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Phosphorus Measurements in Aqueous Media Using Inorganic Phosphorus Sources as Compared to Organic Sources and Resulting Complications

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Abstract:

The phosphorus moiety that exists in both inorganic and organic molecules has significant importance [1]. Phosphorus serves as nutrient [2], a plant building block, a control agent for pests (both plant and insect) [2], and can be an inadvertent cross contaminant in herbicide production, and is often seen as an environmental pollutant [1]. As a cross contaminant, samples suspected of containing the phosphorus moiety are traced to the source of manufacture. Upon suspicion of the source, serious consequences for the manufacturer can develop including loss of relationships, heavy fines and legal matters. Quantitation of phosphorus is not straightforward. Phosphorus can be present in the environment and in samples in either the organic or inorganic form. Segregation of organic and inorganic phosphorus plays a role in the issues that surround reliable quantitation. Both sources are often times simultaneously quantified as total phosphorous and can lead to exaggerated or erroneous results [3]. It is the purpose of this paper to investigate the challenges that exist in quantifying phosphorus as phosphate moieties, in the range of one to ten μg ml^{-1}, using a Perkin Elmer Optima 8000 inductively coupled plasma using optical emission spectrometer, owned by Nufarm Inc. using an existing methodology while investigating a new strategy for quantitation and addressing some of the challenges found in the current method.

Keywords: glyphosate, inductively coupled plasma, matrix matching

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Contents

Importance of Phosphorus

Phosphorus is the twelfth most abundant element [4] and is a key component of all forms of organisms on the planet [2]. It was discovered from the distillation of urine by Hennig Brandt in 1669 [5]. Brandt heated the mixture until it was red hot and thought he had the key to making gold from other metals, however it did not work [5].

Similar to nitrogen, the availability of phosphorus is also cyclical [5]. Erosion of sedimentary rocks plays an important role in introduction of phosphorus into the environment [6]. Once trace dissolution of rocks like apatite occurs, phosphorus is released into the environment and then is converted to phosphates in water sources [5]. Once in the water it serves as an essential nutrient to phytoplankton that serve as the base of the ocean's food chain [7].

Both in water and on land, phosphorus is an important nutrient for plants and makes up about 0.2% of a dried plants weight [8]. Sugar metabolism, characteristic of plants, would not occur without the presence of phosphorus as a phosphate moiety [9]. Interestingly though an essential nutrient to the growth of the plant, application of phosphate as a fertilizer only 20% is used; the remainder is converted to an unusable form for plants [8]. Phosphorus that is used for fertilizer is in the phosphate form, to be more specific it is often encountered in the poly-phosphoric form [10]. Phosphorus is not only used as a fertilizer, but is also used in the manufacture of matches and anionic surfactants.

Pure phosphorus is manufactured in large quantity in five crystalline forms (white, red, other forms of red, violet, and black) [11]. White phosphorus (P_4) is waxy, toxic, metastable and is the standard to which others are compared [10]. At the turn of the 20^{th} century white phosphorus was used in the manufacture of matches [12]. People working in those factories

developed brain damage and necrosis of the jaw from exposure to vapors of phosphorus; currently red phosphorus (non-toxic form) is used for the manufacture of matches [10].

Soaps and surfactants produced by the use of phosphorus derived phosphoric acid are known as anionic surfactants [13]. Surfactants made with the use of phosphoric acid are more readily available for surface active moieties which increases the number of different aqueous formulations available [14]; however, the over-use of anionic surfactants can have environmental impacts.

In the late 1960's algae blooms and poor water quality were the direct result of the use of phosphorus due to human activity [15]. The increased amount of phosphorus, in the form of phosphates, increased the amount of nutrients in the water which lead to a foaming issue. The foaming of several rivers across the United States was linked to the use of phosphate manufactured detergents [16]. Despite the calamities that can take place due to the misuse of phosphorus derived compounds, their usefulness in other structures cannot be ignored [17] [18].

The molecules of interest to this study are relatively small molecules of very high polarity, due to the presence of phosphoric acid moieties (refer to table 1).

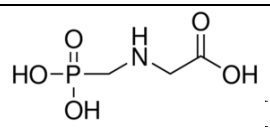
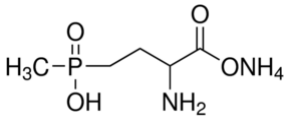
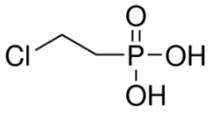
Glyphosate	 [19]
Glufosinate	 [20]
Ethephon	 [21]

Table 1.

Glyphosate is formulated in both forms the mono-isopropyl amine (MIPA) and the potassium salt (K+). Regardless the form, glyphosate is a non-specific herbicide. Nonspecific in the notion that any plant that has glyphosate on the foliar region will uptake glyphosate through its plasma membrane [22] and eventually die. Entry of either compound of interest is not a simple matter. Commonly plants have a waxy exterior [23] that must be considered before the molecule can perform its intended action. It is the organic phosphorus moiety that impairs the ability of glyphosate to be active within the target plant species unless the appropriate surfactant and or wetting agent is used [22]. It is the addition of surfactant in intended formulation that increases the solubility of glyphosate and glufosinate, but at the same time complicates the analysis for total phosphorus content [24].

Restorative experiments performed by Cornish et. al focused on the effects of transplanting four types of Australian native restorative perennials into soils that were treated with increasing amounts of glyphosate [25]. Empirical observation and statistical analysis done by Cornish et. al demonstrated that sensitivity to glyphosate was not universal. Species dependent sensitivity started with as low as a concentration of 18 mgL-1 up to 360 mg/L-1 and regardless of species anything above 360 g/L^{-1} died.

Quantitative experiments using a combination of anion exchange chromatography with post eluent colorimetric modification done by Coutinho C.F et. al, reported a limit of detection for glyphosate at a concentration of 0.38 μgml^{-1} [26] in water. Similar the US-EPA outlines ion chromatography method 300.1 to quantitate the phosphate ion but only for Ortho Phosphate and likewise in water [27]. Sancho et al performed experiments using precolumn fluorogenic labeling and coupled-column liquid chromatograph, reporting sub μgml^{-1} levels and again the matrix was water (to complicate the preparation was a derivatization technique) [28]. Zhong et. al also confirmed the sub μgml^{-1} levels (0.7 μgml^{-1}), also in water, using ion chromatography inductively coupled plasma and mass spectrometry without any derivatization agents[29].

The obvious strengths of these methods is their respective selectivity to the phosphate ion using an ion exchange methodology in an aqueous media. The weakness of each of the methods becomes evident when the simplest matrix to be considered by this work will be a mixture of Chicago Heights municipal water approximately 46.8% , approximately 39.8 % 2,4-dichlorophenoxyacetic acid, 12.9 % dimethylamine, 0.5 % of a proprietary surfactant, prior to the addition of a separate glyphosate or glufosinate formulation.

Glufosinate comes in the ammonium salt form and is blended with various surfactants. Much like glyphosate, glufosinate is also a non-specific herbicide, its mode of action is also foliar contact equated to plant death [30].

Ethephon is quite different than either glyphosate or glufosinate; it is a plant growth regulator [31]. Ethephon's mode of action is to penetrate the surface of the plant, decompose to ethylene and begin the ripening of fruit [32], [33], [34], [35].

Overview of Method Validation

In order to determine if a method is valid there are preemptive requirements that are set before any work is done to ensure that the method is fit for its intended purpose [37]. Examples would be what is the working range, and what level of precision is required? These are only two particular questions surrounding the validation of a method and it is only compounded if there is need to submit the method to exterior regulatory agencies. An overall review of studies on specificity, linearity, accuracy, range, precision and robustness need to studied prior to being reported [37], [38],[39].

Method Comparison Schema

Prepare the calibration curve and recovery samples as outlined by method 720 as provided by Nufarm (an internal standard method) and compare those results against an intentional product dilution (IPD) of a spiked sample. The outline that will be used is to perform the internal standard as prescribed, determine the limit of detection (LOD), LOQ and perform recovery observations. Next will be to perform the calibration by using IPD methodology. Then prepare recovery samples using the IPD approach. Then compare the results of each technique and then observe sample stability as a function of time for the internal standard methodology.

An intentional production dilution (IPD) is the intentional use of a formulated product as a spike to another herbicide product that should not have any residue of the target analyte. In this work,, 18% Grass Weed Vegetation Herbicide (GWVH) which is a 18.76% active ingredient monoisopropyl amine salt of glyphosate which typically contains 4.4 percent by weight ethoxylated tallow amine surfactant will be introduced, as a spike, by weight into a triple active phenoxy based formulation (Lazer MC) that does not contain glyphosate.

IPD Sample Preparation and Calibration

First, 2.1543g of the 18% GWVH was weighed into an 11 dram sample vial and without tarring the scale added to the same vial sufficient Lazer MC until a total weight of 26.550 was achieved. This resulted in a Lazer MC sample containing 16,448.6 mgL^{-1} by weight active glyphosate content (Stock Spike Sample – R_1). Then weigh out 2.5324g of R_1 and dilute with additional Lazer MC to a total weight of 50.0184g resulting in a concentration of 773.6 mgL^{-1} glyphosate (this solution was R_1W). Again using R1 2.0342g into a total weight of 24.4212 g of Lazer MC resulted in a concentration of 1370.1684 mgL^{-1} (this solution was R_2). From R2, 1.4628g was weight in to an 11 dram sample vial and the total weight was brought up to 20.0146g resulting in a concentration of 100.2 mgL-1 glyphosate (R_3). Next 2.0042g of R_3 was added to a fresh 11 dram sample vial and the final concentration was brought up to 19.9989 g of Lazer MC resulting in a concentration of 10.0 mgL^{-1} (R_4). For the remaining concentrations for the IPD method please refer to table 2.

Sample	Initial wt. ,g	Origin	Final wt. ,g	Glyphosate , mgL^{-1}
R_1	2.1543	18% LWVH	26.5220	16,448.6
R_1W	2.5324	R_1	50.0184	773.6
R_2	2.0324	R_1	24.4212	1370.1684
R_3	1.4638	R_2	20.1046	100.2
R_4	2.0042	R_3	19.9989	10.0
R_5	2.0034	R_4	20.0671	1.0019
R_6	2.0278	R_5	20.2213	0.1005

Table 2

Method 720

Preparation of 100 mgL^{-1} yttrium standard

Pipette 10.0 ml of 1000 mgL-1 yttrium solution into a 100 volumetric flask, fill to the mark and mix thoroughly.

Calibration Blank

Pipette 500 µL of 100 mgL-1 yttrium internal standard into a suitable flask or bottle and bring up to a total volume of 50 ml, mix thoroughly.

Phosphorus Standard 1

Pipette 0.4 mL of purchase Perkin Elmer phosphorus 1000 mgL-1 standard into a 100 mL volumetric flask. Dilute to the mark and mix. This is the 4 mg/L phosphorus standard. Convert to equivalent glyphosate content using the following example: 4 (169/31) = 21.8 mgL-1 as glyphosate.

Phosphorus Standard 2

Pipette 2.0 mL of 1000mgL standard solution into a 100 mL volumetric flask and dilute to the mark and mix. This is the 20 mgL-1 phosphorus standard. Convert to equivalent glyphosate content using the following example 20 (169/31) = 109 mgL-1 as glyphosate.

Method 720 - Samples and Standards Preparation

Both samples and standards are diluted as described below prior to introduction into the ICP. Pipette 2.5 mL of sample (or standards) into a suitable flask, pipette 500 µl of yttrium internal standard, bring the final volume up to 50 ml.

Instrument Specifics, Settings and Warm up Procedure -IPD

The instrument used in this experiment was a Perkin Elmer Optima 8000 dual view inductively coupled plasma with an S10 auto sampler. It is also important to note that this instrument is a sequential analyzer not continuous. (Sequential ICP instruments go to the first wavelength make consecutive measurements and then the prism is moved to the next wavelength where consecutive measurements are taken and so on and so forth. A continuous ICP in essence takes a snap shot of all available wavelengths at the same time.) After the instrument has been turned on and the torch has successfully generated a plasma allow to sit idle for one hour. After one hour, apply the following settings: argon flow rate of 10 L min^{-1}, nebulizer flow rate of 1.0 L min^{-1}, auxiliary flow 0.4 Lmin^{-1}, sample flow of 1.0 ml min^{-1}, a z position of +0.5 mm, with a

RF power of 1500 Watt, set the view to axial and the purge to high. Next, using a 1:10 dilution of a multi-element standard, must contain Mn, in a 2% nitric solution perform an alignment view and allow to run to completion. Based on the instrument response adjustment in the z direction of the torch may be necessary.

Instrument Specifics, Settings and Warm up Procedure – Method 720

After the instrument has been turned on and the torch has successfully generated a plasma allow to sit idle for one hour. After the hour apply the following settings: argon flow rate of 18 L min^{-1}, nebulizer flow rate of 0.4 L min^{-1}, auxiliary flow 0.2 L min^{-1}, sample flow of 1.0 ml min^{-1}, a z position of +0.5 mm, with a RF power of 1350 Watt, set the view to radial and the purge to high. Next, using a 1:10 dilution of a multi-element standard, must contain Mn, in a 2% nitric solution perform an alignment view and allow to run to completion. Based on the instrument response adjustment in the z direction of the torch may be necessary.

Results – Method 720 performed on 11/28/2014

Calibration Blank details

Sample	Replicate #	Analyte	Net Intensity	Corrected Intensity	Concentration mg L^{-1}
Calib. Blank 1	1	Y 371.029	32916.6	32916.6	
Calib. Blank 1	1	P 213.617+	23.8	25.7	0.00
Calib. Blank 1	2	Y 371.029	34901.6	34901.6	
Calib. Blank 1	2	P 213.617+	28.7	29.2	0.00
Calib. Blank 1	3	Y 371.029	36130.4	36130.4	
Calib. Blank 1	3	P 213.617+	19.3	19.0	0.00
Calib. Blank 1	4	Y 371.029	36699.8	36699.8	
Calib. Blank 1	4	P 213.617+	29.8	28.9	0.00
Calib. Blank 1	5	Y 371.029	37058.7	37058.7	
Calib. Blank 1	5	P 213.617+	23.5	22.6	0.00
					Standard Dev.
Average		Y 371.029		35541.4	1682.01
		P 213.617+		25.1	4.32
RSD		Y 371.029	4.74%		
		P 213.617+	17.25%		
LOD		P 213.617+	7.57		
LOQ		P 213.617+	23.1		

Table 3

Phosphorus Standard 1 details

Sample	Replicate #	Analyte	Net Intensity	Corrected Intensity	Concentration mg L^{-1}
Phos Std 1	1	Y 371.029	71671.5		
Phos Std 1	1	P 213.617+	208	78.1	0.00
Phos Std 1	2	Y 371.029	73741		
Phos Std 1	2	P 213.617+	208.9	75.6	0.00
Phos Std 1	3	Y 371.029	73332.0		
Phos Std 1	3	P 213.617+	205.6	74.6	0.00
Phos Std 1	4	Y 371.029	73054.1		
Phos Std 1	4	P 213.617+	199.7	72.1	0.00
Phos Std 1	5	Y 371.029	72758.0		
Phos Std 1	5	P 213.617+	207.8	76.5	0.00
					Standard Dev.
Average		Y 371.029		72911.3	782.05
		P 213.617+		75.4	2.24
RSD		Y 371.029	1.07%		
		P 213.617+	2.97%		

Table 4

Phosphorus Standard 2 details

Sample	Replicate #	Analyte	Net Intensity	Corrected Intensity	Concentration mg L^{-1}
Phos std 2	1	Y 371.029	74782.4		
Phos std 2	1	P 213.617+	905.9	405.5	110.179
Phos std 2	2	Y 371.029	75912.2		
Phos std 2	2	P 213.617+	925.0	408.0	110.179
Phos std 2	3	Y 371.029	75860.0		
Phos std 2	3	P 213.617+	925.9	408.7	110.179
Phos std 2	4	Y 371.029	76201.7		
Phos std 2	4	P 213.617+	921.3	404.6	110.179
Phos std 2	5	Y 371.029	76659.7		
Phos std 2	5	P 213.617+	919.2	401.1	110.179
					Standard Dev.
Average		Y 371.029		75883.2	692.38
		P 213.617+		405.6	3.04
% RSD		Y 371.029		0.91	
		P 213.617+		0.75	

Table 5

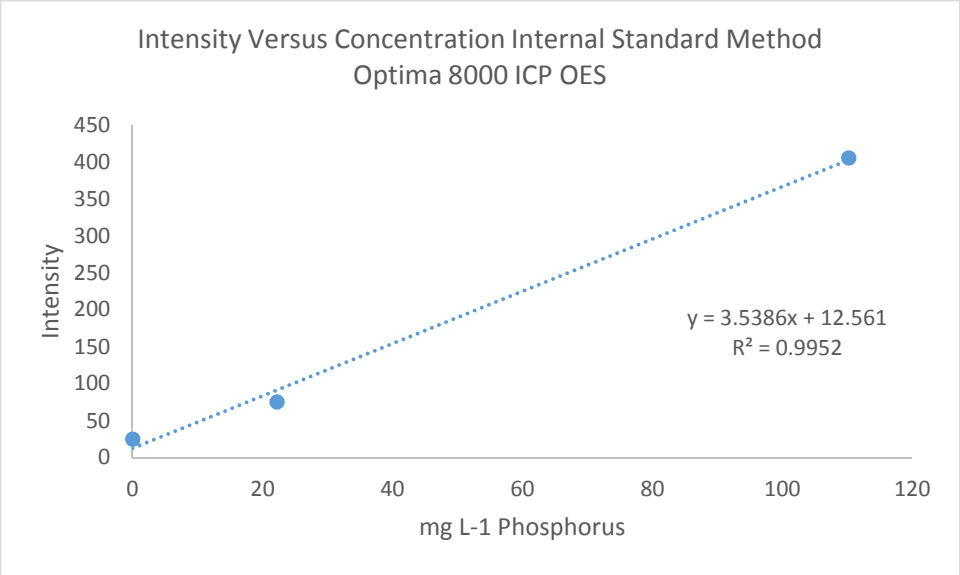


Figure 1: Calibration Curve Int. Std. 1

Summarized Recoveries – Method 720

Recovery samples were prepared in accordance to the internal standard methodology and analyzed on the Optima 8000 ICP-OES.

Sample	Prepared concentration, mg/L	Measured concentration mg/L	% Recovery
Calibration blank	0.00	0.00	N/A
R1	16564.95	Not analyzed	N/A
R2	1390.05	1128	81.2
R3	101.59	104.1	99.5
R4	10.18	9.694	95.3
R5	1.02	2.363	31.7
R6	0.11	Not analyzed	N/A
RoW	0.00	-0.694	N/A

Table 6: Method 720 Recoveries

Results – IPD Method

Blank

Sample	Repl#	Analyte	Net Intensity	Corrected Intensity	Concentration mg L^{-1}
DI water	1	P 213.617	16.3	16.3	0.00
DI water	2	P 213.617	47.5	47.5	0.00
DI water	3	P 213.617	49.6	49.6	0.00
DI water	4	P 213.617	23.8	23.8	0.00
DI water	5	P 213.617	78.4	78.4	0.00
					Standard Dev.
Average		P 213.617		43.1	24.5
RSD		P 213.617	56.81%		
LOD		P 213.617	11.8		
LOQ		P 213.617	31.1		

Table 7

Calibration Curve – IPD Method table 8

Sample	Repl#	Analyte	Net Intensity	Corrected Intensity	Concentration mg L^{-1}
CH1W1	1	P 213.617	63619.8	63576.7	16448.6
CH1W1	2	P 213.617	63494.3	63451.2	16448.6
CH1W1	3	P 213.617	63838.1	63795.0	16448.6
CH1W1	4	P 213.617	63990.5	63947.3	16448.6
CH1W1	5	P 213.617	63856.0	63812.9	16448.6
					Standard Dev.
Average		P 213.617		63716.6	199.18
RSD		P 213.617	0.31%		

Table 8

Sample	Repl#	Analyte	Net Intensity	Corrected Intensity	Concentration mg L^{-1}
CH2W1	1	P 213.617	4853.8	4810.6	1370.168
CH2W1	2	P 213.617	4820.0	4776.9	1370.168
CH2W1	3	P 213.617	4916.2	4873.0	1370.168
CH2W1	4	P 213.617	4865.9	4822.8	1370.168
CH2W1	5	P 213.617	4937.3	4894.2	1370.168
					Standard Dev.
Average		P 213.617		4835.5	47.63
RSD		P 213.617	0.99%		

Table 8

Sample	Repl#	Analyte	Net Intensity	Corrected Intensity	Concentration mg L^{-1}
CH3W1	1	P 213.617	468.0	424.9	100.1598
CH3W1	2	P 213.617	485.0	441.8	100.1598
CH3W1	3	P 213.617	461.4	418.2	100.1598
CH3W1	4	P 213.617	437.4	394.3	100.1598
CH3W1	5	P 213.617	479.5	436.4	100.1598
					Standard Dev.
Average		P 213.617		423.1	18.61
RSD		P 213.617	4.40%		

Table 9

Sample	Repl#	Analyte	Net Intensity	Corrected Intensity	Concentration mg L^{-1}
CH4W1	1	P 213.617	132.2	89.1	10.0360
CH4W1	2	P 213.617	142.0	98.9	10.0360
CH4W1	3	P 213.617	142.3	99.2	10.0360
CH4W1	4	P 213.617	146.4	103.2	10.0360
CH4W1	5	P 213.617	123.8	80.7	10.0360
					Standard Dev.
Average		P 213.617		94.2	9.18
RSD		P 213.617	9.75%		

Table 10

Sample	Repl#	Analyte	Net Intensity	Corrected Intensity	Concentration mg L^{-1}
CH5W1	1	P 213.617	64.2	21.1	1.0019
CH5W1	2	P 213.617	107.1	64.0	1.0019
CH5W1	3	P 213.617	60.9	17.8	1.0019
CH5W1	4	P 213.617	121.8	78.6	1.0019
CH5W1	5	P 213.617	104.5	61.3	1.0019
					Standard Dev.
Average		P 213.617		48.6	27.42
RSD		P 213.617	56.47%		

Table 11

Sample	Repl#	Analyte	Net Intensity	Corrected Intensity	Concentration mg L^{-1}
CH6W1	1	P 213.617	92.0	48.9	0.1005
CH6W1	2	P 213.617	129.4	86.3	0.1005
CH6W1	3	P 213.617	69.0	25.8	0.1005
CH6W1	4	P 213.617	48.2	5.0	0.1005
CH6W1	5	P 213.617	90.8	47.6	0.1005
					Standard Dev.
Average		P 213.617		42.7	30.28
RSD		P 213.617	70.85%		

Table 12

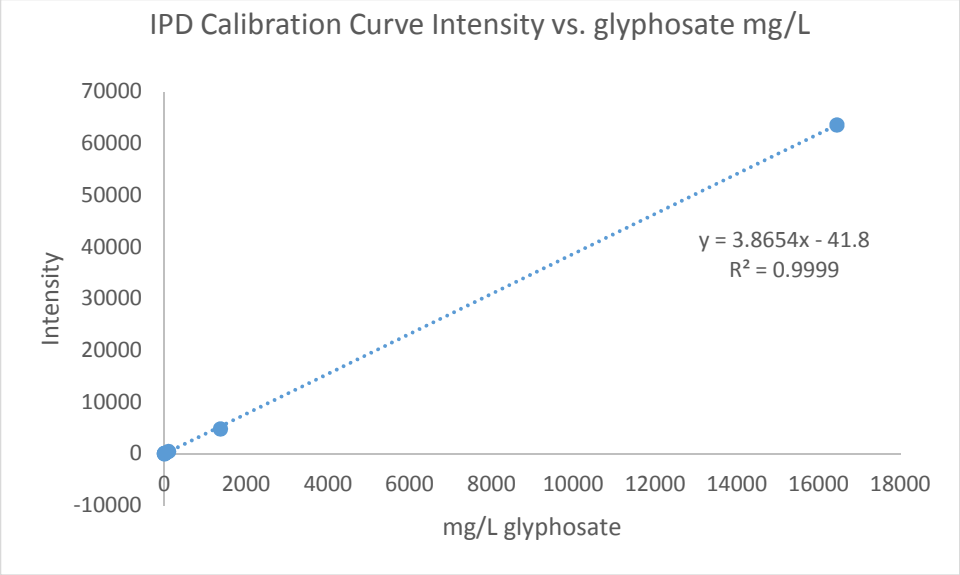


Figure 2: IPD Calibration Curve

Recoveries – IPD Method

Recovery for the external method was done by preparing a calibration curve by means of standard addition (product serial dilution) and determining a calibration curve. The data points for the standard addition are listed below. Afterwards each standard was subjected to one to ten dilution and analyzed on the Optima 8000 ICP-OES.

Sample	Prepared concentration, mg/L
CH1W1	16448.6
CH2W1	1390.05
CH3W1	101.59
CH4W1	10.18
CH5W1	1.02
CH6W1	0.11

Table 13

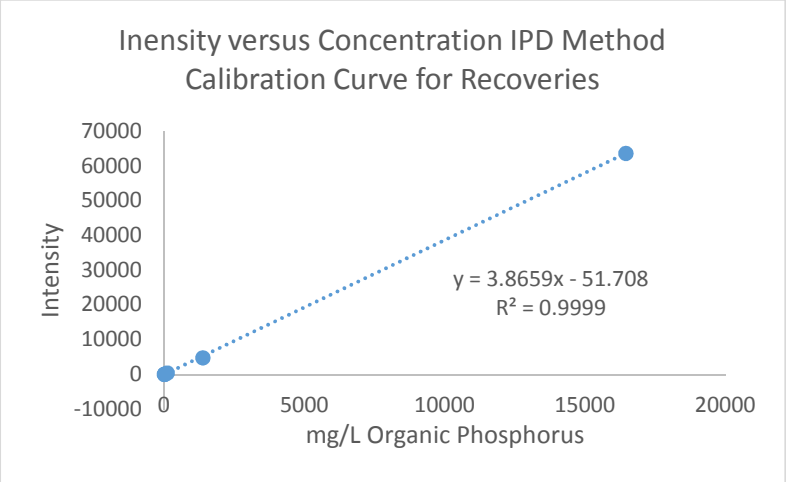


Figure 3

Sample	Prepared concentration, mg/L	Avg.Measured concentration, mg/L	% Recovery
RCV	61.0	55.04	90.22
RCV 2	1.162	2.879	147.8
RCV 3	3.0365	2.9748	98.0
0.131g 18.76%	2284	2320	98.4

Table 14

Results Stability Monitoring – Method 720

A sample was prepared according to method 720 and made up to a volume of 200 mL for the purpose of monitoring intensity over a given time frame. The large volume sample was prepared in a 200 mL volumetric flask by scaling up the required amounts of ingredients to have

the same net concentration as the samples at 50 mL. The required amount of sample was 10.0 mL, 2.0 g of internal standard and diluting to the mark with deionized water. Below is the monitoring of the same sample post internal standard calibration.

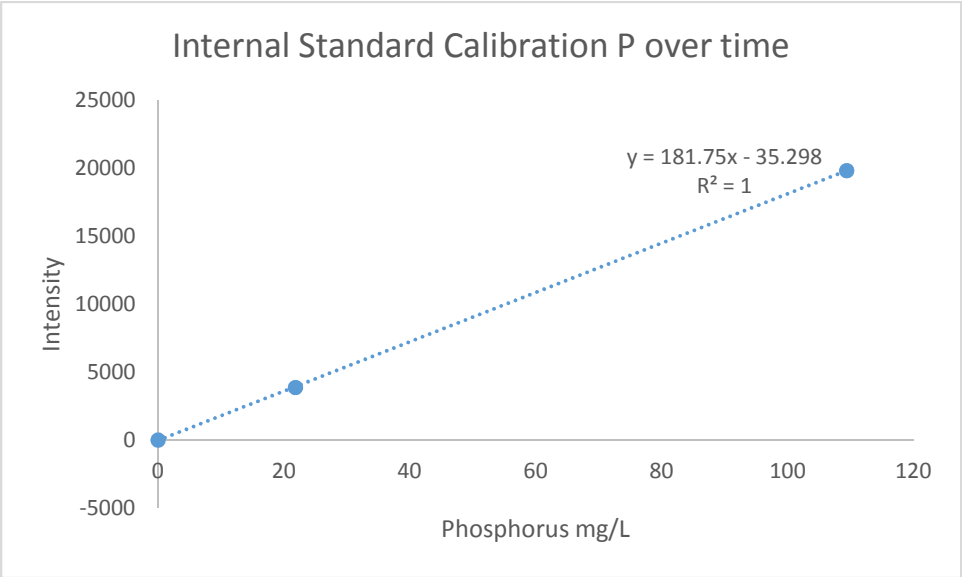


Figure 4 Calibration curve Phosphorus sensitivity over time

F(P) time	Intensity
0	2067.9
30	1953.9
60	2118.2
90	2082.8
120	323.6
150	298.0

Table 15

Conclusion

It is the purpose of this work to investigate the challenges that exist in quantifying phosphorus as phosphate moieties, in the range of one to ten µg ml^{-1}, using a Perkin Elmer Optima 8000 inductively coupled plasma using optical emission spectrometer, owned by Nufarm Inc. using an existing methodology while looking to a new strategy and addressing some of the issues that have surfaced. Both methods that were observed IPD and Method 720 were evaluated using the guidelines outlined by the overview of method validation discussion aforementioned.

The correlation values (demonstration of linearity) for each of the calibration curves were examined. At first assessment, the internal standard calibration curve appears more accurate for the internal standard however, when graphed on the same scale the overall picture is quite different.

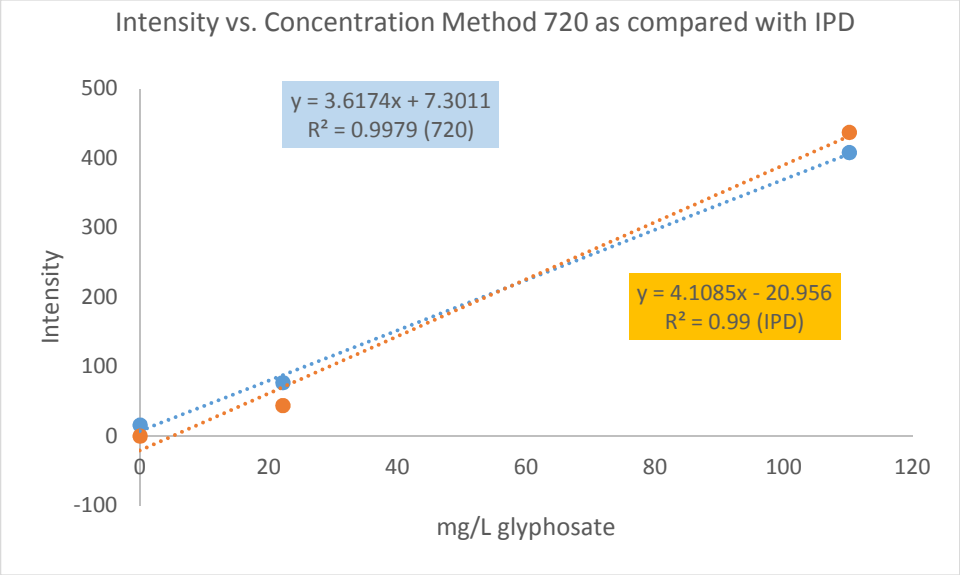


Figure 5, Working range linearity comparison

From figure 5 above it is reasonable to assume that the linearity of the IPD method in the concentration region of interest is equally linear.

Then the sensitivity of each method was considered. The recovery values for internal standard methodology did drop off as predicted by the determination of LOD and LOQ being 7.57 and 23.1 mg/L, respectively. The recovery values for the IPD methodology yielded an LOD and LOQ; 11.8 and 31.1 mg/L, respectively.

Author	Technique used	Reported LOD	Reported LOQ
Coutinho C.F. et al	Post eluent modification	0.38 μg ml^{-1}	Not reported
Sancho et. al	Fluorogenic labeling	0.7 μg ml^{-1}	Not reported
Zhong et al	ICP/MS	0.7 μg ml^{-1}	Not reported
Akudi – method 720	ICP AES	7.6 μg ml^{-1}	23.1 μg ml^{-1}
IPD method	ICP AES	11.8 μg ml^{-1}	31.1 μg ml^{-1}

Table 16 LOD and LOQ comparison

In table 16 a direct comparison of the overall sensitivity of each method can be easily done. In terms of method validation is the fit for use notion [36] that drives the need for comparison of the LOD and LOQ's of the reported methods. As was previously mentioned was that the range was from 1 to 10 μg ml^{-1} at this point in time both methods (720 and IPD) are at least 10 fold less sensitive than what was required.

A study of the robustness of the sample was observed for the internal standard methodology to verify an observation that one of the samples that was prepared with the internal standard technique (the IPD methods were found to be stable for several days of observation). From the data in figure 4, it can be observed that the sample has a lifetime of about 120 minutes

which strongly suggests that the preparation technique is not very robust, this can be observed in figure 4 below.

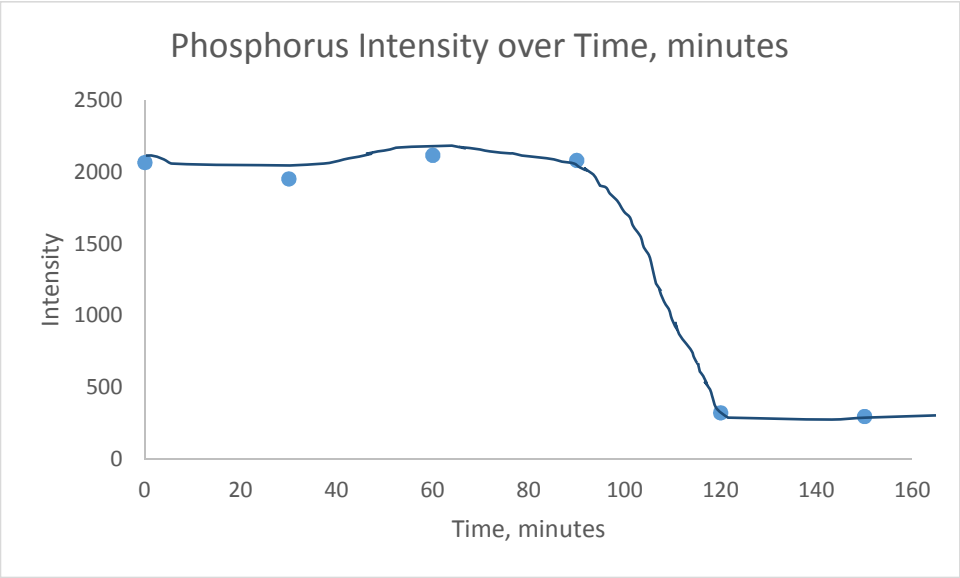


Figure 4 Method 720 Intensity Change over Time

It was believed at first that the IPD would afford greater sensitivity through matrix matching [40]. The matrix of a sample can be considered everything else, but the analyte/s [40]. As the name implies the calibration matrix should be as close to a match as your sample as possible [40]. However matrix matching assumes that the user has experience in determining if spectral interferences have occurred and to take corrective action [41], [42]. The corrective action for this work was to use matrix matching in such that the analyte, formulated glyphosate, was intentionally added to Lazer MC. This effort would closely resemble the manufacturing conditions in which the sample would have been subjected to.

By adding the glyphosate formulation of interest into a matrix sample both of significant pH difference, glyphosate formulations have an inherent pH of 4.5 to 5.2 where the product matrix has a pH of 9.0 it was demonstrated that the internal standard method would yield more

reliable results, but only for a short amount of time. Thus verifying results would rely solely on the sample preparation.

It was also learned that through Perkin Elmer that the purchased standard is made with Ammonium Dihydrogen Phosphate and diluted with Type 1 water at 18 Ω and was doubly deionized. It is not clear if this plays a role at lower concentration levels. Perhaps additional study into the limit of detection of external standard techniques using the same water source may be beneficial in reducing the overall background.

I had the privilege to have contact with I.B.Brenner whom during the talk he gave at PittConn in February 2014, suggested that matrix effects would be lower if axial viewing is used [43]. What was found was that when the Perkin Elmer Phosphorus standard was measured axially and directly the result was an error message that read code 5. Code 5 means that the sample emission is saturating the detector. What has yet to be determined is that if the purchased standard is serially diluted would it match the reported detection limit of 6.4 μgL^{-1} [43]. Other suggestions brought forth by Brenner's talk was that perhaps evaluating the type of nebulizer and nebulizing chamber may be in order. An overall 20% increase in nebulization efficiency can be observed by switching from a standard nebulizer to an ultrasonic nebulizer [43] and may be a point of future work.

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