

Phosphate Testing for Cooling Waters

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Introduction

Several articles have appeared in *The Analyst*^{1,2} emphasizing the importance of proper testing and describing some special problems in regard to phosphonates. These reports are well worth reading again and can form a good foundation for understanding the following observations.

The recognition of AMP and HEDP phosphonates as highly effective scale control agents was a major advance in water treatment technology. To a great extent, these products have now been replaced or supplemented by PBTC because of its greater stability in the presence of stressed or oxidizing conditions.

Inorganic phosphates have long been used for corrosion control, but the organic phosphorus inhibitor Belcor 575

(HPA) is displacing the inorganic phosphates because of its enhanced ability to resist degradation and precipitation. And finally, to complete the treatment package, a number of new copolymers offer greatly improved dispersion, especially for phosphorus containing complexes. The combined impact of these three contributions has been substantial and the synergisms are widely recognized.

Test procedures for determining phosphonate concentration were designed for AMP and HEDP. It is now necessary to establish and publish conversions more closely related to the lower phosphate content of PBTC, HPA, PCM, MAPA, DTMP/MDTP, and one PCA. POCA and other PCAs have even lower phosphorus

Table 1. Organic Phosphorus Containing Products³

Type (a)	Commercial Product (b)	Mol Wt (c)	"P" Groups (d)	Active Phosphonate (e)	100 % Active		Commercial	
					% PO ₄ (f)	% P (g)	% PO ₄ (h)	% P (i)
AMP	Dequest® 2000	299	3	0.50	95.2	31.2	47.7	15.6
HEDP	Dequest® 2010	206	2	0.60	92.2	30.1	55.3	18.1
PBTC	Bayhibit® AM	270	1	0.50	35.2	11.5	17.5	5.7
HPA	Belcor® 575	156	1	0.50	61.0	19.9	30.5	10.0
PCA-500	Belclene® 500	410	1	0.35	23.1	7.5	11.6	3.8
PCA-161	Belsperse® 161	1820	1	0.48	5.2	1.7	2.5	0.8
PCA-400	Belclene® 400	1530	1	0.50	6.2	2.0	3.1	1.0
PCM	Bricorr® 288	260	1	0.30	36.7	12.0	11.0	3.6
DTMPA/MDTP	BPS® 319	426	4	0.36	89.2	29.1	32.1	10.5
MAPA	Versenex® CSI	475	5	0.42	99.8	32.6	41.9	13.7
POCA	Belclene® 499	2500	1	0.50	3.8	1.2	1.9	0.6

- Calculations are based on the functional activity of the theoretical formulas and/or on values provided by the manufacturer. The vendors have not disclosed some of the specifications; therefore, estimates are subject to revision.
- If the molecular weight (c), number of phosphorus groups (d), and activity (e) of a phosphonate are known, its PO₄ content may be calculated as follows: Belcor 575 = (1)(95)(0.50)/(156) = 30.5.
- $g = (31)(d)(10^2)/(c)$; $i = (g)(e)$; $f = (3.06)(g)$; $h = (3.06)(i)$.
- Orthophosphate ions present in some materials (e.g., 3 % in HPA and 10 % in MAPA) must be considered.
- The commercial products described are registered to Monsanto, Bayer, BioLab, Rhodia, Buckman and Dow (or their successors).

content, in general too low for accurate monitoring at recommended treatment levels. All of these products are described in Table 1.

There are two general approaches to testing for phosphonates. Both methods will be considered in this article, and ideally, they should give the same results. Serious challenges remain in the use of drop tests for combined and low phosphate products, and hopefully more complete guidance will soon be available.

Good results have been obtained in the digestion tests, but limited success with drop tests. Considerable information has been published on this topic, but has not been fully assimilated. Comparisons and adjustments are difficult since some tests report phosphonate concentration as "P" and some as "PO₄". Other variations are misunderstandings about 100 % active materials and the dilute commercial versions. And finally, some readings are designed to be multiplied by a conversion factor and others divided by a conversion factor. All of this indicates the need for carefully recording all pertinent specifications for testing and calculating.

Digestion

The first procedure requires the conversion of phosphonate to the orthophosphate form. This is performed through the addition of persulfate and the use of ultraviolet (UV) radiation followed by reaction with thorium or other agents. The resulting digestion is expressed as orthophosphate content on a properly calibrated colorimeter. These readings are then adjusted with factors supplied with the kit or calculated below.

Because of its relatively high cost, the danger of exposure to UV rays, and the testing time required, the digestion procedure is usually limited to permanent laboratory installations. The results provide the total mg/L of organic PO₄ but do not provide the number of different phosphonates present or their structure.

Reasonably accurate results are obtained if careful attention is given to the instructions provided with the testing equipment. Each sample must be protected from any interference, guarantee the cleanliness of the glassware, provide for the introduction of adequate reactant, and allow a sufficient period of UV radiation.

Though these tests do not lead to the determination of an unknown formula, they can be used to maintain control of a system when the treatment formula is known and the applicable phosphate levels have been calculated.

Field Testing

A second method is the drop test - more portable, easier, faster, less expensive, and hopefully with minimal loss of accuracy. There are many kits available, usually based upon the complexation of organic phosphorus components. They are currently being adjusted to accommodate the growing use of PBTC and HPA. Unfortunately, little success has been found in testing for combinations of two or more organophosphates at the same time.

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Hopefully, in the near future a drop test can be developed to accurately determine the total PO_4 content under these circumstances. If phosphate content is to be a guide to the combined amount of organic phosphorus present, and obviously it should be, it is expected that one drop of the titrant will, at least, indicate more of a low phosphorus material than of a high phosphorus material. Until such time as a field test can more closely meet these expectations, the approach taken may suggest a better estimate than any other.

It may be that multiple tests will also have to be performed to set a standard that assures reliability in the field. Tests should be performed for each formula and the results recorded in tables and graphs. It is entirely possible that all of the phosphorus present will not react to a single test, but that there will be a consistent pattern in the portion that does.

Be aware that there is a higher incidence of significant testing error inherent at low levels of phosphorus (or any other ingredient). To some extent, adjustments may be made through the choice of sample size and attendant multiplier.

Formula Percentages and System Concentrations (% by weight)

To obtain proper control in a system, it is necessary to determine:

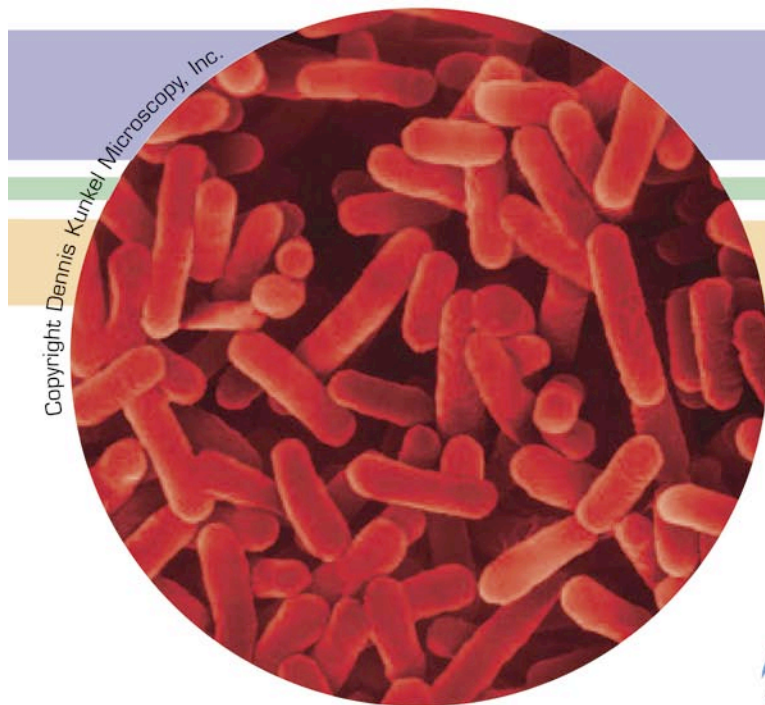
- The number of Cycles of Concentration (B) expected to achieve for Formula (A),
- The level of each (100 % active) additive desired in a system (C) or (F)
- The type and rate of chemical feed chosen:
 - Weight – e.g. 100 milligrams (mg) per liter (L)
 - Volume – e.g. one pint (pt) per 2000 gallons (gal)

The production formula to be utilized for Product 904

Weight – [(E %) or (H %)]

Volume – [(E %)/(U) or (H %)/(U)]
 ("U" is the weight factor to be developed later)

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As a start, specifications are provided for the phosphorus portion of:

A	Formula	904
B	Cycles of Concentration	6
C	100 % PBTC in System	4.2
D	50 % PBTC in System (C/K)	8.4
E	50 % PBTC in Feed (D/B)	1.4
F	100 % HPA in System	8.4
G	Belcor 575 (50 % HPA) in System (F/K)	16.8
H	Belcor 575 in Feed (G/B)	2.8

Only the ingredients in the formula that contribute to phosphonate readings have been shown. Not included are the complex inorganic phosphates that call for reversion by heat/acid. If orthophosphate ions are present, by choice or chance, they will add their PO₄ content to the phosphonate readings and must consequently be subtracted or zeroed out.

The purpose of the “control,” “background” or “blank” determination is to record and eliminate any phosphate introduced by water used in the testing procedure. If the blank is diluted with DI water, no phosphate is added and the process, presumably, contributes to the general balancing.

If this formula is fed at the rate of 100 mg/L and recycled as indicated, the following level will be present in the system:

I	100 % Active Phosphonate (C + F)	12.6
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Color development in these tests should reflect the actual phosphate shown in the following PO₄ conversion values:

J	Phosphonate	HEDP	PBTC	HPA
K	Activity (as a decimal)	0.600	0.500	0.500
L	Com. Prod. (PO ₄)	0.553	0.175	0.305
M	Dry Basis PO ₄ (L/K)	0.922	0.352	0.610
N	Multiplier (1/M)	1.085	2.841	1.639
O	Com. Prod. Multiplier (N/K)	1.808	5.682	3.278

One drop of color indicator signals the equivalent mg/L of 100 % active product present at the levels shown in Row “N”. These results can also be converted to mg/L of commercial product at the rate shown in Row “O”. BioLab’s *Waterfront Bulletin*⁴ “Testing Belcor 575” verifies that HPA multiplier is 1.6 for Belcor 575 as measured by Masters and Palintest test kits.

For present and later consideration are the conversion factors specified by test kit manufacturers. Those for Hach come from UV digestion tests while the others are for field-testing. It appears that the divergence comes from the use of special (undisclosed) reactants. Masters indicates that their factors for each phosphonate can be combined to describe a blend.

	HEDP	PBTC	HPA
N (from above)	1.085	2.841	1.639
N/1.085	1.00	2.62	1.51
Hach	1.08	2.84	1.49
Taylor K-1584	0.80	0.80	0.60
Palintest PK-158	0.92	2.61	1.56
Masters PDQ	1.00	1.40	1.00

Even in the most sophisticated chemical laboratories there are inaccuracies due to systematic errors, which should be control and random errors whose presence must be recognized and quantified. With this in mind, the proposed drop range is shown in row “S”, rather than the questionably precise value shown in row “R”. Mike Scott commented⁵ that a possible error of ±1 in 10 drops was a common range for dropper tips.

P	Drops for PBTC (C/N)	1.48
Q	Drops for HPA (F/N)	5.12
R	Sum of Drops (P + Q)	6.60
S	Expected Range of Drops	5 - 8

If the drop count substantially exceeds these values, dosage and/or cycling should be reduced, and the converse is also true. If conditions will not tolerate the number of cycles specified, this may indicate that the hardness in the recirculating water is higher than anticipated or that there are other limiting factors. This may require increasing dosage or changing to a formula better suited to the water being used. Be warned that in a new system, residuals are slow to develop and must be patiently monitored.

Volumetric Feeding

If this product is to be introduced at one pint per multiple of 1,000 gallons of makeup water, the level of drops should be adjusted to anticipated a specified level of feed:

T	Pounds per Gallon	9.1
U	Weight Factor*	0.68
V	One pint /2000 gal. (RxU)	4.49
W	Range of Drops for V	3 - 6
X	One pint/1000 gal (2xRxU)	8.98
Y	Range of Drops for X	7-10
Zee,	we told you that it would all work out!	O.K.?

* Conversion from 100 mg/L to one pint/2000 gallons
 $= [(9.1)(10^6)]/[(8)(2)(8.3282)(10^3)]$
 $= (9.1)/(10^3)/(133.251)$
 $= 68 \text{ mg/L.}$

The product was originally designed to be fed at 100 mg/L. Feeding volumetrically resulted in a light dosage (68 mg/L) at one pint per 2000 gallons and a heavy dosage (136 mg/L) at one pint per 1000 gallons. Close correspon-

dence to the original (mg/L) guidelines could, in this case, be obtained by feeding one pint for about 1360 gallons. ♦

Robert R. Cavano is president of Scranton Associates, Incorporated. Mr. Cavano has been the recipient of many awards for his contribution to the water treatment industry, and especially his technical contributions to AWT. He can be contacted by phone at [216] 252-2120.

References:

1. M. Scott, "What's in Your Toolbox? Test Methods For Industrial Water Analysis," The Analyst XII, 3 (2005): p 9.
2. G. Garcia, "Phosphonate Testing and Analysis," The Analyst XII, 3 (2005): p 19.
3. Dequest® 2000 and Dequest® 2010 are registered trademarks of Solutia; Bayhibit® AM is a registered trademark of Bayer Corporation; Bricorr® 288 is a registered trademark of Rhodia Corporation; BPS® 319 is a registered trademark of Buckman Laboratories, Inc.; Belclene® 499, Belclene® 500 and Belsperse® 161 are registered trademarks of Great Lakes Chemical Corporation; Versenex® CSI is a registered trademark of Alco Chemical Corporation.
4. Biolab Waterfront Bulletin are not numbered, dated or give any indication when they have been published.
5. Robert R. Cavano, Scranton Associates Inc., correspondence to Michael Scott, Taylor Technologies, Inc., April, 2006.

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