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(DEHPA) Bis(2-ethylhexyl Phosphoric Acid)

(C₈ H₁₇)₃P=O (TOPO) TriOctyl Phosphine Oxide

(C₄ H₉O)₃P=O (TBP) TriButyl Phosphate

TBP

TBP

()

Summary

Nuclear magnetic resonance spectroscopy (NMR) was applied in this work to the industrial process of extraction of uranium from phosphoric acid and to the process of the purification of the phosphoric acid for food proposes. The structural changes of used extraction materials and the organic content of the final product was studied. ¹³C, ¹H and ³²P- spectra of all material during the process were recorded. The spectra of the three used extraction materials Bis(2-ethylhexyl Phosphoric Acid)) DEHPA, TriOctyl Phosphine Oxide (TOPO) (C₈ H₁₇)₃P=O and TriButyl Phosphate (TBP) (C₄ H₉O)₃P=O show a partial degradation during the process. The final product (Phosphoric acid for Food proposes) doesn't contain any organic solvents or extraction material.

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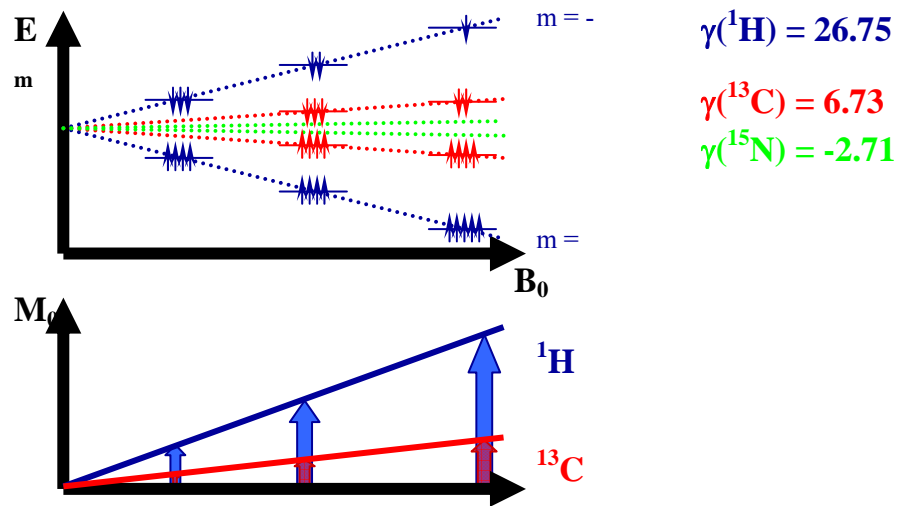
.....

. [1,2,3]

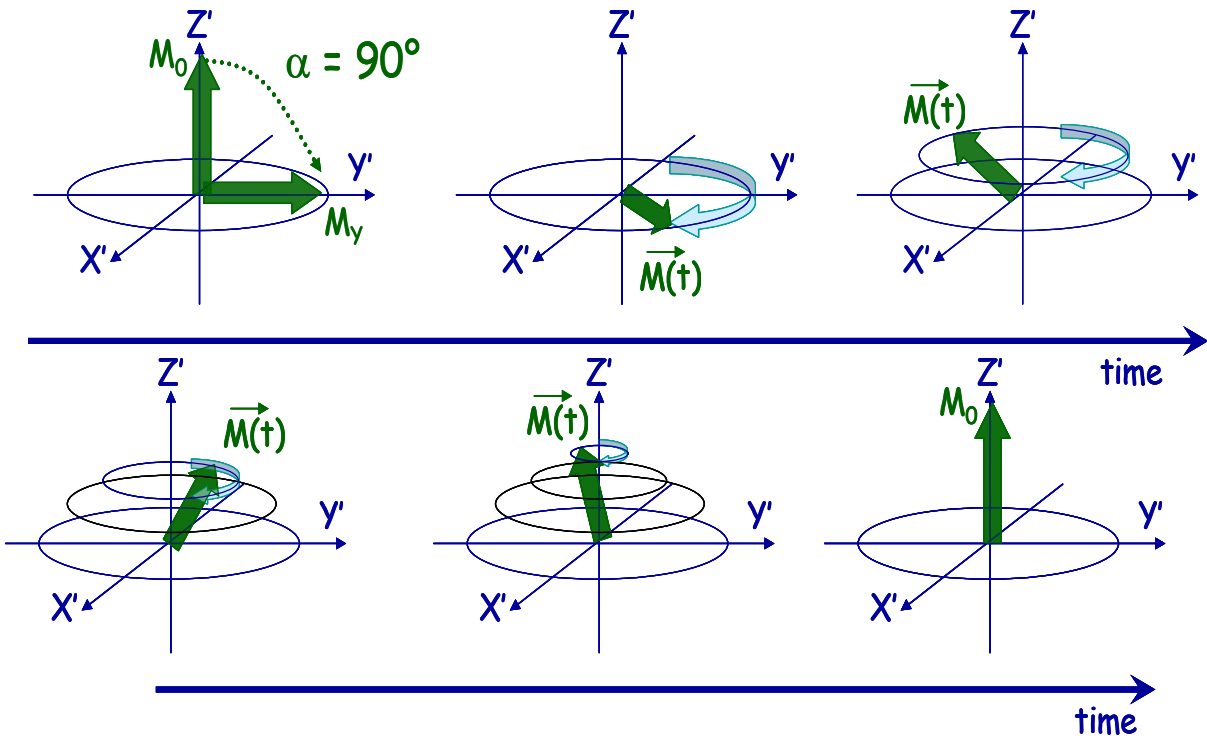
Spin Precession and

Spin Relaxation

. [4]



T_1 Relaxation

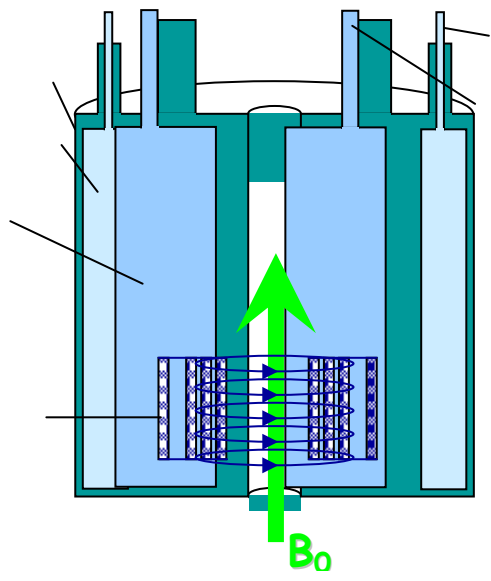


-)
(-) ()
()

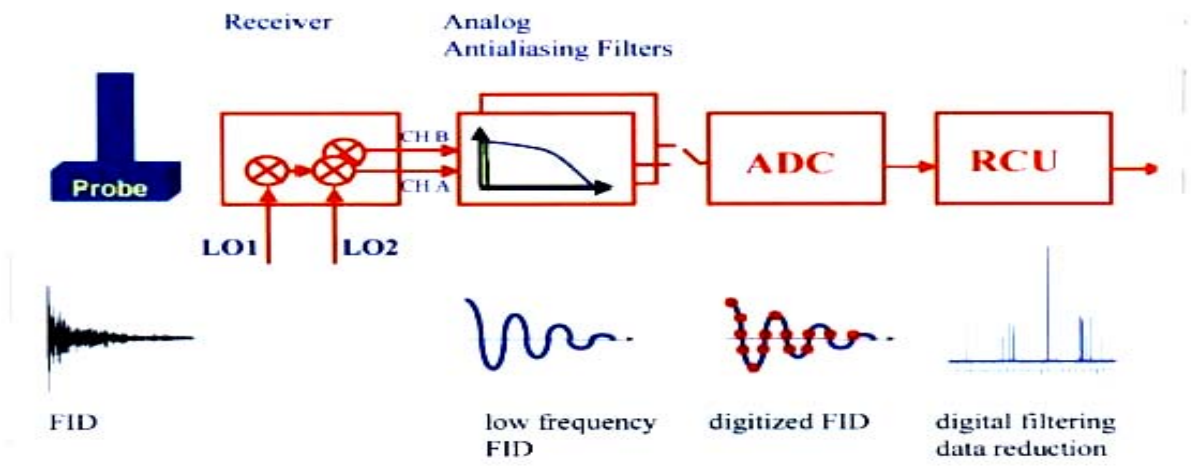
ADC

FID

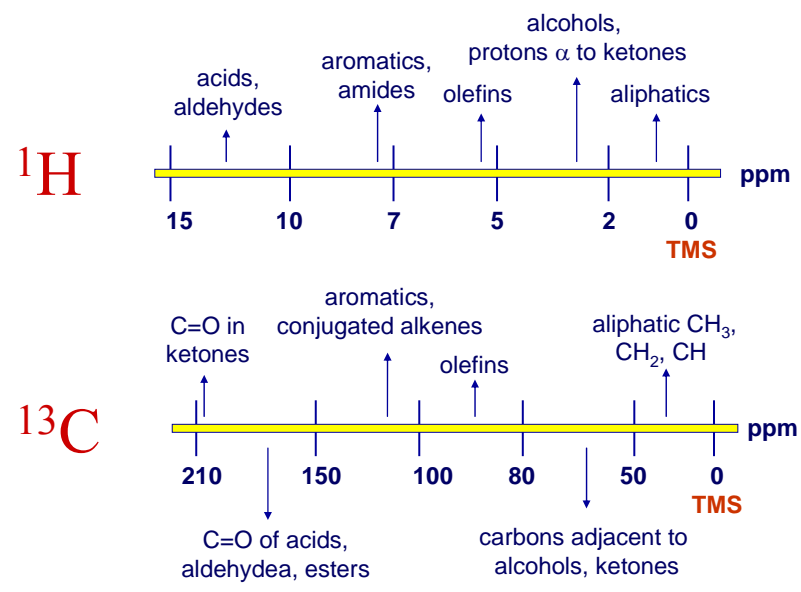
()



:



chemical shift



	:	/	/
^1H ^1D		H	
^{13}C ^1D		C	1 D
DEPT, APT		CH, CH ₂ , CH ₃	
COSY		H-H	
TCOSY		H-(-) _n H	2D
HMQC, HSQC		C-H	
HMBC		C-(-) _n H	
ROSEY, NOESY		H...H	

^1H ^{13}C

[3,5]

^{31}P ^{15}N

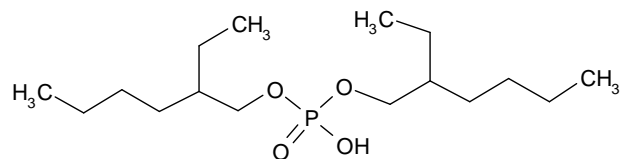
[4,6,7]

)

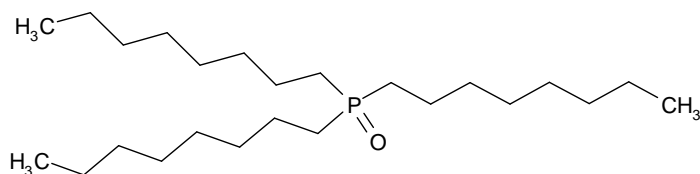
(

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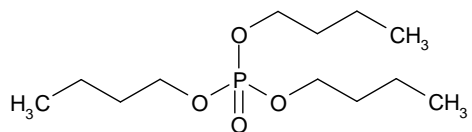
(DEHPA) Bis(2-ethylhexyl Phosphoric Acid) (. -) •



($\text{C}_8 \text{H}_{17}$) $_3\text{P}=\text{O}$ (TOPO) TriOctyl Phosphine Oxide •

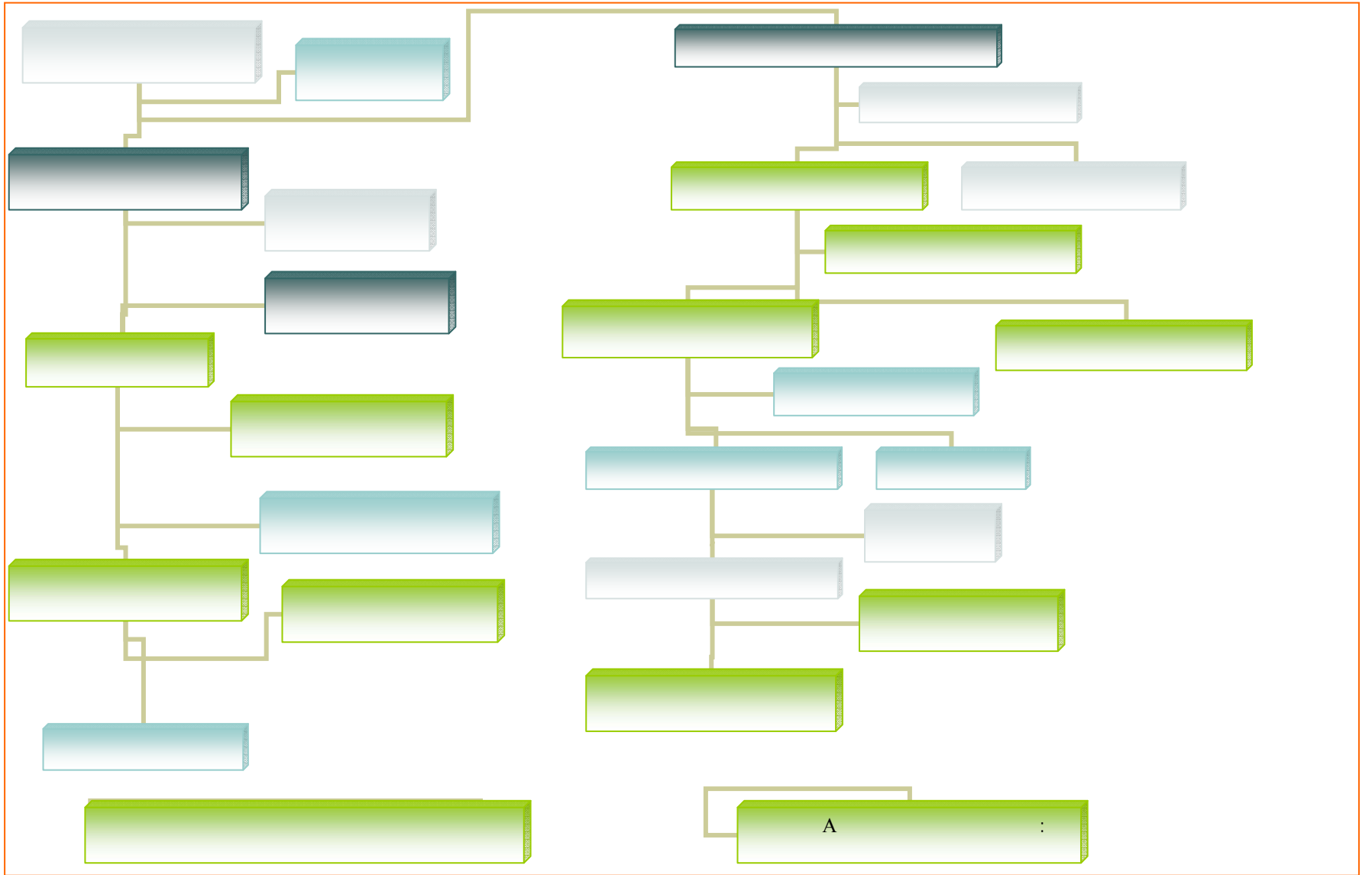


($\text{C}_4 \text{H}_9\text{O}$) $_3\text{P}=\text{O}$ (TBP) TriButyl Phosphate •



NMR

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DEHPA/TOPO

TBP

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•	•	•	•
•	•	•	•
	•		•
	•		•
	•		•

D-

(HNMR)

(C13APT)

(C13DEPT)

H

(,) NMR

(C13CPD) H

(Attached Proton Test)

(Distortionless Enhancement by Polarization Transfer)

.DEHPA/TOPO TOPO DEHPA

.(P31CPD)

.P31CPD C13DEPT C13APT C13CPD H

:

•

: TOPO/DEHPA NMR

TOPO/DEHPA .

.TOPO ppm , DEHPA ppm ,

TOPO/DEHPA .

.TOPO DEHPA

TOPO DEHPA

SDBS 25.16

ppm , ,

-) , NMR

SDBS (

.ppm , , (<http://www.aist.go.jp/RIODB/SDBS>)

J

NMR

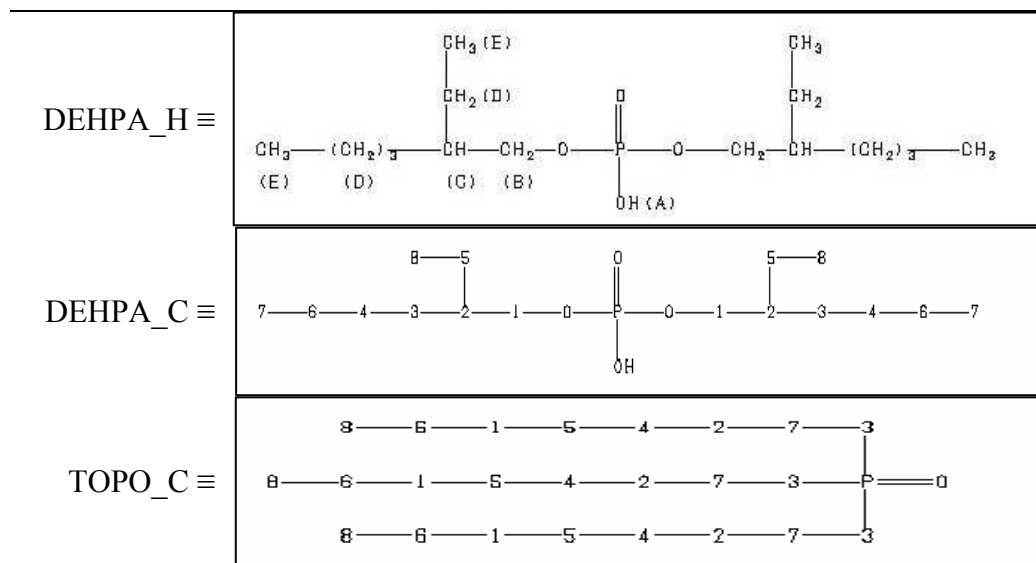
NMR = J_{C-P}

(-) ,

-) , NMR SDBS

.(

: SDBS



SDBS

DEHPA TOPO

SDBS				NMR	
DEHPA	DEHPA	TOPO	DEHPA/TOPO	DEHPA/TOPO	
H	C	C	C	C	H
A 12.2		31.84 741 1	10.92	10.92	0.872
B 3.93	69.77 257 P 1	31.52 333 P 2	14.06	14.07	0.906
C 1.46	69.53 277 P 1	30.98 318 P 2	14.09	14.11	0.865
D 1.42 to 1.21	40.31 381 P 2	29.34 274 P 3	21.70	21.60	1.517
E 0.90	40.02 366 P 2	29.11 1000 4	21.85	21.63	1.517
	29.98 777 3 *	5	22.67	22.69	1.254

28.98	911	4 *	26.77	274 P	3	23.04	23.03	1.271
23.33	772	5 #	22.67	701	6	23.33	23.27	1.364
23.04	1000	6 #	21.85	308 P	7	26.77	26.83	1.724
14.06	817	7	21.70	308 P	7	29.34	27.47	1.708
10.92	733	8	14.09	259	8	28.98	28.94	1.254
						29.11	29.15	1.264
						29.98	29.94	1.290
						30.98	31.08	1.376
						31.52	31.22	1.376
						31.84	31.87	1.241
						40.02	40.07	1.548
						40.31	40.15	1.548
						69.53	69.43	3.896
						69.77	69.49	3.895

ppm , DEHPA () .

.ppm , - TBP ppm , TOPO

() TBP

ppm , , ,

ppm , , ()

- , - TOPO DEHPA

TBP . TBP ppm , , ,

.(Raffinite)

() .

TOPO DEHPA ppm , , ,

ppm , - , -

P-P

.DEHPA

TOPO DEHPA

ppm

()

.ppm , - , -

(&)

.ppm ()

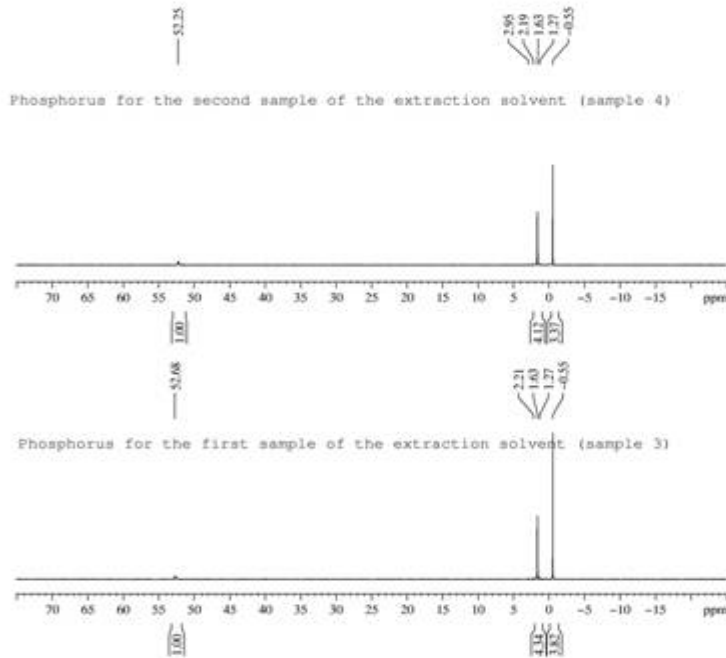
()

TBP

(&)

TOPO DEHPA

TBP



```

===== CHANNEL 1 =====
NAME      ElectroMAG
SAPNO     1
FACNO     1
F2 - Amplification Parameters
DATE_     2205001
TIME      16.30
INSTRUM   W400
PROBHD    5 mm BBO BB-1H
PULPROG   zgpg30
TD        65536
SOLVENT   CDCl3
NS        10
DS        0
SWH        16233.761 Hz
F2FREQ    0.047798 Hz
AQ        2.1181287 sec
RG        13024
DM        80.800 usec
DE        6.00 usec
TE        0.0 K
QT        2.0000000 sec
SI        0.0000000 sec
DELTA     1.8999999 sec
PCPROG    5.0000000 sec
PCWPRG    7.0100000 sec

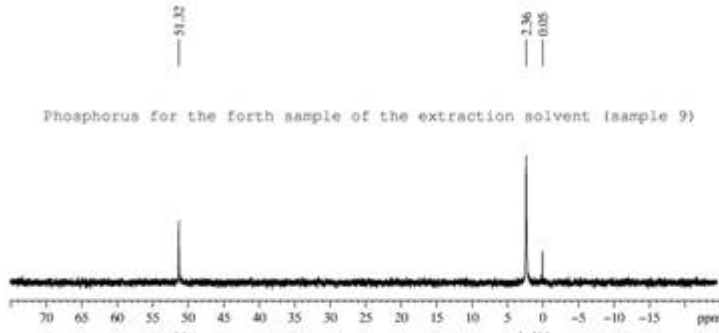
===== CHANNEL 2 =====
NAME      waltz16
SAPNO     1
FACNO     1
F2 - Processing parameters
SI        16384
SF        161.975720 MHz
NUC1      31P
OR        0
SR        1.00 Hz
PC        1.40

```

(&)

DEHPA/TOPO

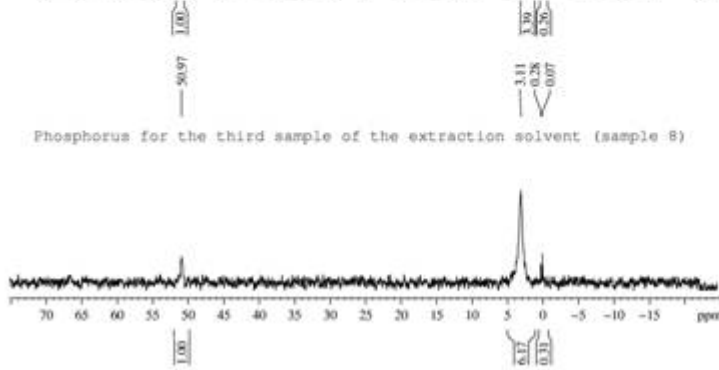
:



Phosphorus for the fourth sample of the extraction solvent (sample 9)

```

===== CHANNEL F1 =====
NAME      P100Organic
EXPNO     1
PROCNO    1
F2 - Acquisition Parameters
Date_     2004021
Time      16.30
INSTRUM   mv400
PROBHD    5 mm BBO 50-14
PULPROG   zgpg30
TD        65536
SOLVENT   DMSO-d6
NS        10
DS        4
SWH        14237.747 Hz
F2FREQ    50.137500 MHz
AQ        2.0185587 sec
RG        13004
SM        30.800 usec
DE        6.00 usec
TE        300.2 K
PC        2.0000000 sec
SFO       500.1360000 MHz
DELLA     1.8999998 sec
WALTZ16   0.3000000 sec
MORPH     0.3000000 sec
MORPH2    0.3000000 sec
===== CHANNEL F2 =====
NAME      P100Organic
EXPNO     1
PROCNO    1
F2 - Processing parameters
SI        14284
SF        141.9733710 MHz
WDW        0
SSB        0
LH        1.00 Hz
GB        0
PC        1.40
  
```

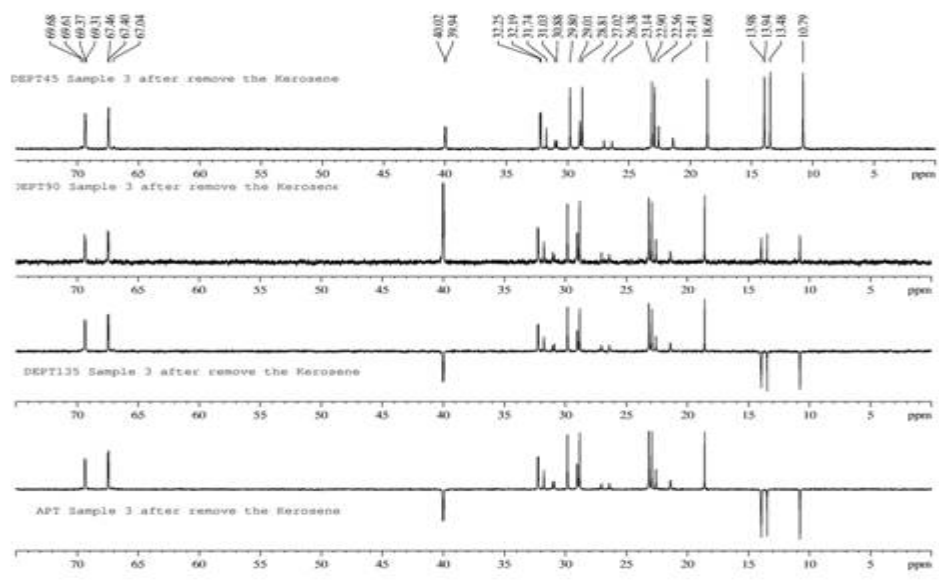


Phosphorus for the third sample of the extraction solvent (sample 8)

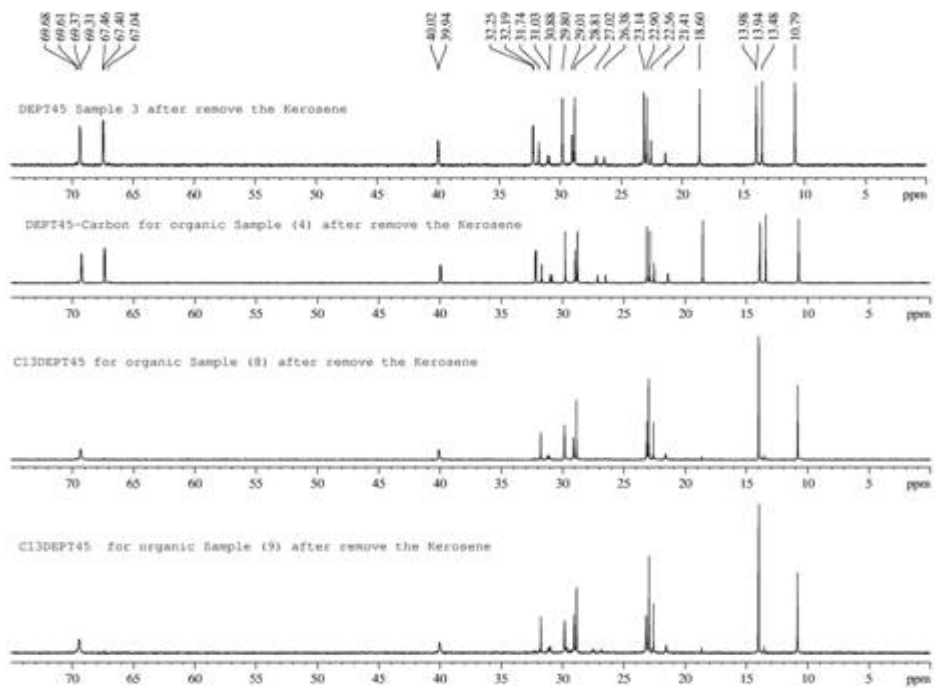
```

===== CHANNEL F1 =====
NAME      P100Organic
EXPNO     1
PROCNO    1
F2 - Acquisition Parameters
Date_     2004021
Time      16.30
INSTRUM   mv400
PROBHD    5 mm BBO 50-14
PULPROG   zgpg30
TD        65536
SOLVENT   DMSO-d6
NS        10
DS        4
SWH        14237.747 Hz
F2FREQ    50.137500 MHz
AQ        2.0185587 sec
RG        13004
SM        30.800 usec
DE        6.00 usec
TE        300.2 K
PC        2.0000000 sec
SFO       500.1360000 MHz
DELLA     1.8999998 sec
WALTZ16   0.3000000 sec
MORPH     0.3000000 sec
MORPH2    0.3000000 sec
===== CHANNEL F2 =====
NAME      P100Organic
EXPNO     1
PROCNO    1
F2 - Processing parameters
SI        14284
SF        141.9733710 MHz
WDW        0
SSB        0
LH        1.00 Hz
GB        0
PC        1.40
  
```

(&) DEHPA/TOPO :



() DEHPA/TOPO :



DEHPA/TOPO :

NMR :

TBP

, () , () , : ()

///

.() , ()

() COSY

ppm ,

ppm ,

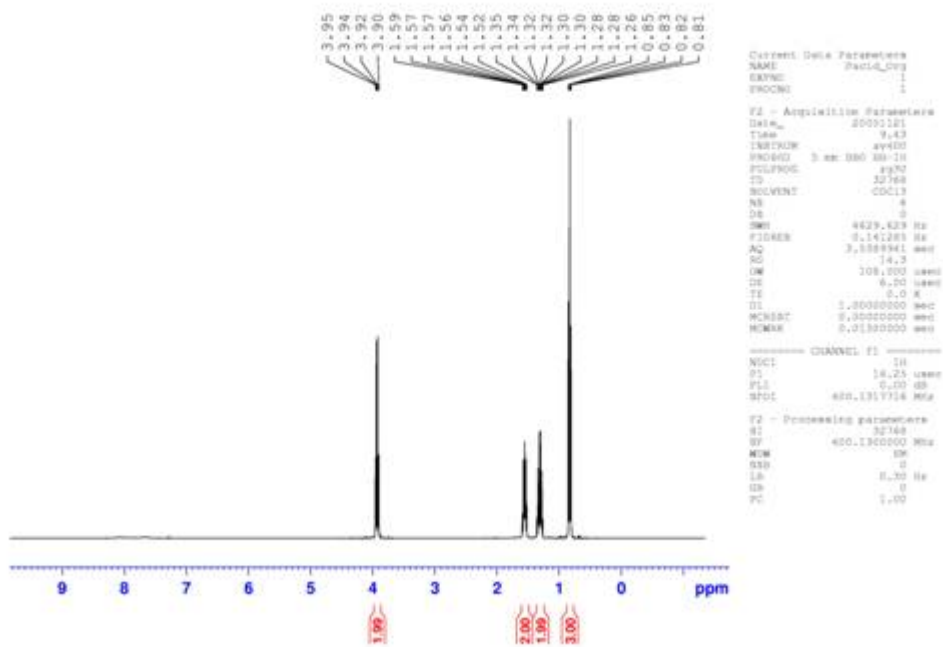
ppm ,

.ppm

ppm ,

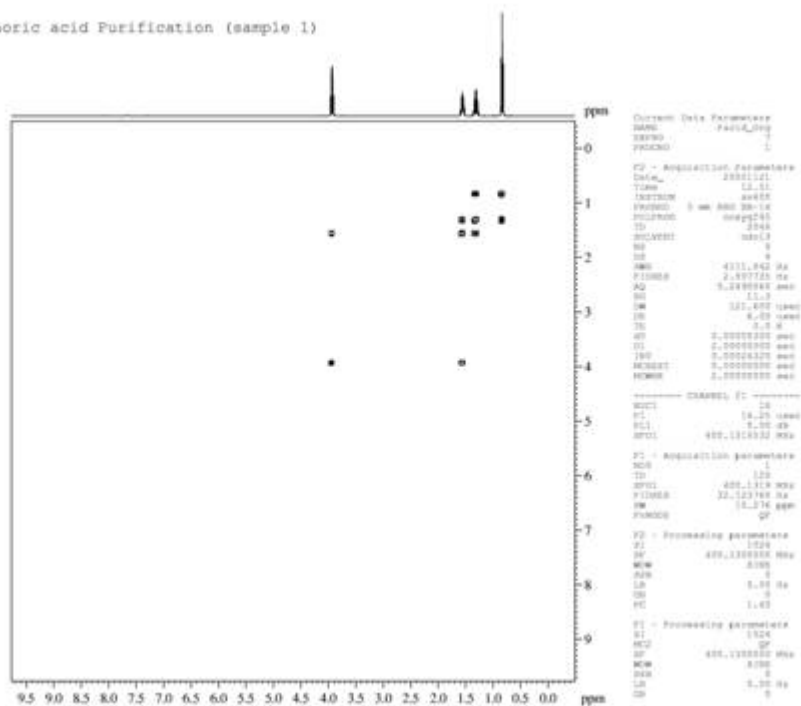
. ppm ,
 : () H - .
 .() , () , () , () ,
 CH2 ppm , CH3
 C- () HSQC .() DEPT45 (90, 135) APT
 , , , , H
 . , , , ,
 . /
) H - ppm , - .
 , .()
 . ppm , ,
 ppm , /

Proton: Phosphoric acid Purification (sample 1)

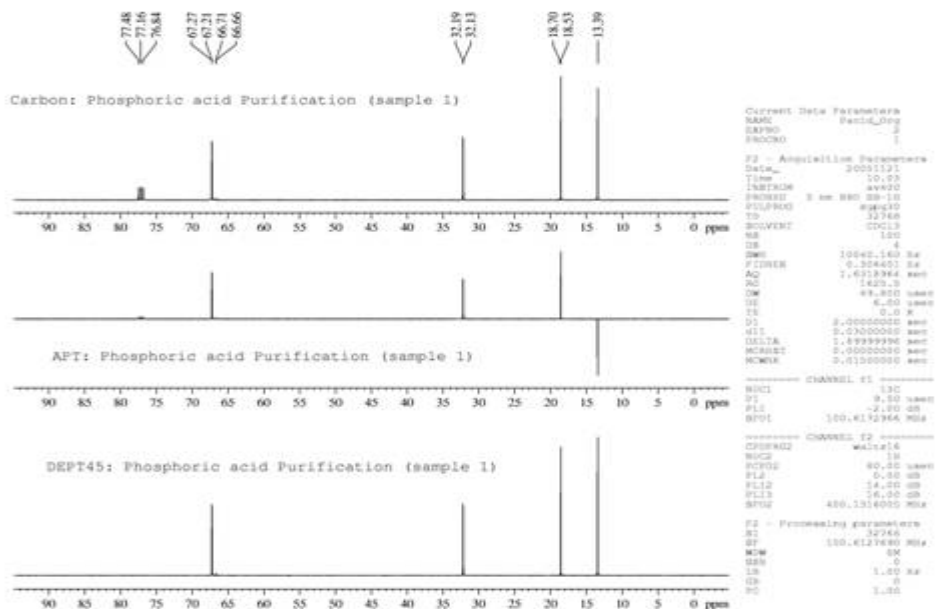


TBP :

COSY: Phosphoric acid Purification (sample 1)

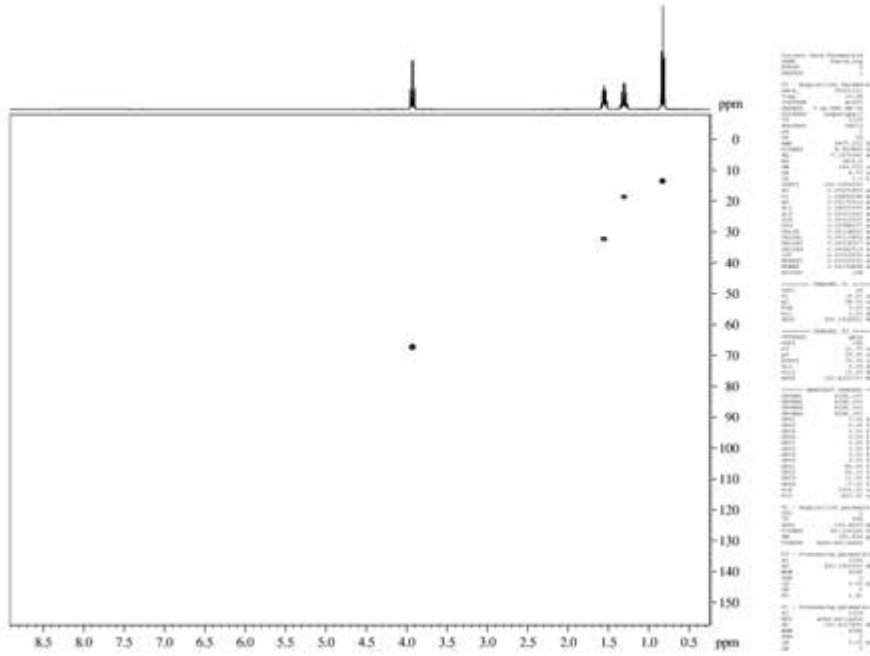


TBP H-H :



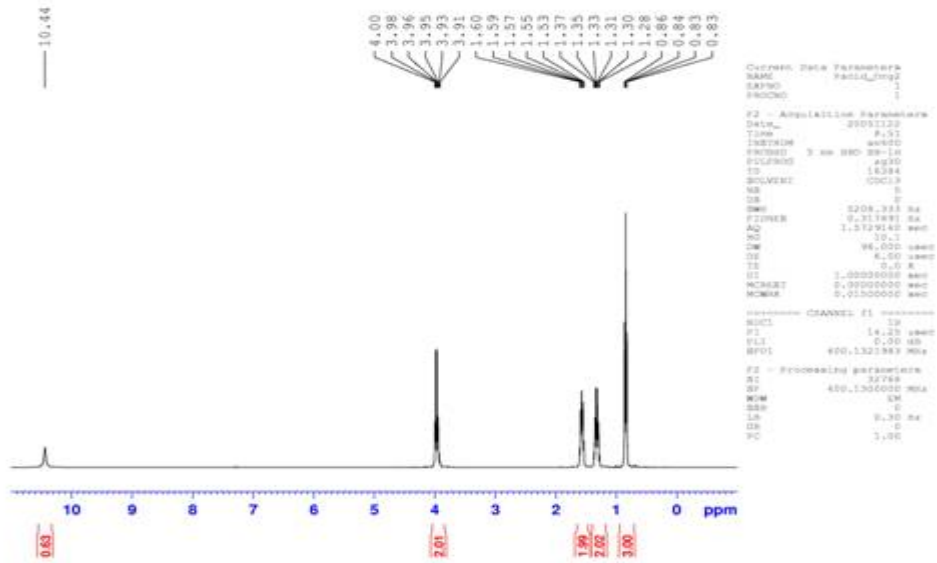
TBP :

HSQCETGPI2: Phosphoric acid Purification (sample 1)

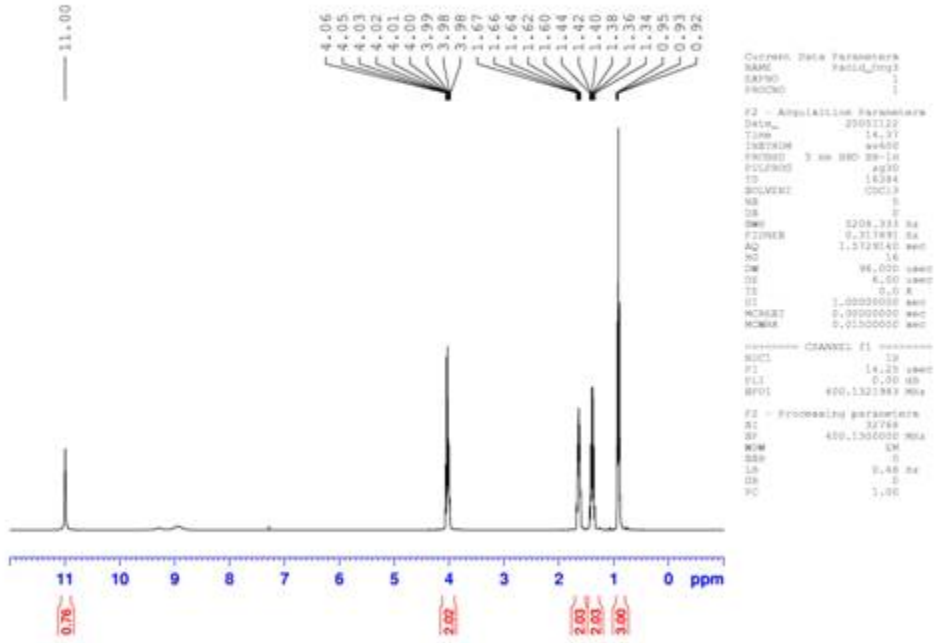


TBP C-H :

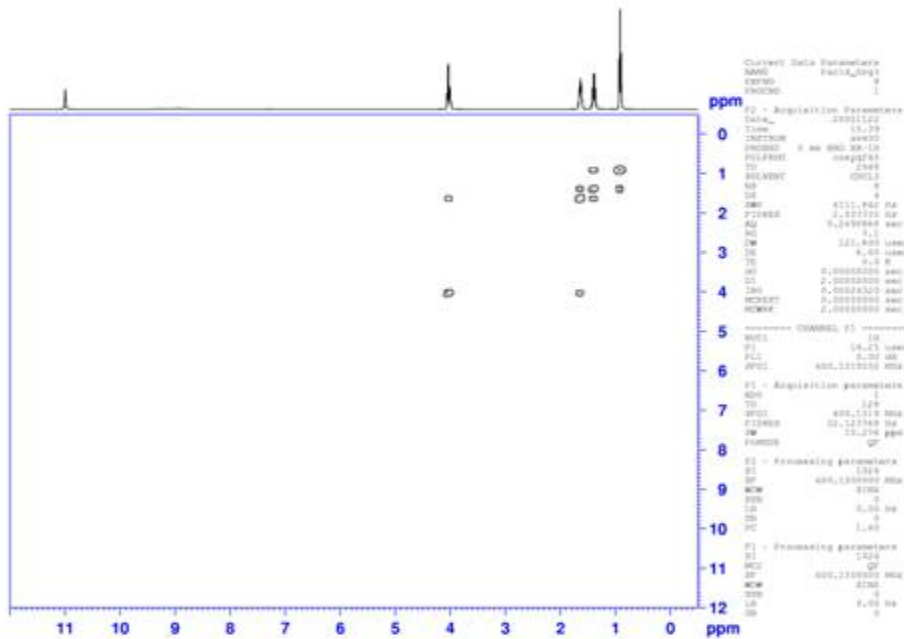
Proton: Charged Solvent of The P acid Purification (Sample 4 # 6)



Proton: Washed Charged Solvent of P acid purification (sample 8 # 9)

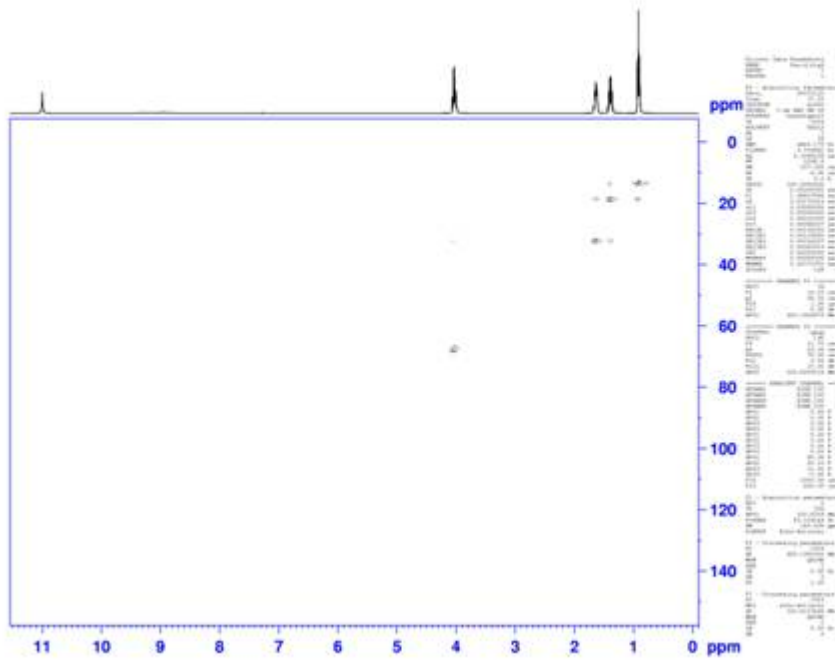


COSY: Washed Charged Solvent of P acid purification (sample 8 # 9)



COSY :

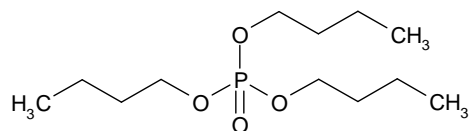
HSQC: Washed Charged Solvent of P acid purification (sample 8 # 9)



HSQC :

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NMR



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TBP

(O=P(-OH; -OR;-OR*) OH) ppm ,

) TBP

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ppm ,

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:ppm , -

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H

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:ppm 0.70

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) H

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:ppm ,

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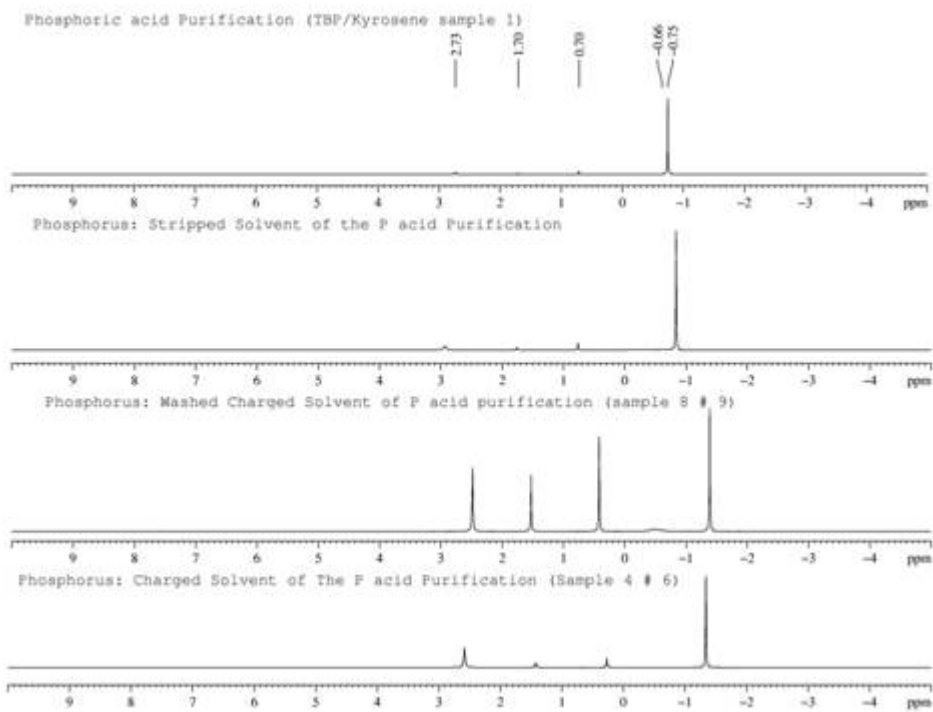
) H

.(

:ppm ,

H

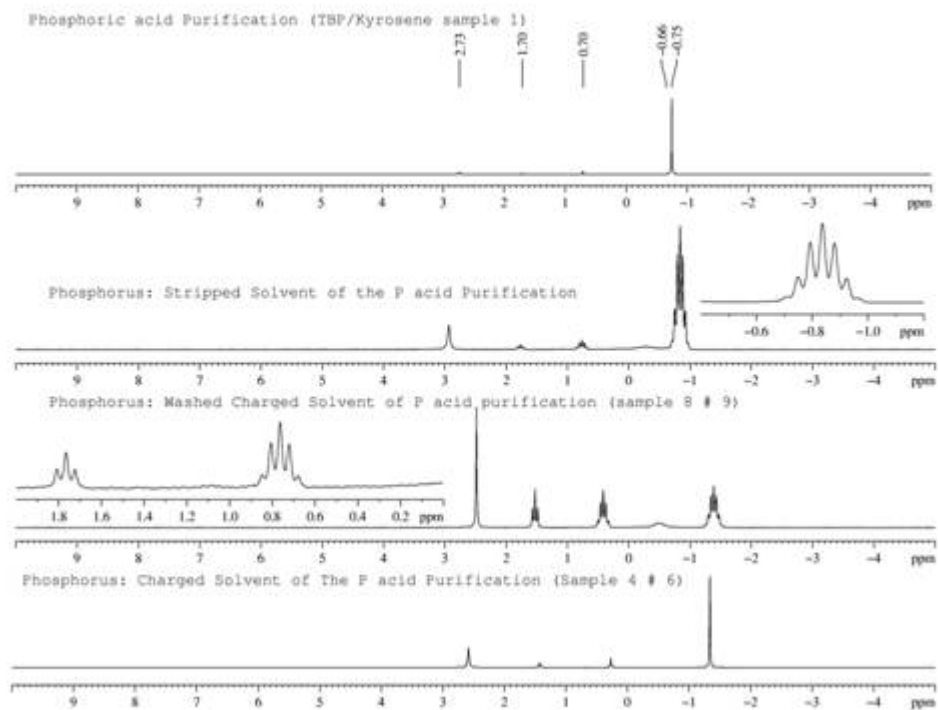
.()



H-P

TBP

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H-P

TBP :

()

TBP

.()

ppm ,

(ppm , & ,)

(ppm ,) :()

(ppm , & ,)

$$J_{P-H}=41.2 \text{ Hz}$$

(CH₃-

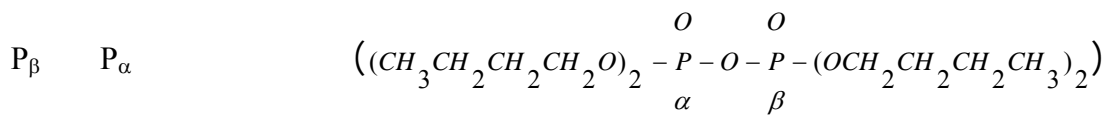
⁵J_{P-H} ⁴J_{P-H}

(-CH₂-O)_n-P=O

TBP

CH₂-CH₂-CH₂-O)_n-P=O

TBP



$J_{P-H} \quad J_{P-P}$

P-H

$P_{\alpha}-P_{\beta}$

$\beta \quad \alpha$

H-H

H-P

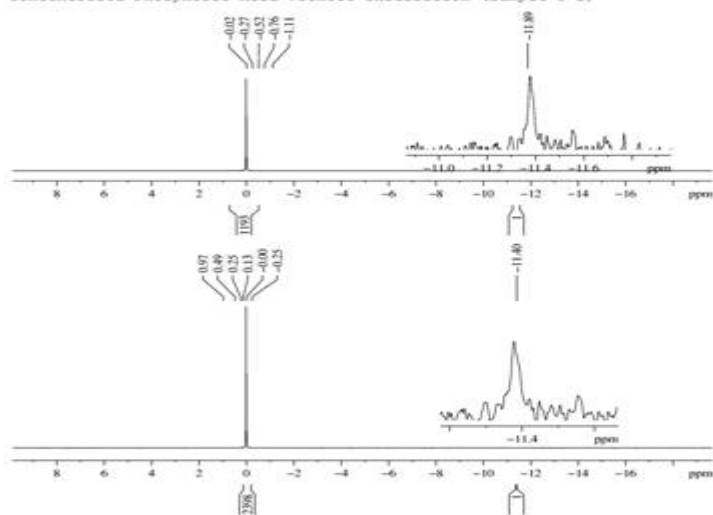
) ppm , & ,

()

(P-H

.() P-H

Concentrated Phosphoric Acid without Oxidization (sample 5-2)



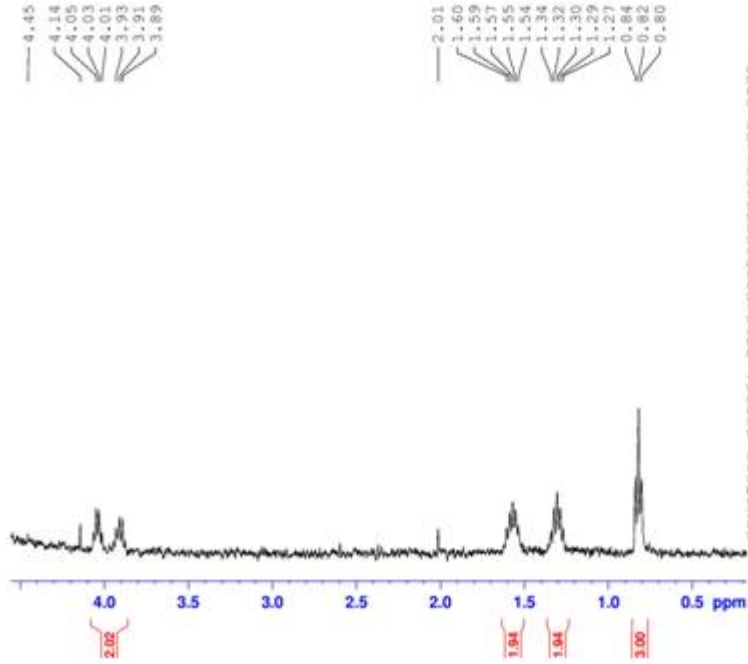
```

Current Data Parameters
NAME          5_2acid
EXPNO         10
PROCNO        1
----- Acquisition Parameters -----
Date_         20051109
Time          12.24
INSTRUM       spect
PROBHD        5 mm BBO GP-1H
PULPROG       zgpg30
TD            65536
SOLVENT       H2O
NS            500
DS            10
SWH           34482.738 Hz
F2FREQ        62.826342 MHz
AQ            1.9023940 sec
RG            1280.0
AQ            14.3000000 sec
SI            6.0000000 sec
TE            0.0 K
D1            0.00000000 sec
d11           0.02000000 sec
DELTA         1.49999996 sec
NUC1          31P
NUC2          31P
MORPHET       0.00000000 sec
MORPHET       0.01000000 sec
----- CHANNEL f1 -----
NUC1          31P
P1            4.0000000 sec
PL1           4.0000000 dB
SFO1          161.9764434 MHz
----- CHANNEL f2 -----
CPDPRG2       waltz16
NUC2          31P
P2            4.0000000 sec
PL2           4.0000000 dB
PL12         14.0000000 dB
PL13         14.0000000 dB
SFO2          400.1416000 MHz
----- Processing parameters -----
SI            65536
SF            161.9764434 MHz
GB            0
WDW           0
SSB           0
LB            1.0000000 Hz
GB            0
PC            1.40

```

³¹P NMR :

Concentrated Phosphoric Acid without Oxidization (sample 5-2)



Current Data Parameters
 NAME: P_0011
 EXPNO: 12
 PROCNO: 1

F2 - Acquisition Parameters
 Date_ : 2005109
 Time : 14.52
 INSTRUM : av400
 PROCNO : 3 ac 000 00-10
 PULPROG : zgpg30
 TD : 32768
 SOLVENT : H2O+D2O
 NS : 10
 DS : 2
 SWH : 8278.144 Hz
 FIDRES : 0.305278 Hz
 AQ : 0.0496436 sec
 RG : 18
 DW : 80.400 usec
 DE : 6.70 usec
 TE : 30.2 K
 D1 : 5.0000000 sec
 d12 : 0.0000000 sec
 MCHIST : 0.0000000 sec
 MCHKA : 0.0100000 sec

----- CHANNEL f1 -----
 NUC1 : 1H
 P1 : 14.23 usec
 PL1 : 0.00 dB
 PL2 : 0.00 dB
 PL3 : 0.00 dB
 PL4 : 0.00 dB
 PL5 : 0.00 dB
 PL6 : 0.00 dB
 PL7 : 0.00 dB
 PL8 : 0.00 dB
 PL9 : 0.00 dB
 PL10 : 0.00 dB
 PL11 : 0.00 dB
 PL12 : 0.00 dB
 PL13 : 0.00 dB
 PL14 : 0.00 dB
 PL15 : 0.00 dB
 PL16 : 0.00 dB
 PL17 : 0.00 dB
 PL18 : 0.00 dB
 PL19 : 0.00 dB
 PL20 : 0.00 dB
 PL21 : 0.00 dB
 PL22 : 0.00 dB
 PL23 : 0.00 dB
 PL24 : 0.00 dB
 PL25 : 0.00 dB
 PL26 : 0.00 dB
 PL27 : 0.00 dB
 PL28 : 0.00 dB
 PL29 : 0.00 dB
 PL30 : 0.00 dB
 PL31 : 0.00 dB
 PL32 : 0.00 dB
 PL33 : 0.00 dB
 PL34 : 0.00 dB
 PL35 : 0.00 dB
 PL36 : 0.00 dB
 PL37 : 0.00 dB
 PL38 : 0.00 dB
 PL39 : 0.00 dB
 PL40 : 0.00 dB
 PL41 : 0.00 dB
 PL42 : 0.00 dB
 PL43 : 0.00 dB
 PL44 : 0.00 dB
 PL45 : 0.00 dB
 PL46 : 0.00 dB
 PL47 : 0.00 dB
 PL48 : 0.00 dB
 PL49 : 0.00 dB
 PL50 : 0.00 dB
 PL51 : 0.00 dB
 PL52 : 0.00 dB
 PL53 : 0.00 dB
 PL54 : 0.00 dB
 PL55 : 0.00 dB
 PL56 : 0.00 dB
 PL57 : 0.00 dB
 PL58 : 0.00 dB
 PL59 : 0.00 dB
 PL60 : 0.00 dB
 PL61 : 0.00 dB
 PL62 : 0.00 dB
 PL63 : 0.00 dB
 PL64 : 0.00 dB
 PL65 : 0.00 dB
 PL66 : 0.00 dB
 PL67 : 0.00 dB
 PL68 : 0.00 dB
 PL69 : 0.00 dB
 PL70 : 0.00 dB
 PL71 : 0.00 dB
 PL72 : 0.00 dB
 PL73 : 0.00 dB
 PL74 : 0.00 dB
 PL75 : 0.00 dB
 PL76 : 0.00 dB
 PL77 : 0.00 dB
 PL78 : 0.00 dB
 PL79 : 0.00 dB
 PL80 : 0.00 dB
 PL81 : 0.00 dB
 PL82 : 0.00 dB
 PL83 : 0.00 dB
 PL84 : 0.00 dB
 PL85 : 0.00 dB
 PL86 : 0.00 dB
 PL87 : 0.00 dB
 PL88 : 0.00 dB
 PL89 : 0.00 dB
 PL90 : 0.00 dB
 PL91 : 0.00 dB
 PL92 : 0.00 dB
 PL93 : 0.00 dB
 PL94 : 0.00 dB
 PL95 : 0.00 dB
 PL96 : 0.00 dB
 PL97 : 0.00 dB
 PL98 : 0.00 dB
 PL99 : 0.00 dB
 PL100 : 0.00 dB

F2 - Processing parameters
 SI : 32768
 SF : 400.1418550 MHz
 KW : 30
 SSB : 0
 LB : 1.00 Hz
 GB : 0
 PC : 1.00

HNMR :

:

1. R. Ernst, Nuclear Magnetic Resonance Fourier Transformation Spectroscopy, *Anewandte Chemie*, vol. 31, Nr. 7, 805-930, 1992
2. H. Kessler, M. Gehrke and C. Giesinger, Zweidimensionale NMR-Spektroskopie, *Anewandte Chemie*, **vol.** 100/4 , 507-554, 1988.
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5. D.E. Leyden and R.H. Cox, Analytical Applications of NMR, John Wiley, 1987
6. S. Braun, H. O. Kalinowski, S. Berger, 150 and more basic NMR-Experiments, Wiley-VCH, 1998.
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8. SDBS Information at <http://www.aist.go.jp/RIODB/SDBS/>

TBP,

DEHPA, TOPO

TBP, DEHPA, TOPO

Phosphor investigation in the production of Syrian phosphoric acid using Nuclear Magnetic Resonance

Dr. Oussama Alhaasanieh, Mohammed Al-Hameish

Atomic Energy Commission – Chemistry Department

Nuclear magnetic resonance spectroscopy (NMR) was applied in this work to the industrial process of extraction of uranium from phosphoric acid and to the process of the purification of the phosphoric acid for food proposes. The structural changes of used extraction materials and the organic content of the final product was studied. ^{13}C , ^1H and ^{32}P - spectra of all material during the process were recorded. The spectra of the three used extraction materials DEHPA, TOPO and TBP show a partial degradation during the process. The final product (Phosphoric acid for Food proposes) doesn't contain any organic solvents or extraction material

Key words: Phosphoric Acid, Extraction materials TBP – DEHPA-TOPO, Nuclear Magnetic Resonance, ^{13}C ,

^1H and ^{32}P - spectra

SYRIAN ARAB REPUBLIC
ATOMIC ENERGY COMMISSION
DAMASCUS- P.O.BOX: 6091



Report on Scientific Laboratory Study
Department of Chemistry

Phosphor investigation in the production of Syrian phosphoric acid using Nuclear Magnetic Resonance

Dr. Oussama Alhaasanieh
Mohammed Al-Hameish