POLYPHOSPHATES: RATIONALE FOR USE AND FUNCTIONALITY IN SEAFOOD AND SEAFOOD PRODUCTS

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Food Grade Phosphates

Among the legitimate functional goals for the use of phosphates in seafoods are retention of natural moisture and flavor, inhibiting fluid losses during shipment and prior to sale, emulsification, inhibiting oxidation of flavors and lipids by chelation of heavy metals and cryoprotection, thereby; extending shelf-life. Properly used, phosphates impart no flavor.

Recently, the use of phosphates in some segments of the seafood industry has been subject to government scrutiny. When improperly used, excessive absorption of moisture may lead to charges of economic fraud by the U.S. Food and Drug Administration. It is important to note, however, that seafood myofibrillar proteins readily denature at refrigeration temperatures (5°C) and may lose up to 80% of their water-binding capacity within five days (10) while similar changes to beef muscle take in excess of 45 days at >20°C (8). Failure to protect these delicate proteins leads to significant overpack to meet net stated weight and negative economic consequences to seafood processors.

Phosphates are refined from calcium phosphate which is mined. Through varying degrees of neutralization of phosphoric acid with either alkali metal ions (i.e., sodium or potassium) or alkaline earth metals (i.e., calcium), two general classes of phosphates (simple and condensed) are formed (7). Simple phosphates consist of a phosphorous atom surrounded by four oxygens and valences that can be filled by metal ions or hydrogen. Condensed or combined phosphates are short to long chains or rings, the latter forms have the broadest applications in the seafood industry.

Application of Phosphates

Phosphates are generally applied by dipping in, spraying with or tumbling in a phosphate solution. Injector needle systems may also be used with and without added tumbling. Dry addition is used in comminuted meat systems, e.g., surimi and sausage formulations.

The most predictable way to apply phosphates is through vacuum tumbling, if done properly and the structure of the flesh can withstand mechanical action. Contrary to some practices, tumbling in an excess of solution results in protein extraction rather than absorption of solution. This uniform and rapid means of treating the muscle offsets the inefficiency of protracted holding in phosphate-based solutions (soaking).

It has been demonstrated that treating finfish prior to smoking requires different phosphate concentrations depending on the dimensions of the fillets and/or pieces. For example, with the same size pieces of flesh (within selected species), a 5% phosphate dip requires 24 hours treatment time while a 25% phosphate dip requires only two seconds (16) to reach equal processing effects, i.e., inhibition of surface curd formation and reduced cook-cool losses. This is especially valuable when delicate muscle structure eliminates tumbling as an option. Caution should be exercised when applying phosphates to fish of different muscle thickness, muscle types (e.g., interspecies variation) and initial moisture content (spawning).

Methods to Determine Phosphate Application

Some methods to monitor phosphate use are based upon total moisture content of the muscle. One example would be the French HP (9) method which is used to monitor the ratio of protein to water within muscle. In scallops, the ratio is considered to be between 4.0 and 4.9: 1.0 (water: protein). The moisture content of commercially harvested seafood muscle is 80% or greater in species including, but not limited to, soft-shell blue crab, some mollusks and post-spawned finfish. Webb et al., (21) determined that the moisture content of bay scallop meats was significantly different at the 5% level between harvest years, sounds, locations within the sounds and among months and within locations. These researchers (21) also determined that the moisture content (monthly sampling) of land-shucked bay and Calico scallops ranged between 74.15 to 83.66 and 76.12 to 81.86%, respectively.

The HP ratio then would not be realistic for many species or at certain times of year. This value is based upon Kjeldahl protein to moisture (overnight drying at 100 to 105°C).

In theory, determination of total phosphorous in seafoods might be a useful marker of phosphate treatment; however, it is not necessarily accurate. For example, Crawford (4) determined that the natural level of phosphorous in fresh shrimp (Pandulus jordani) ranged from 537 to 727 mg/100 gm. Shrimp of the same history showed increases of 81±39 and (base not given) ±110 mg of phosphorous, respectively after treatment with either 1.5 or 6% phosphate solutions for five minutes. In shrimp (Pandulus jordani), the natural variation in phosphorous exceeded that added by responsible treatment.

Total natural phosphorous has also been reported to vary in lobster, blue mussels, squid, anchovies, carp, capelin, catfish, Atlantic cod, eel, hake, herring, yellow leatherjacket, European pilchard and albacore tuna (13). Penetration of phosphate, and therefore phosphorous content, will also vary according to concentration of solution used, variations in muscle thickness, subsequent processing, etc.

Other methods to screen for added phosphates include high pressure liquid chromatography (HPLC), ion chromatography and thin layer chromatography. Wood and Clark (22) have reviewed the difficulties associated with these phosphate determinations.

Biochemical decomposition of condensed phosphates necessitates assaying immediately after treatment of the seafood species. Hydrolysis of condensed phosphates occurs due to muscle alkaline phosphatase activity during the post-treatment (lag) time prior to cooking. Sutton (15) determined that sodium tripolyphosphate is rapidly hydrolyzed to pyrophosphate (phosphate dimer) and orthophosphate (phosphate monomer) in cod muscle at either zero or 25°C.

It has also been determined that after two weeks of frozen storage (-26°C), only 12% of the total phosphorous in raw shrimp muscle corresponded to the originally added sodium tripolyphosphate. By ten weeks, phosphorous levels corresponded to 45% orthophosphate (17). Clearly, in treated seafood muscle, the condensed phosphates were unstable over time.

Mechanism of Action

Offer and Trinick (11) determined that pyrophosphate [(10 mM), (from beef myofibrils)] in combination with reduced levels of sodium chloride, extracted the A-band completely beginning at both ends. This effect was confirmed by Voyle et al. (1984) with pork. In the absence of pyrophosphate, however, only the center of the A-band was extracted. Lewis et al. (1986) determined from 5 gm pork, beef, chicken and cod samples that an A/I overlap composed of denatured actomyosin and connectin was formed while unassociated myosin and actin were probably dispersed (sol) through the meat structure in the form of a water-holding gel (post heat treatment).

Trout and Schmidt (18) concluded that at high ionic strengths (>0.25), pyrophosphate affected hydrophobic interactions which stabilize the protein structure, and thus, the thermal stability of the protein. Elevating pH (1M NaOH), in combination with pyrophosphate, increased the temperature (from 70 to 87°C) for, and the extent of, protein aggregation. Yagi et al. (25) confirmed that inorganic polyphosphate offered a high degree of protection (to carp myofibrils) from thermal denaturation.

Water retention is correlated with increased pH and normally associated with the use of alkaline polyphosphates such as sodium tripolyphosphate. Orthophosphates have virtually no effect on water-binding (12). Pyrophosphates are associated with improved protein solubility (myosin) and water binding. Consequently, water binding is dependent upon the type of phosphate used and specific physicochemical reactions may require the use of blends.

Phosphates as Processing Aids

This area will be given only a cursory mention since it is a topic of a later presentation. Crawford (4) was instrumental in developing a protocol for the treatment of Pacific shrimp (Pandulus jordani) to be mechanically cooked and peeled. By the responsible use of phosphates in treating Pacific shrimp to be mechanically cooked and peeled, meat yield increased an average of 12%. There was no significant uptake of moisture, and there was an added ex-plant income (in Oregon alone) of greater than 65 million dollars in the first eight years of use (1).

Preservation of Freshness

A process for using low concentrations (1 to 2%) of sodium tripolyphosphate in either flaked or crushed ice was patented by Stone (14). Use of this ice increased the yield of shrimp and effectively reduced moisture and nutrient loss. Shrimp stored in phosphated ice could be over-exposed to polyphosphates if treated again during further in-plant processing which could cause either off-flavor, >0.5% residual phosphate or both.

Specialty Blends

Among products for extending the shelf-life of fish fillets, Crawford (2, 3) developed a patented blend consisting of sodium tripolyphosphate, sodium hexametaphosphate, citric acid and potassium sorbate (FISH-PLUS™, BK Ladenburg Corporation). Fish fillets were dipped into either distilled water or (ca.) 12% treatment solutions. The shelf-life (aerobic plate count $\leq 1 \times 10^6$ CFU/g) for treated samples was 12.4 days and that of the control (water-dipped) was 6.8 days. Both control and treated fillets increased in weight by 4% after 60 seconds of immersion. Those dipped in the patented blend remained at their stated package weight throughout the 14 days of storage at 5°C, while the controls, dipped in water, dropped below the initial weight within four days of chill storage. Shelf-life extension would most likely be increased due to, first, the antimicrobial activity contributed by the sorbic acid, and second, the sequestration by phosphates of enzyme (metal) co-factors.

Frozen Seafoods

Researchers at Texas A&M University reported that sodium tripolyphosphate dissolved slowly in seawater (6). In addition, fresh, shell-on and peeled shrimp (Gulf of Mexico) became translucent and slippery to the touch after dipping in solutions of phosphate-sea water. This led to subsequent treatments which included five minute dips in water and 2, 4 or 5% condensed phosphates. Using a blend of sodium tripolyphosphate and hexametaphosphate (BRIFISOL™ 512, BK Ladenburg Corporation) resulted in rapid solubilization of the condensed phosphate, and more desirable sensory (touch) properties. The dipped shrimp were frozen and stored at -26°C for two weeks. Upon thawing and cooking (four mins), those shrimp dipped in the 4% blend for five minutes lost 0.8% weight after frozen storage (control, 2.0% loss) and 19.8% after cooking (control, 25.3% loss). It was concluded that addition of these phosphate blends imparted a cryoprotective effect.

Woyewoda and Bligh (24) dipped Atlantic cod fillets into 12% solutions of sodium tripolyphosphate, sodium metaphosphate blends or no solution (FREEZ-GARD‘ FP-19, FP-65 [Rhone-Poulenc] and a control, respectively) for 45 seconds and stored each treatment at either -12°C or -30°C for up to 26 weeks. Phosphate-treated cod showed decreased thaw, and cooked drip loss and resulted in higher moisture content in both raw and cooked product. After 26 weeks (at -30°C), all phosphate treated fillets were judged the most tender and highly acceptable by sensory evaluation. The use of tripolyphosphate significantly reduced expressible water after holding at -30°C up to 26 weeks and up to 24 days at -12°C.

Thermally Processed Seafoods

Struvite, or magnesium ammonium phosphate, may be formed in thermally processed seafoods (e.g., canned tuna and crab). Sodium acid pyrophosphate can be used to sequester magnesium ions and thus, inhibit struvite crystals, which resemble broken glass.

Salmon may develop a surface curd (denatured protein) if either held on ice for a protracted length of time and/or frozen prior to canning. The curd may constitute up to four percent of the pack, by weight, and may be considered questionable by many consumers.

Curd was significantly ($P \leq 0.05$) reduced by dipping sockeye salmon steaks for 2 to 120 seconds in 15 to 20% solutions of condensed phosphate (BRIFISOL™ 512 [sodium tripolyphosphate and sodium hexametaphosphate], BK Ladenburg Corporation) and by dipping for 30 to 120 seconds in 5 to 10% solutions (19). To avoid dipping, Wekell and Teeny (19) verified that there was a 68% reduction in curd formation by dry addition of the phosphate blend prior to sealing the can. Although it was estimated that 1.0% polyphosphate would be needed to completely inhibit curd formation, this would exceed the legal limits for phosphate in canned salmon.

Domestically, phosphate is not uniformly allowed in canned salmon except for a temporary allowance granted to several processors. Its use in canned salmon has, however, been given provisional approval by the Canadian government.

Phosphates provide significant benefit to the seafood industry when there is a large harvest within close proximity, and conversely, there are limited quotas (i.e., freezing fillets to extend wholesale/retail availability). Spawning salmonids may represent one of the most important applications since the muscle has been physico-chemically altered. Such finfish contain reduced levels of myofibrillar proteins which lead to impaired muscle water holding capacity. This is parallel with elevated levels of sarcoplasmic proteins and total moisture, a combination conducive to curd development.

Troubleshooting

Often when phosphates are added in excess, a glassine look develops. This is particularly noticeable on shrimp. There are regulatory constraints to the use of polyphosphates along with organoleptic problems (a soapy taste) if the phosphates are used in excess. The glassine appearance probably occurs more in error than through intentional overuse of phosphates since there are no standard or defined procedures for their application. Most industrial protocols have been developed by trial and error and/or have been based upon far more resilient terrestrial muscle.

Combining sodium tripolyphosphate with sea water will frequently promote the formation of a "floc" on the surface of certain species. Mineral content and pH of the muscle will exacerbate the formation of this crystalline precipitate.

Polyphosphate insolubility is related to water quality and to the individual type of condensed phosphate. Minerals in hard water will compete with some types of polyphosphate for solubility. In addition, not all forms of polyphosphate are readily soluble in water.

Erratic functionality of phosphates also may be caused by either heating phosphates to promote solubility or using old solutions. Many of the polyphosphates are prone to hydrolysis, and the monomeric forms will not perform the same as the polymers.

The maximum permitted legal level in processed meat and poultry is 0.5% by weight of the final product and serves as the current guideline where their use is permitted. Polyphosphates are not allowed in breaded shrimp and in certain other species (5). They are, however, self-limiting. If much more than 0.5% of the high pH phosphates, such as sodium tripolyphosphate, is used, flavor and appearance will be adversely affected.

Summary and Conclusions

Phosphates are valuable to maintenance of the functional properties of seafood myofibrillar proteins which preserve the natural muscle juices. Inhibiting drip loss in the fresh state, while thawing and in cooking is important to prevent economic loss. Phosphates increase the thermal stability of proteins which, in seafoods, are normally lower than that of terrestrial muscles. Improper use of phosphates leads to sensory defects and the potential for charges of economic fraud.

Literature Cited

CRAWFORD, D.L. 1988. Personal Communication.

2. CRAWFORD, D.L. 1985. U.S. Patent 4,517,208.

3 CRAWFORD, D.L. 1984. U.S. Patent 4,431,679.

4. CRAWFORD, D.L. 1980. Meat yield and shell removal functions of shrimp processing. Oregon State University Extension Marine Advisory Program. Special Report 597. 6 p.

5. CODE OF FEDERAL REGULATIONS. 1991. 21 CFR 161.30 to 161.190.

6. DUXBURY, D. 1986. Phosphate blends in shrimp, fish reduce thaw shrink, cook loss. research evaluates cryoprotection. Food Processing. 47:18.

7. DZIEZAK, J.D. 1990. Phosphates improve many foods. Food Technology. 44:79.

8. LAMPILA, L.E. Comparative microstructure of red meat poultry and fish muscle. Journal of Muscle Foods. 1:247.

9. LEWIS, D.F., K.H.M. GROVES and J.H. HOLGATE. 1986. Action of polyphosphates in Meat Products. Food Microstructure. 5:53.

10. LOREAL, H. and ETIENNE, M. 1990. Added water in frozen scallop muscles: French specifications and methodology. 20th WEFTA Meeting. Reykjavik, Iceland.

11. MOREY, K.S., L.D. SATTERLEE and W.D. BROWN. 1982.Protein quality of fish in modified atmospheres as predicted by the C-PER assay. Journal of Food Science. 47:1399.

12. OFFER, G. and TRINICK, J. 1983. A unifying hypothesis for the mechanism of changes in the water-holding capacity of meat. Journal of the Science and Food and Agriculture. 34:1018.

13. REGENSTEIN, J.M. 1984. Protein-Water interactions in muscle foods. Reciprocal Meat Conference Proceedings. 37:44.

14. SIDWELL, V.D. 1981. Chemical and Nutritional Composition of Finfishes, Whales, Crustaceans, Mollusks, and Their Products. NOAA Technical Memorandum NMFS F/SEC-11. U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Marine Fisheries Service.

15. STONE. 1981 U.S. Patent 4,293,578.

16. SUTTON, A.H. 1973. The hydrolysis of sodium triphosphate in cod and beef muscle. J. Food Technology. 8:185.

17. TAYLOR, P. 1990. Personal Communication.

18. TENHET, V., G. FINNE, R. NICKELSON, and D. TOLODAY, 1981. Phosphorous levels in peeled and deveined shrimp treated with sodium tripolyphosphate. Journal of Food Science. 46:350.

19. TROUT, G.R. and SCHMIDT, G.R. 1987. The effect of cooking temperature on the functional properties of beef proteins: The role of ionic strength, pH, and pyrophosphate. Meat Science. 20:129.

20. VOYLE, C.A., P.D. JOLLEY and G.W. OFFER. 1984. The effect of salt and pyrophosphate on the structure of meat. Food Microstructure. 3:113.

21. WEBB, N.B., F.B. THOMAS, F.F. BUSTA and R.J. MONROE.1969. Variations in proximate composition of North Carolina scallop meats. Journal of Food Science. 34:471.

22. WEKELL, J.C. and TEENY, F.M. 1988. Canned salmon curd reduced by use of polyphosphates. J. Food Sci. 53:1009.

WOOD, H.G. and CLARK, J.E. 1988. Biological aspects of inorganic polyphosphates. Ann. Rev. Biochem. 57:235.

WOYEWODA, A.D. and BLIGH, E.G. 1986. Effect of phosphate blends on stability of cod fillets in frozen storage. J. Food Sci. 51:932.

25. YAGI, H., SAKAMOTO, M, WAKAMEDA, A., and ARAI, K.1985. Effect of inorganic polyphosphate on thermal denaturation of carp myofibrillar protein at low ionic strength. Bulletin of the Japanese Society of Scientific Fisheries. 51:667.