

The background is a light blue gradient with several realistic water droplets of various sizes scattered across the surface. The droplets have highlights and shadows, giving them a three-dimensional appearance.

Phosphorus by Microwave Digestion and Analysis by ICP or ICP-MS

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Phosphorus Digestion

TKN (EPA 351.2) & TOTAL-P (EPA365.4)

- 1) 25ml Sample + 5ml Digestion Reagent
- 2) Step 1- heat to 160C and hold for 90 minutes
- 3) Step 2 – heat to 380C and hold (120 minutes total)
- 4) Total Digestion about 3 hours 45 minutes
- 5) Cooling Time 1.5 – 2 hours
- 6) 40 Sample positions max
- 7) 25ml Final volume

MICROWAVE

- 1) 25ml Sample + 1.50ml HNO₃ & 1.00ml HCl
- 2) Step 1- heat to 160C for 10 minutes
- 3) Step 2 – heat to 170C for 10 minutes
- 4) Total Digestion 20 minutes
- 5) Cooling Time 30 minutes
- 6) 14 – 40 Sample positions max (Mars 5 or Mars 6)
- 7) 30 -50ml Final volume (closed vessel)



EPA 3015A Doesn't specifically list Phosphorus

But, in Section 1.1-

“OTHER ELEMENTS AND MATRICES MAY BE ANALYZED BY THIS METHOD IF PERFORMANCE IS DEMONSTRATED FOR THE ANALYTE OF INTEREST, IN THE MATRICES OF INTEREST, AT THE CONCENTRATION LEVELS OF INTEREST (SEE SEC. 9.0).”

EPA 200.7 Metals by ICP

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is used to determine metals and some nonmetals in solution.

This method is a consolidation of existing methods for water, wastewater, and solid wastes.1-4

(For analysis of petroleum products see References 5 and 6, Section 16.0)

This method is applicable to the following analytes:

Analyses	Chemical Abstract Services Registry Number (CASRN)
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Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Boron (B)	7440-42-8
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Cerium (Ce)	7440-45-1
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4

Analyses	Chemical Abstract Services Registry Number (CASRN)
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Manganese (Mn)	7439-96-5
Mercury (Hg)	7439-97-6
Molybdenum (Mo)	7439-98-7
Nickel (Ni)	7440-02-0
Phosphorus (P)	7723-14-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silica (SiO ₂)	7631-86-9
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Strontium (Sr)	7440-24-6
Thallium (Tl)	7440-28-0
Tin (Sn)	7440-31-5
Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

Phosphorus Analysis

Flow/segment analyzer

Wave length 880nm

MRL is 30ppb

Curve: 30ppb – 500ppb

Rinse out: Good

Sample Load: 14-18 per hour

Reagents needed: a lot

ICP

Wave length 214.9 or 213.6

MRL is 10 – 20ppb

Curve: 20ppb – 10,000ppb

Rinse out: Great

Sample Load: 14-18 per hour

Reagents needed: Acid rinse

ICP-MS

Mass 31

MRL is 5ppb

Curve: 5ppb – 10,000ppb

Rinse out: Great

Sample Load: 18-22 per hour

Reagents needed: Acid rinse

Stream Line Work Flow

- 85% of samples needing Total-P also needed Hardness (Ca & Mg by ICP). Hence, the Microwave Digestion was already done on the sample. Just needed to turn on Phosphorus lines.
- Only 15% of samples needing Total-P needed TKN as well. Hence, 85% of the Total-P Kjeldahl digestions could be eliminated.
- Microwave Digestion done in about 1 hour whereas the Total-P Digestion takes about 5.5-6 hours.
- Clean-up of Microwave Teflon vessels very fast. Total-P glassware needs special acid soaking.

	Nutrients TOT-P		ICP TOT-P (200.7)	ICP-MS TOT-P (200.8)	ICP-MS TOT-P (200.8)
	EPA 365.4		Acid= 1.50ml HNO3	Acid= 1.50ml HNO3	Acid= 0.500ml HNO3
	STD MTHD 4500-P (E)(F)		1.00ml HCl	1.00ml HCl	0.250ml HCl
	MRL = 0.030ppm		MRL= 0.020ppm	MRL= 0.0050ppm	MRL= 0.0050ppm
Matrix	Curve= 0.030 - 0.600ppm		Curve= 0.020 - 10.0ppm	Curve= 0.0050 - 2.0ppm	Curve= 0.0050 - 2.0ppm
	PPM (mg/L)		PPM (mg/L)	PPM (mg/L)	PPM (mg/L)
Wilamette	0.056		0.057	0.0617	0.0649
River			0.061	0.0615	0.0657
"	0.055		0.051	0.0567	0.0608
Columbia	0.021		0.022	0.0213	0.0219
River	0.027		0.020	0.0205	0.0220
"	0.025		0.017	0.0242	0.0214
"	0.024		0.018	0.0184	0.0194
"	0.026		0.017	0.0182	0.0196
La Grande	4.32		4.41	4.59	
CL2 EFF			4.35	4.62	

	EPA 365.4	Acid= 1.50ml HNO3	Acid= 1.50ml HNO3	Acid= 0.500ml HNO3
	STD MTHD 4500-P (E)(F)	1.00ml HCl	1.00ml HCl	0.250ml HCl
	MRL = 0.030ppm	MRL= 0.020ppm	MRL= 0.0050ppm	MRL= 0.0050ppm
Matrix	Curve= 0.030 - 0.600ppm	Curve= 0.020 - 10.0ppm	Curve= 0.0050 - 2.0ppm	Curve= 0.0050 - 2.0ppm
	PPM (mg/L)	PPM (mg/L)	PPM (mg/L)	PPM (mg/L)
TC CL2 EFF	1.46	1.36	1.42	1.40
1 EFF	7.52	7.50	7.80	7.84
COL CL2 EFF	1.22	1.25	1.27	1.22
1 EFF	7.94	8.19	8.25	8.57
1 EFF	5.07	5.25		4.81
FANNO Creek	0.100		0.0832	
FANNO Creek	0.120		0.0997	
FANNO Creek	0.130		0.112	
Surf. Water COG	0.081	0.076		
Surf. Water COG	0.104	0.096		

INSTRUMENT:		P.E. 5300 ICP
Sample ID	Dil	P 213.617
CAL BLK	1	0.0000
Calib Std 1 (0.020)	1	0.020094
Calib Std 2 (0.100)	1	0.097441
Calib Std 3 (0.400)	1	0.40192
Calib Std 4 (2.00)	1	2.03214
0.250ppm P ICV	1	0.2411
CCB 1	1	-0.001327
0.020ppm P CCV 1	1	0.020435
0.100ppm P CCV 1	1	0.099006
0.400ppm P CCV 1	1	0.39704
CCB 2	1	-0.001411
0.020ppm P CCV 2	1	0.019927
0.100ppm P CCV 2	1	0.099878
0.400ppm P CCV 2	1	0.40152
CCB 3	1	-0.002584
0.020ppm P CCV 3	1	0.019074
0.100ppm P CCV 3	1	0.10191
0.400ppm P CCV 3	1	0.40345

Instrument: ICAP-Q								
		6Li	31P	45Sc	71Ga	115In	195Pt	209Bi
Sample List		KED	KED	KED	KED	KED	KED	KED
Label	DIL	%	ppb	%	%	%	%	%
Cal BLK	1	100	-0.248	100	100	100	100	100
5.00 ppb STD	1	102.3	4.997	104.4	104.2	103.3	99.8	100.5
20.0 ppb STD	1	102.9	20.42	104.2	104.4	103.4	100.0	101.2
100 ppb STD	1	102.7	104.9	103.8	103.6	103.0	99.3	102.2
400 ppb STD	1	103.0	405.4	104.9	104.2	104.5	101.0	103.6
2000 ppb STD	1	102.0	1983	103.4	104.2	104.3	100.7	104.8
10,000 ppb STD	1	98.1	9792	100.1	100.7	101.5	98.4	102.5
ICB	1	100.7	0.0140	101.1	100.8	100.0	98.9	100.6
5.00 ppb MRL Check	1	99.7	5.011	101.7	101.2	100.3	97.6	100.7
250 ppb ICV	1	101.1	249.54	102.6	102.3	101.6	98.7	101.3
SRM1@50	0.110151	93.7	216312	107.6	101.5	97.8	92.3	116.8
	mg/Kg		23827					
SRM2@50	0.106847	90.8	217626	103.7	98.5	95.4	92.0	116.9
	mg/Kg		23253					
B15F271-BLK1 @5	0.025	91.2	0.170	90.1	91.2	92.8	94.1	97.2
	mg/Kg		0.004					
W15F024-01@40	0.157134	95.1	118965	100.4	99.6	98.5	96.0	115.5
	mg/Kg		18693					
B15F271-DUP1@40	0.153563	95.3	124851	100.4	99.6	97.7	94.3	114.5
	mg/Kg		19172					
B15F271-DUP2@40	0.158053	96.2	120994	101.2	100.0	97.8	95.1	114.3
	mg/Kg		19123					
B15F271-MS1@40	0.158053	97.2	143012	102.2	100.0	97.2	92.5	109.4
	mg/Kg		22603					
CCB 1	1	103.4	0.248	103.9	101.6	99.2	96.8	98.8
5.00 ppb CCV 1	1	105.3	5.100	105.1	102.5	100.2	96.5	99.2
20 ppb CCV 1	1	106.9	20.64	106.2	103.0	101.1	98.0	99.1

			SOLIDS (BPC & Digester)	
		Nutrients TOT-P	ICP TOT-P (200.7/6010)	ICP-MS TOT-P (200.8/6020)
		EPA 365.4	Acid= 3.00ml HNO3	Acid= 3.00ml HNO3
		STD MTHD 4500-P (E)(F)	2.00ml HCl	2.00ml HCl
		MRL = 0.030ppm	MRL= 0.020ppm	MRL= 0.0050ppm
Sample ID	Matrix	Curve= 0.030 - 0.600ppm	Curve= 0.020 - 10.0ppm	Curve= 0.0050 - 2 or 10ppm
		PPM (mg/Kg)	PPM (mg/Kg)	PPM (mg/Kg)
SRM1 6/18/15	SRM 2781		25300	23800
SRM2 6/18/16	SRM 2781		24900	23300
SRM1 5/21/15	SRM 2781		24000	24000
SRM2 5/21/15	SRM 2781		23800	23600
SRM3 5/21/15	SRM 2781		23400	23900
SRM4 5/21/15	SRM 2781		23100	23200
SRM1 5/12/15	SRM 2781		24800	
SRM1 2/03/15	SRM 2781		24000	
SRM2 2/03/15	SRM 2781		25500	
SRM3 2/03/15	SRM 2781		24600	
SRM4 2/03/15	SRM 2781		24500	
Expected value for SRM 2781			24200	24200

				SOLIDS (BPC & Digester)		
		Nutrients TOT-P		ICP TOT-P (200.7/6010)		ICP-MS TOT-P (200.8/6020)
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		STD MTHD 4500-P (E)(F)		2.00ml HCl		2.00ml HCl
		MRL = 0.030ppm		MRL= 0.020ppm		MRL= 0.0050ppm
Matrix		Curve= 0.030 - 0.600ppm		Curve= 0.020 - 10.0ppm		Curve= 0.0050 - 2 or 10ppm
		PPM (mg/Kg)		PPM (mg/Kg)		PPM (mg/Kg)
BPC		17300		17500		
dup		16400		17400		
Digester		27400		27100		
dup		27000		26400		
BPC		19200		19000		18700
dup				19400		19200
BPC		16600		18080		
DIG		17200		16620		
DIG		30100		27800		
BPC		26300				28900

What to watch out for with Phosphorus on ICP

- There is a Titanium (Ti) line 213.572 under/next to the Phosphorus 213.618 line. You may have to offset the point on the peak (run it on the shoulder) for quantification.
- Run a custom IEC solution. Don't run a 200ppm(Fe, Ca, Mg, K, Al & Na and Ti at 20ppm IEC solution. To better match surface waters run it at 10- 20ppm(Fe, Ca, Mg, K, Al & Na) and Ti at 0.50ppm for an IEC solution. Spike the IEC with P at 0.100 – 0.200ppm.

What to watch out for with Phosphorus on ICP-MS

- The curve acid mix should match the injected sample acid mix. When injecting samples with an acid mix of 1.50ml HNO₃/1.00ml HCl against a curve with an acid mix of 0.500ml HNO₃/0.250ml HCl the Phosphorus results will be about 10-15% suppressed. You can run high acid samples on a dilution in order to match the curve acid mix.

Conclusion

- Microwave digestion done in 50 minutes (20 minutes cooking + 30 minutes cooling) versus 5.5 -6 hours with Kjeldahl digestion (cooking and cooling).
- Clean-up with the Teflon microwave vessels is much easier.
- Both ICP and ICP-MS can deliver a lower MRL as well as a higher working curve (up to 10-20ppm).
- Read back of MRL standards is much better with an ICP or ICP-MS.
- Minimal carry-over issues with high level samples when using ICP or ICP-MS