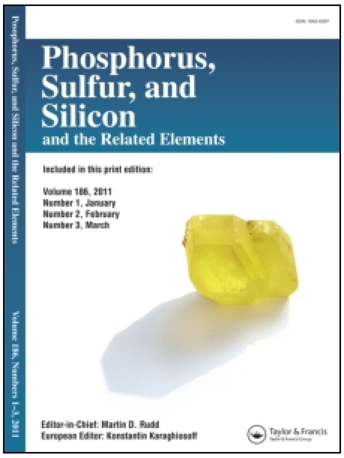

# Phosphorus, Sulfur, and Silicon and the Related Elements

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## PosterPresentations

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# STRUCTURES OF TRIMETAPHOSPHATES-TELLURATES

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Telluric acid has the property to give addition compounds with inorganic phosphates, arsenates, sulfates and iodates. The structural common characteristic for all compounds is the coexistence of two different kinds of anions : $TeO_6$ octahedra and phosphate, sulfate, arsenate or iodate anions.

In the phosphate-tellurates obtained by addition of telluric acid and monophosphates or condensed phosphates (up to now $P_2O_7$-$P_3O_9$ and $P_4O_{12}$) we had interest for trimetaphosphate-tellurates of monovalent cations. We describe the crystal structures of :

$Te(OH)_6.2Na_3P_3O_9.6H_2O$ : hexagonal, P63/m,
a = 11.67(1) , b = 12,12(1) Å    Z = 2

$Te(OH)_6.K_3P_3O_9.2H_2O$ : monoclinic, P21/c,
a = 15.61(5) , b = 7.456(1) , c = 14.84(8) Å    Z = 4
β = 108.01(4)°

$Te(OH)_6.Rb_3P_3O_9.H_2O$ : monoclinic, P21/a,
a = 15.56(1) , b = 8.358(3) , c = 13.72(1) Å    Z = 4
β = 113.27(5)°

$Te(OH)_6.2(NH_4)_3P_3O_9$ : rhombohedral, R3
a = 8.773(5)Å α = 100.37(5)°    Z=1

# STRUCTURAL CHEMISTRY OF SOME NEW TYPES OF TETRAMETAPHOSPHATES

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Four new structural types of tetrametaphosphates have been investigated :

$SrNa_2P_4O_{12}$ : tetragonal P4/nmb
a = 9,838(5), c = 5,003(3) Å    Z = 2

$SrNa_2P_4O_{12}.6H_2O$ : orthorhombic I2mm
a = 7,332(5), b = 7,663(5) , c = 14,408(8) Å    Z = 2

$Zn_2P_4O_{12}.8H_2O$ : triclinic $P\bar{1}$
a = 8,610(5), b = 7,137(5) , c = 7,108(5) Å
α = 96.09(5) , β = 105,99(5) , γ = 100,49(5)    Z = 1

$Zn_4Na_4(P_4O_{12})_3$ : cubic $I\bar{4}3d$
a = 14, 570(6) A    Z = 4

Detailed atomic arrangements are presented for these four compounds.

## POTASSIUM MONO-, DI-, AND TRIPHOSPHATE IN VIEW OF THEIR USE AS LIQUID FERTILIZERS.

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The use of simple and multicomponent liquid fertilizers is finding ever-increasing application. Therefore, the system $K^+, H^+ \| PO_4{}^{3-}, P_2O_7{}^{4-}, P_3O_{10}{}^{5-} - H_2O$ (I) was studied. The agrochemical demands on the pH of the solutions used (5-10) then led to the study of solubility in the partial system

$$K_2HPO_4 - KH_2PO_4 - K_3HP_2O_7 - K_2H_2P_2O_7 - K_4HP_3O_{10} - K_3H_2P_3O_{10} - H_2O \quad \text{(II)}$$

The solubility was studied mainly at temperatures below 273 K. It has been found that the agrochemical demands are best satisfied by solutions in which tetrapotassium hydrogentriphosphate, $K_4HP_3O_{10}$, crystallizes. Another advantage for agrochemical use of solutions from this region of system(II) is a low temperature-dependence of the solubility.

In connection with the application of liquid potassium fertilizers, the problem of the solubility of potassium chloride in these systems gains importance. Therefore, the solubility was studied in the $KCl - K_2H_2P_2O_7 - H_2O$ and $KCl - K_3H_2P_3O_{10} - H_2O$ systems and the results were compared with those published for the $KCl - KH_2PO_4 - H_2O$ system. It has been found that the solubility of potassium chloride in samples of the above systems decreases with increasing degree of polymerization of the phosphate anion.

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## HYDROLYSIS STUDY OF INORGANIC CYCLIC PHOSPHATES

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Munakata, Fukuoka 811-41 (Japan)

Hydrolysis reaction of inorganic cyclic phosphates was studied by liquid chromatography. Parent compound and hydrolysis products were separated by anion exchange chromatography. Phosphorus content in the column effluent was determined automatically with the use of Mo(V)-Mo(VI) reagent. Hydrolysis reactions in acidic aqueous solutions were first order. First order rate constant in 0.1M HCl solution decreases from trimeta- to hexametaphosphate with the increased ring, however, that of octametaphosphate increases again. In neutral solution, ring stability increases with the ring increase. An affinity of cyclic phosphates with hydrogen ion, which extremely accelerates the P-O-P bond cleavage by reducing an electron density around P atoms, increases with the ring increase. Thus, octametaphosphate hydrolysis rate becomes faster.

From the temperature dependence of the rate constants of trimeta-, tetrameta-, hexameta- and octametaphosphate, Arrhenius activation energy in 0.1M HCl solution was determined as $20 \sim 25$ kcal/mol.

PHOSPHORUS - DETECTION AND ESTIMATION by Erol KURAL, Azot Sanayi T.A.S., Samsun, Turkey.

Detection : The general procedure for detecting phosphorus in any compound is based on the reaction between orthophosphoric acid and molybdate to give a yellow precipitate in strongly acid solution.

Element : Phosphorus may be detected by its property of burning in air to give white fumes. The varieties are spontaneously combustible at room temperature, but both the red and black varieties have to be heated to cause ingnition.

Various Oxidation States : Mixtures of the acids and/or salts of phosphorus in various states of oxidation have been separated and detected by electrophoretic and diffusion paper chromatography.

Estimation : Quantitative determination of total phosphorus often reported as phosphorus pentoxide and sometimes, in the case of fertilizer, as bone phosphate of lime, is required for a great variety of materials.

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## ON THE CATALYTIC EFFECT OF SODIUM ION ON THE AMMONOLYSIS OF TRIMETAPHOSPHATE.

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The catalytic effect of sodium ions on the rate of the ammonolysis of trimetaphosphate ($P_{3m}$) molecules in aqueous ammonia (5 mol/dm$^3$) has been investigated at 30.0 ± 0.1°C and ionic strength of unity with tetramethylammonium chloride solution. The reaction product, monoamidotriphosphate, and $P_{3m}$ have been separated and determined by use of a high-performance liquid chromatography. The rate constants determined by measuring the disappearance of $P_{3m}$ was of first order in the concentration of $P_{3m}$. The rate constant increased as the sodium ion concentration increased and ion-pairs of Na-$P_{3m}$ and $Na_2$-$P_{3m}$ together with $P_{3m}$ anions are found to participate in the reaction. The stability constants of Na-$P_{3m}$ and $Na_2$-$P_{3m}$ ion-pairs estimated by the kinetic study were much smaller than the ones evaluated potentiometrically by use of Na-glass electrode. This discrepancy indicates that only a small fraction of sodium ions bound to $P_{3m}$ anions is considered to be in direct contact with non-bridging oxygen atoms and effective as the catalysts. Formation of the contact ion-pair with no intervening solvent molecules increases the electropositive character of phosphorus atom, which facilitates the nucleophillic attack of ammonia to phosphorus atom.

## SOLID STATE PHOSPHORUS-31 NMR OF SINGLE CRYSTALS: $KH_2PO_4$, $NaH_2PO\ H_20$, AND Na KURROL'S SALT.

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Magic angle orientation and high power heteronuclear decoupling techniques were applied to single crystal preparations of the above three phosphates and fully deuterated preparations of the two ortho salts. $KH_2PO_4$ yields a first-order quartet of line width at half height = 13,363 Hz when the long axis of the crystal is oriented along the NMR magic angle of 54.7°. H-1 decoupling at 400 watts reveals the multiplet to be proton coupled ($J_{HP}$ = 3938 and 5156 Hz). Upon decoupling the linewidth is narrowed to 1456 Hz revealing two residual chemical shift tensors from the two nonequivalent phosphate groups of the crystal unit cell. A long $T_1$ of 356 s was measured by the inversion-recovery method; $T_2$ was too short to determine ($< 200$ μs). The sodium salt exhibited a narrow H-1 coupled multiplet of 39 Hz. $T_1$ of 1.48 s was much shorter and $T_2$ of 0.25 s was much longer than those of the analogus potassium salt. Kurrol's salt demonstrated the greatest chemical shift anisotrophy, with the narrowest line width obtained by placing the crystal long axis at 35.3 with respect to Ho. This suggests that the resultant crystal shift tensor is aligned orthogonal to the crystal long axis, and this interpretation is supported by the known X-ray crystallographic data. The narrow line width of 150 Hz allows for the determination of middle and branch phosphate functional groups within the crystal. The $T_1$ relaxation is 240 ms; $T_2$ is shorter at 8.8 ms. Supported by: NIH EY 03988 and ESO 2397 and the United Cerebral Palsey Foundation.

## MECHANISM AND KINETICS OF THERMAL DEHYDRATION OF $Ca(H_2PO_4)_2.H_2O$ AND DOUBLE SUPERPHOSPHATE.

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Investigating thermal dehydration of $Ca(H_2PO_4)_2.H_2O$ and its mixtures with $Mg(H_2PO_4)_2.2H_2O$, $SiO_2$, KCl, natural phosphates and fluorite, the peculiarities of dehydration mechanism under the influence of additions are ascertained. The influence of $SiO_2$ on the phosphate ion condensation and KCl on the formation of free phosphoric acids is specified. In mixtures with natural materials depending on the reactivity of the basic mineral and the presence of impurities, their interaction with heating products up to the completion of dehydration can be observed.

Investigating the thermal dehydration of double superphosphate (DC), the influence of the rate of temperature increase, duration of heating and conditions of contact with the gaseous phase on the composition and properties of heating products was established. By short-term heating of granulated DC in a fluidized bed at 250-350°C it is possible more fully to decompose phosphate rock, to control the rate of phosphate solubility and to get a product with water-soluble or a set correlation of water and citrate-soluble $P_2O_5$ forms. Distribution of various phosphates along the section of heated samples is determined. Ammoniation of the product promotes an increase of solubility and a decrease of hydroscopicity. The kinetics of hydrolytic degradation of condensed phosphates is investigated; as a result, solubility becomes equal to that of the initial DC.

# NEW DERIVATES OF THE MOLECULAR HEPTAPHOSPHIDES $P_7(MR_3)_3$

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In a heterogeneous reaction of solid $M_3P_7$ with suitable reactants RX (eg. $ClSime_3$) solutions of $R_3P_7$ are obtained, from which the crystalline compounds $R_3P_7$ result. A direct path via substituent exchange then leads from these materials to new compounds, often with high yields. Examples are the complete series $P_7(Mme)_3$ with M=Si, Ge, Sn, Pb as well as $P_7(Mph_3)_3$ with M=Si, Ge, Sn. In these series, surprisingly the stability of the compounds in air increases. The silicon compounds decompose instantaneously into phosphane and siloxane; the lead compounds in contrast, however, react only in the course of some days. The i.r. spectra show the expected shift of the M-P and M-C vibrations with atomic mass, whereas the vibrations of the $P_7$-cages remain completely unaffected by the substitution.