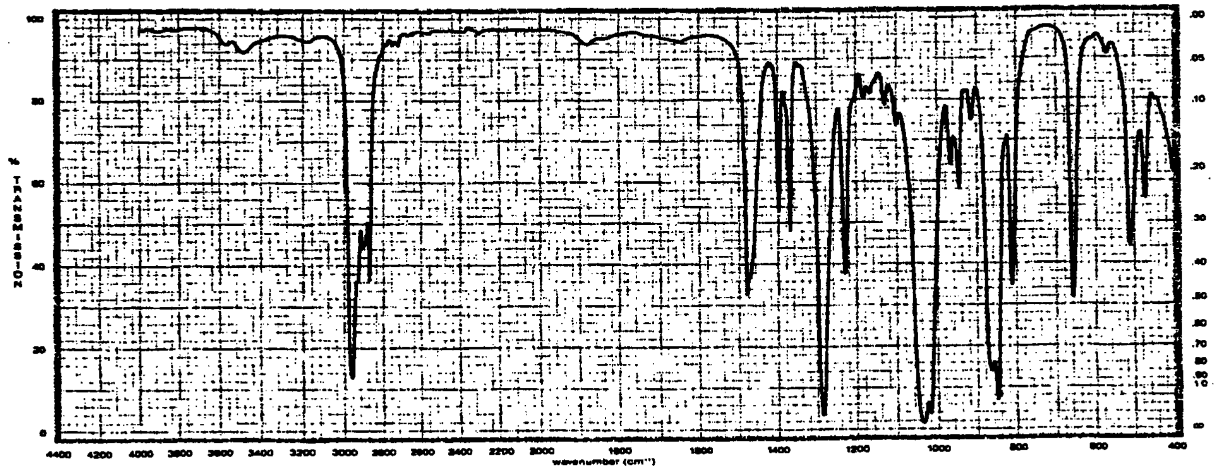

Figure 90 ISOBUTYL *t*-BUTYLPHOSPHONOFLUORIDATE, LIQUID, CF/KBr

4.8 Isobutyl Hydrogenmethylphosphinate $CH_3P{=}O(H)[OCH_2CH(CH_3)_2]$

The infrared spectrum for isobutyl hydgogenmethylphosphinate is reproduced as ***Figure 91***. The band assignments for the compound are as follows: 3408 cm^{-1} vw (H_2O), 2962 cm^{-1} m (ν_{as} CH_3), 2877 cm^{-1} w (ν_{sy} CH_3), 2349 cm^{-1} vw (ν P-H), 1472 cm^{-1} w (δ OCH_2 and δ_{as} CH_3), 1414 cm^{-1} vw (δ_{as} P-CH_3), 1397 cm^{-1} vw (partly ω OCH_2 and δ_{sy} CH_3 isopropyl), 1369 cm^{-1} vw (δ_{sy} CH_3 isopropyl), 1302 cm^{-1} m (δ_{sy} P-CH_3), 1231 cm^{-1} s (ν P=O), 1048 cm^{-1} ms (ν P-O-C), 995 cm^{-1} s (P-H deformation), 964 cm^{-1} sh (ν C-C of O-isobutyl), 883 cm^{-1} vvw (CH_3 rock of isopropyl group), 849 cm^{-1} m (P-CH_3 rock), 822 w (POC), 728 cm^{-1} vw (ν P-C).

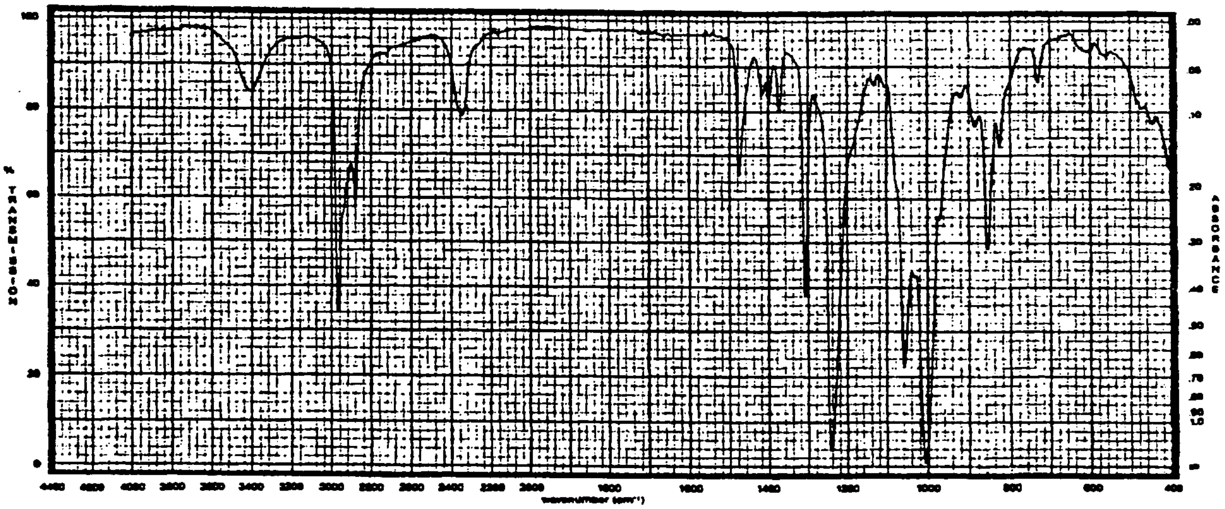

Figure 91 ISOBUTYL HYDROGENMETHYLPHOSPHINATE, LIQUID ,CF/KBr

The infrared spectra representing the effect of atmospheric moisture on isobutyl hydrogenmethylphosphinate are given by ***Figures 92A*** through ***92D***. After 24 hours of exposure to atmospheric moisture the infrared spectrum of the compound shows a broadened P=O stretching band now at 1211 cm^{-1}. Some P-OH bands are evident near 2700 cm^{-1} and under the P-H stretch at 2369 cm^{-1} (indicated by a broadening of the band) and by a weak broad band near 1680 cm^{-1}. After 12 days of exposure to atmospheric moisture the spectrum of the sample showed bands indicative of a P-acid. This observation also holds for the sample exposed to atmospheric moisture for 25 and 39 days. The hydrolysis product after 39 days (which appears to be the driest sample) has the following bands: 2964 cm^{-1} vvw and 2922 vvw (ν_{as} and

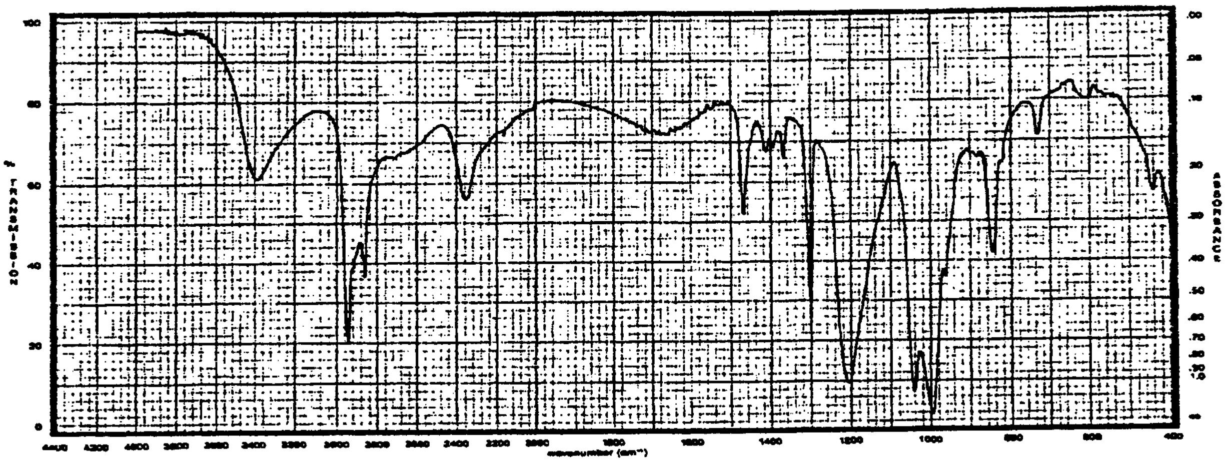

Figure 92A ISOBUTYL HYDROGENMETHYLPHOSPHINATE, LIQUID, CF/KBr, AFTER 24 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

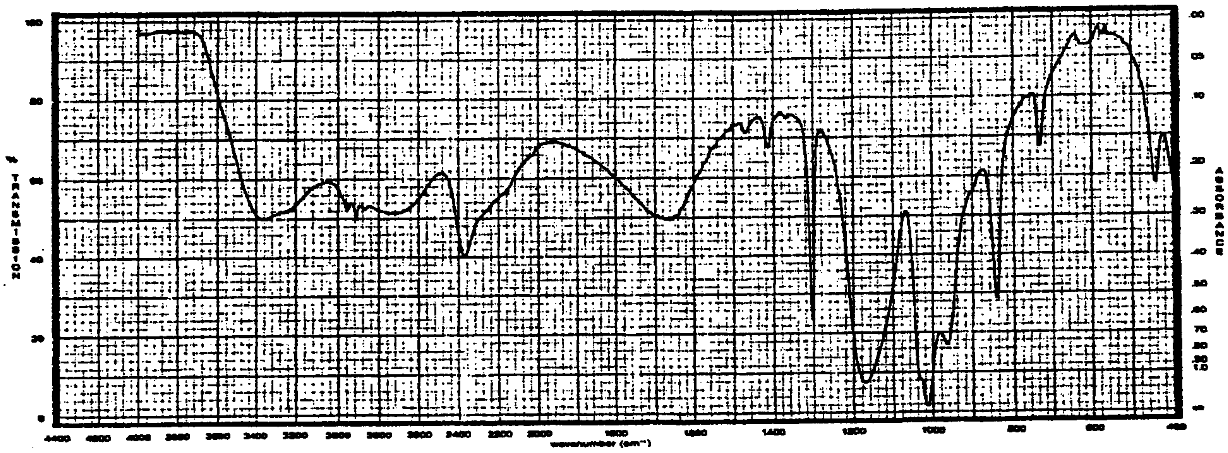

Figure 92B ISOBUTYL HYDROGENMETHYLPHOSPHINATE, LIQUID, CF/KBr, AFTER 12 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

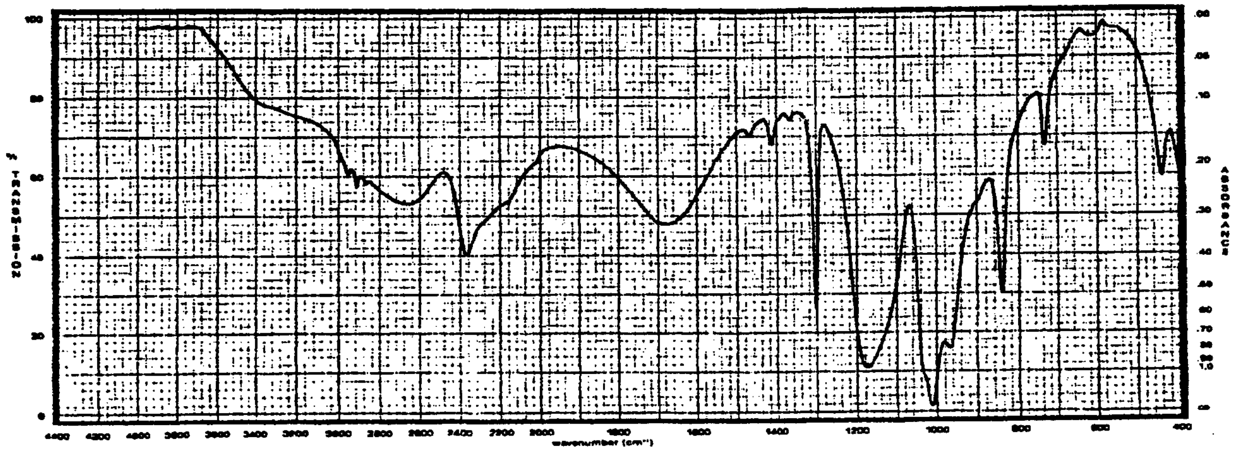

Figure 92C ISOBUTYL HYDROGENMETHYLPHOSPHINATE, LIQUID, CF/KBr, AFTER 25 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

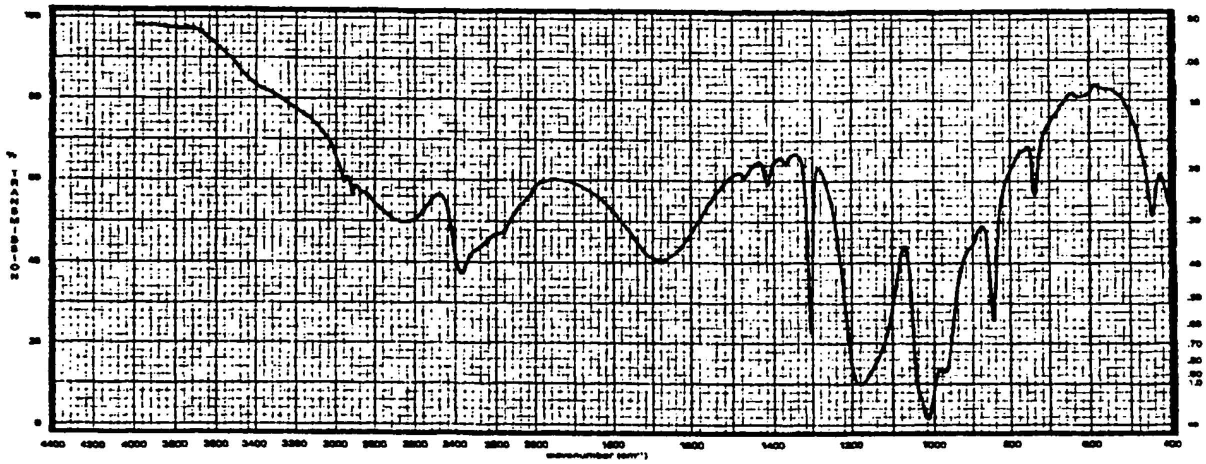

Figure 92D ISOBUTYL HYDROGENMETHYLPHOSPHINATE, LIQUID, CF/KBr, AFTER 39 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

ν_{sy} CH_3), 2645 cm^{-1} w broad (P-OH), 2381 cm^{-1} w (ν P-H, this band is somewhat broad in shape and is also partly due to P-OH), ca 1680 cm^{-1} w broad (P-OH), 1416 cm^{-1} vvw (δ_{as} CH_3), 1305 cm^{-1} m (δ_{sy} P-CH_3), 1180 cm^{-1} ms broad (ν P=O), 1017 cm^{-1} s (P-H deformation), 972 cm^{-1} sh (ν P-OH), 844 cm^{-1} m (P-CH_3 rock), 736 cm^{-1} w (ν P-C), 442 cm^{-1} w (P=O deformation ?). The hydrolysis product appears to be methylphosphinic acid, $CH_3P{=}O(H)(OH)$. The hydrolysis may thus be summarized as follows:

$CH_3P{=}O(H)[OCH_2CH(CH_3)_2]$ -HOH-> $CH_3P{=}O(H)(OH)$ + HO-$CH_2CH(CH_3)_2$.

5. CONCLUSIONS

The infrared spectra for a number of G-type compounds and well as precursors, impurities and decomposition products were presented and discussed. The effect of atmospheric moisture on the infrared spectra of these compounds was also examined and illustrated by spectra taken at various times of atmospheric exposure. It was shown, that when CsI windows were used to support the liquid films for spectral examination, Cs_2SO_4 and $CsNO_3$ (to a lesser degree) were also produced. The effect of grinding on some of the solid materials was also illustrated by representative infrared spectra.

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