The values of γ calculated from the Born-Huang theory for the phase III of ammonium fluoride with rigid ions and polarizable ions are summerized in Table 1. The calculated value of γ with rigid ions is 20% larger than the measured value. But the value of γ calculated with polarizable ions is deviated from the measured value with only 5%, which is in experimental error. This result provides a strong evidence that the phase III would be a CsCl-like structure. However, in order to determine the structures of the high pressure phases of ammonium fluoride conclusively, high pressure X-ray or neutron scattering studies would be required.

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A New Quantitative Analysis of Phosphates by ^{31}P-NMR Spectroscopy[1]

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A quantitative analysis of phosphates is generally well established by conventional wet chemistry for a long time because of their important role in all areas of chemistry.[2] The ASTM D 515,[3] which measures the total orthophosphate of sample by oxidation or hydrolysis, is very sensitive method, but it has many interferences and no selectivity. These drawbacks could be overcome by the several useful method such as anion-exchange chromatography,[4] paper chromatography,[5] and TLC.[6] However, all of these mentioned are time-consuming and inconvenient methods.

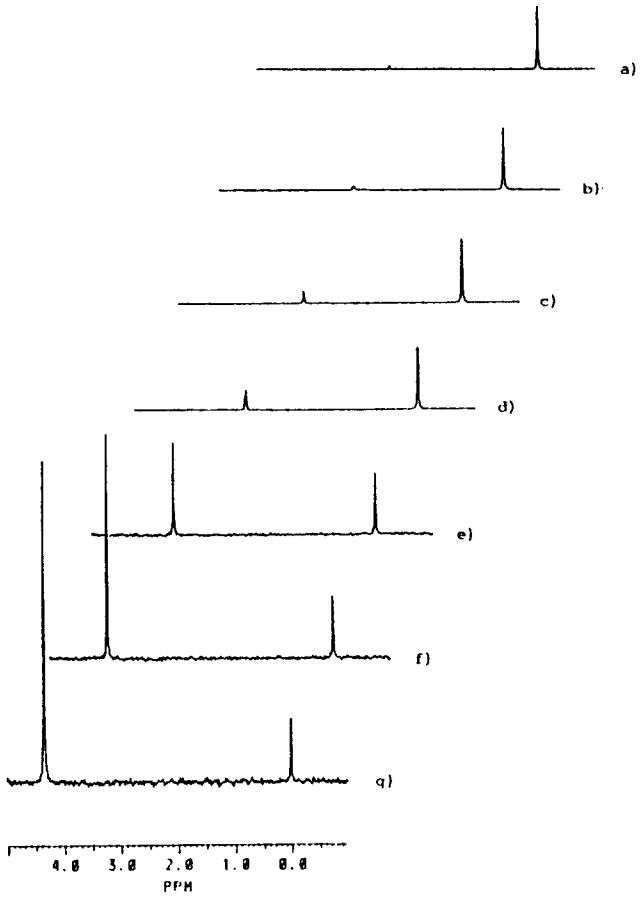

Figure 1. ^{31}P-NMR spectra of trisodium orthophosphate at various concentrations with 500 ppm phosphoric acid as an external standard. The concentrations (a-g) are 10, 20, 50, 100, 250, 500, and 1000 ppm as phosphorus.

NMR is generally much less sensitive than other analytical methods. However, rapid growth during the last decade in NMR technique, most notably in the increasing use of a high-field spectrometer with further hardware developments, reduced the absolute detection thresholds drastically and made the NMR technique a viable alternative and a preferred technique in all areas of chemistry. With these advantages, the use of ^{31}P nucleus, which has 100% natural abundance, relatively high sensitivity, and wide chemical shift range in NMR, has become more and more popular in chemistry.[7]

In this communication, we now report what appears to be the new preferred alternative method for the quantitative analysis of phosphates. The phosphates studied were trisodium orthophosphate, tetrasodium pyrophosphate, and pentasodium tripolyphosphate in H_2O/D_2O (50%, v/v). The representative ^{31}P-NMR spectra of orthophosphate obtained on a Bruker AM-300 spectrometer at 121 MHz are shown in the Figure 1. The upfield singlet is the peak of the 500 ppm phosphoric acid which is contained at 3 mm tube (inside radius 1.75 mm)[8] and placed co-axially in a 5 mm NMR tube containing various concentrations of phosphates. The spectra were accumulated by using 17.8° pulse width and

Table 1. Integration Ratios of Various Phosphates to 500 ppm Orthophosphoric Acids in Several Concentrations (50% D_2O Solvent)

Conc. (ppm)	Integration Ratio		
	Na_3PO_4	$Na_4P_2O_7$[a]	$Na_5P_3O_{10}$[a]
1000	5.6	6.0	6.0
500	2.9	3.1	3.1
250	1.4	1.7	1.4
100	0.52	0.60	0.55
50	0.27	0.27	0.28
20	0.11	0.099	0.086
10	0.056	0.045	–
r[b]	0.9998	0.9993	0.9996
a[b]	−4.34E-03	0.0218	−0.0405
b[b]	5.64E-03	6.04E-03	6.07E-03

[a] Obtained at pH 12, [b] Linear regression parameters: r, correlation coefficient; a, axis intercept of calibration line; b, slope of calibration line.

2.7 sec repetition time.[9] The pH of pyro- and tripolyphosphate solution was held at 12 to optimize the spin-lattice relaxation time[10] and the signal separation. Under all these conditions described, we ensured that the peak area measurement can be used for a quantitative analysis.

Integration ratios of individual three phosphates at various concentrations to the 500 ppm phosphoric acid as an external standard are given in the Table 1. The linear regression parameters are also given in the Table 1. It is clear that this method has a great advantage over the other conventional methods in terms of the linear regression parameters. Thus, the excellent linear relations (r>0.9993) show the great usuable range from 2 ppm to the percent order of phosphorus.[11] Furthermore, the low values of axis intercept (a), indicating the free of interferences, give a great chance to use this method for various samples. The slightly different slope of calibration line for the orthophosphate clearly indicates that construction of calibration plot is necessary for individual phosphates to analyze mixture.[12]

We applied calibration results described in the Table 1 to five mixture samples of ortho-, pyro-, and tripolyphosphate. The results expressed in percent recovery are summarized in the Table 2 with the relative standard deviation in parentheses. Since the contribution of pyrophosphate in commercial tripolyphosphate to the peak area is significant,

Table 2. Phosphate Species Analysis by ^{31}P-NMR

Sample No.	Recovery (%) (% RSD)[a]		
	Orthophosphate	Pyrophosphate[b]	Tripolyphosphate
1[c]	101 (1.5)	101 (1.5)	98 (3.4)
2[c]	100 (1.0)	104 (2.7)	102 (4.3)
3[c]	96 (2.5)	100 (2.4)	100 (4.0)
4[c]	100 (2.4)	104 (1.2)	102 (1.2)
5[c]	104 (2.3)	104 (0)	102 (1.0)

[a] Average of three runs. Percent relative standard deviation, [b] Results were corrected by separating the contribution by tripolyphosphate, [c] Added concentrations of ortho-, pyro-, tripolyphosphate in ppm as phosphorus were No. 1; 1000,1000,1000, No. 2; 500,500,500, No. 3; 250,250,250, No. 4; 250,250,500, No. 5; 250,250,1000.

the result of the analysis of pyrophosphate in the Table 2 was corrected. Relative standard deviations and relative percent accuracy were within 5%.

In Table 3, we showed comparison data between NMR and the ASTM D 515 for the analysis of three mixture samples. Thus, the result by this NMR method is in good agreement with that of the ASTM D 515 method in general. Although the limiting factor for this analysis is the time required for NMR acquisition,[13] by using a wide NMR probe[13] with high field instrument, this problem could be solved significantly.

In conclusion, the accuracy and precision of the ^{31}P-NMR method are either comparable or superior to that of the ASTM D 515. Especially, the advantages of this approach over the other analytical procedures are the selective analysis of phosphorus compounds and the simple analysis of samples. On the basis of these results, further studies are currently being pursued to apply this method on real samples.

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Table 3. Phosphate Species Analysis by ^{31}P-NMR and ASTM D 515[a]

Sample. No.	Recovery (%) (% RSD)[b]					
	Orthophosphate		Hydrolyzable phosphate		Total phosphate	
	ASTM	^{31}P-NMR	ASTM	^{31}P-NMR	ASTM	^{31}P-NMR
1[c]	108 (2.2)	96	96	100	100 (0)	99
2[c]	108 (0)	100	99	103	101 (0.6)	102
3[c]	112 (0)	104	102	102	103 (0.4)	103

[a] By the colorimetric ascorbic acid reduction method, [b] Average of three runs. Percent relative standard deviation, [c] Added concentrations of orho-, pyro-, tripolyphosphate in ppm as phosphorus were No. 1; 250,250,250, No. 2; 250,250,500, No. 3; 250,250,1000.

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8. This was made from commercially available Pyrex tube. One end of tube was sealed with a gas-oxygen torch and the tube was filled with phosphoric acid solution and the other end of the tube was sealed.
9. In order to determine whether saturation effects may be ignored for our pulse angle and repetition time, the same pulse angles and a pulse repetition rate of 12.7 s were applied to several samples. The change of relative peak intensities was less than 5.9% in all cases.
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11. 2.5 ppm and 5 ppm results were not included in the Table 1 and will be published.
12. After our abstract submission to the 69th Annual Meeting of the Korean Chemical Society, D. R. Gard and *et al.* (*Anal. Chem.*, **64**, 557 (1992)) published results on the application of ^{31}P-NMR for the analysis of pure sample without calibration.
13. For the 2.5 ppm sample, the signal to noise ratio was 3.7 on 37.5 h scan time in 5 mm probe of 121 MHz. In 10 mm probe at 121 MHz, about half of the time was required to get the same signal to noise ratio of 5 mm probe.

Oxidative Lactonization of Diols Using *m*-Chloroperbenzoic Acid and Hydrogen Chloride in *N,N*-Dimethylformamide

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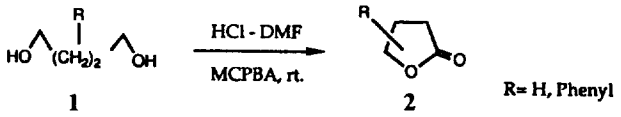
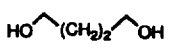
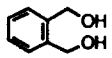
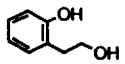
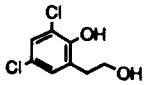
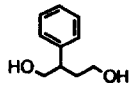
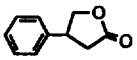
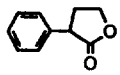
We have recently reported that the combination of dry HCl and *m*-chloroperbenzoic acid (MCPBA) in DMF serves as an effective reagent for the chlorination of phenols,[1] pyrimidine, purine bases and their nucleosides,[2] α-chlorination of ketones,[3] and its oxidation of secondary alcohols.[4] To our knowledge, there is no report on the application of MCPBA for lactonization of diols. In the present study, we wish to oxidative lactonization of diols using HCl/MCPBA/DMF system.

The reaction of diols **1** with dry HCl-MCPBA in DMF at room temperature gave the corresponding lactones **2**. *m*-Chlorobenzoic acid was easily removed by washing with 5% sodium bicarbonate solution.



1 **2** R= H, Phenyl

Table 1. Lactonization of Various Diols Using HCl/MCPBA in DMF[5]

Entry	Diol	Reaction time	Product	Yield (%)[a]
1		0.5 h		87 (55)[b]
2		0.5 h		88 (74)[b]
3		0.5 h		65 (58)
4		0.5 h		62 (55)
				35 (30)

[a]Yields were determined by GC, and values in parentheses are isolated yield, [b]See reference 6.

In a typical run, to a solution of 1,2-bis (hydroxymethyl)benzene (138 mg, 1.0 mmol) in 2.2 m*l* of 0.5 M HCl-DMF (1.1 mmol HCl) was a ded MCPBA (447 mg, 2.2 mmol, 85% purity) in one portion with good stirring at room temperature. The reaction mixture was allowed stirring at room temperature until yellow color disappeared. The reaction mixture was diluted with 5% aqueous $NaHCO_3$ solution and extracted with ether (3×200 m*l*). After removal of solvent *in vacuo*, the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2) to give 99 mg (74%) of γ-lactone (entry 2) as a white solid with low melting point. The lactones obtained were identified by ^{1}H NMR, IR, and mass spectra and/or comparing GC chromatograms with those of authentic samples. The representative results are summarized in Table 1.

The reaction of 1,4-butanediol with HCl-MCPBA in DMF afforded γ-butyrolactone (entry 1) in good yield but the isolated yield was comparatively low because of the difficulties in isolation. In case of symmetrical 1,2-bis(hydroxymethyl) benzene (entry 2), the best result was obtained. On the other hand, unsymmetrical diol, 2-phenyl-1,4-butandiol (entry 4) afforded a mixture of β-phenylbutyrolactone (55%) and α-phenylbutyrolactone (30%). The ratio of β-phenylbutyrolactone increased to *ca.* 70% (determined by GC) by heating (70℃) during the reaction. In case of 2-hydroxyphenethyl alcohol (entry 3), the benzene ring was chlorinated to give 3,5-dichloro-2-hydroxyphenethyl alcohol as expected.[1] The oxidation of alcohol by HCl-MCPBA in DMF seemed to be slower reaction than the chlorination to the aromatic ring. Diols which have a primary and a secondary hydroxy groups such as 2,5-pentandiol and 1-phenyl-1,4-butandiol gave the