LABNOTES
News & Updates of the LabCert Program

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Catching up on Lab-of-the-Year Recipients

There are currently over 300 laboratories in the state that provide chemistry data to DNR to ensure protection of the environment. The Lab-of-the-Year Award recognizes smaller, registered facilities that perform their own testing. Unlike larger environmental labs that typically have many analysts and high technology, registered labs generally may have only a single analyst. And often, that analyst is forced to wear many hats within the community. These folks are plant operators, maintenance workers, and even plow snow. Yet somehow, they still must do their compliance monitoring tests and maintain high quality data standards.

… the 2017 award went to …

In 2017, we were faced with the challenge of identifying a single recipient from a pool of nominations that could be whittled down to two equally deserving (though for different reasons) candidates. So, what did we do? We decided to present two awards!

DNR Secretary Cathy Stepp (L) with Jody Flannery of Rhinelander's WWTP

The first award went to the City of Rhinelander based on a nomination for lab analyst Jody Flannery's long-tenured excellence. Jody and her lab were nominated back in 2013, not selected at that time, but she continues her high standards. If you had a chance to read the nomination, you quickly recognize Jody's organizational skills and attention to detail that is so essential to producing quality lab data. Our DNR field engineer in Rhinelander often uses Jody as a resource to help other labs in the area, especially if they are struggling with the troublesome BOD test, because Jody has figured out all the tricks of the trade. That test is as much art as it is science.

The second 2017 award was presented to the Town of Sullivan for operator/analyst Mike Albert's successes.

DNR Secretary Cathy Stepp (R) with Mike Albert of the Town of Sullivan's WWTP

Town of Sullivan is a very different circumstance. We have had very few one-person operations that have won Lab of the Year. They just wear too many hats to focus on lab work. They run the treatment plant, water utility, plow roads, cut grass…etc.

Three years ago, we were sure we were going to lose this lab. They had a retirement and the new operator was inexperienced and really didn't want to be an operator. It would have been easy for the Town Board to make the decision to shut down the lab and contract out samples, but we met with the Board and they decided to try again and they found Mike Albert at a neighboring treatment plant. The Board gave Mike the resources and support he needed and it has made all the difference.

If you are going to achieve excellence in big things, you develop the habit in little matters. Excellence is not an exception, it is a prevailing attitude.
- Colin Powell

NR 149 Revisions Update

Yes, the process has been a long one, but we took the necessary time to solicit comments on the proposed rule and then to "tweak" the rule in response to comments.

Over 300 individual comments were received on the rule during the public comment process. We have worked diligently to consider each and every comment and, with the advice of our NR149 Workgroup, are in the final stages of making some revisions that will satisfy commenters while maintaining the foundation of what the proposed rule language was attempting to accomplish.

Not every comment was determined to require a revision, but comments will be provided to explain the Program's rationale for not making a change. A complete response to comments will be part of the "green sheet" package which is eventually sent to the Natural Resources Board (NRB) requesting promulgation of the final rule.

It remains our focus to submit the Request for Promulgation to the NRB yet this (2018) spring. When that occurs, we will again alert labs via our website and/or broadcast e-mail so that you can see the final version which we intend to present for promulgation.

If approved by the NRB, we must wait on approval by the legislature. While it is remotely possible we can remain on track for a September 1, 2018 effective date, a Winter 2019 effective date is probably more realistic.

You can follow progress of the rule (and view all documents filed) by accessing the Wisconsin State Legislature's Clearinghouse Rule Page at http://docs.legis.wisconsin.gov/code/chr/all/cr_17_046

Waste Parameter Changes

It's been long overdue to better match the accreditations offered to the waste testing that is actually needed.

Over the last year, the Lab Accreditation Program has worked with the Department's Waste program to ensure that our accreditations suit the needs of the waste program. We identified a number of disconnects in our suite of accreditations offered that required us to discontinue several accreditations (Phase I) and then ensure that labs understand the available accreditations and take the opportunity to add to their scope of accreditations based on testing they perform (Phase II).

Waste testing parameters being eliminated

1. Waste Analysis, Other

Back in the early 1990's, this parameter was known as "waste fingerprinting", and was generally associated with a GC-FID pattern recognition of waste solvents. EPA documents for solid and hazardous waste management, however, refer to "waste fingerprinting" as a suite of testing run by a TSD facility to ensure that the waste product received matches initial expectations. Consequently, this parameter is not readily identifiable and therefore there is no value in issuing accreditation for it.

2. Ignitability of Solids

Under 40 CFR Part 261.21, a solid waste is deemed to exhibit the characteristic of ignitability if it is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture or spontaneous chemical changes and, when ignited, burns so vigorously and persistently that it creates a hazard. There is no generally recognized test method which can quantify whether or not something meets this definition, so we focus on ignitability of liquid wastes.

3. Ignitability, Oxidizers

Under 40 CFR Part 261.21, a solid waste is deemed to exhibit the characteristic of ignitability if it is "an oxidizer." This is not associated with any laboratory test parameter, but rather a class of compounds that yield oxygen readily to stimulate the combustion of organic matter.

Consider adding these waste parameters

There are 32 labs in the program certified to perform one or more waste characteristic tests, but of those labs, **18 labs do not hold accreditation to perform either corrosivity, ignitability, or both**. In order to perform testing to determine whether a waste meets

the corrosivity characteristic, and is therefore hazardous, a lab must hold accreditation for "Corrosivity, Liquids" or "Corrosivity Toward Steel" in the Solid matrix. In order to perform testing to determine whether a waste meets the ignitability characteristic, and is therefore hazardous, a lab must hold accreditation for one or more of the following in the Solid matrix: "Ignitability, Setaflash Closed Cup", "Ignitability, Pensky-Martens Closed Cup," "Ignitability, Small Scale Closed Cup".

In addition, some labs may need to determine whether a waste contains any liquid (landfill requirements) or, for full application of the ignitability characteristic criteria, the percent water of a waste. These tests require a lab to be certified, in the Solid matrix, for "Paint Filters Liquids Test" or "Karl-Fischer Test," respectively.

Check your Scope of Accreditation, and if it lacks one of these tests that you feel you may need, consider submitting a revised application to bolster your accreditations, and ensure that results will be accepted.

EPA promulgates new MDL procedure

On August 28, 2017, the EPA issued a final rule notice that changes the procedure to determine an MDL effective 9-27-2017. We have opted to allow a gradual progression into the new requirement that allows labs to continue with their existing MDL/LODs until September 1, 2018. This date coincides with our projected date that changes to our administrative rule (ch. NR 149, Wis. Admin. Code) would take effect. We ask that labs analyze 2 spiked samples per instrument per test analyte per calendar quarter, beginning now. This will allow calculation of the new MDL_S element. In addition, labs should begin cataloging method blank data in order to determine the new MDL_B element. Additional information is provided below:

Essentially, the old procedure for determining the MDL is now used to generate the MDL "spike" (MDL_S) component.

What has NOT changed

- It's still based on precision (standard deviation).
- You still need to analyze spiked blanks to determine the LOD.
- You still have to do *something* annually (the something has changed).
- It remains in your best interest to perform a "reasonableness" check.

What HAS changed

- Clearly specifies that MDL is inappropriate for Whole Effluent Toxicity (WET), Microbiology, BOD/cBOD), color, pH, specific conductance, and titration methods.
- Provides options/alternatives to determine the initial spiking level to determine the MDL.
- Requires assessment of routine blanks in addition to replicate spiked blanks.
- Blank data is used to determine the LOD_B component
- Requires MDL "spikes" be separated and analyzed over at least 3 separate calendar days.
- Discourages outlier rejection of replicate spikes. Exclusion ONLY if can document a valid reason.
- All instruments in use must be incorporated.
- If you add an instrument: Must prepare/analyze (on different calendar dates) at least 2 spikes and 2 blanks per instrument.
- One prep sample may be analyzed on multiple instruments so long as still have 7 spikes from at least 3 separate batches.
- MDL "spikes" must meet qualitative ID criteria (for each analyte) AND provide a numerical result > zero.
- No more "validation" of the MDL. (i.e. Spike level > MDL > 10% spike level)

<u>What labs need to begin doing NOW:</u>

We will not be enforcing this new protocol until September 1, 2018 to ensure that labs have sufficient time to make the switch. In the interim, we will not require labs to perform the annual update to their LOD. Instead, we asked that labs begin collecting their method blank data and, in addition, begin analyzing at least 2 LOD "spiked samples" (of which you would typically run 7-8 all at once annually) during each calendar quarter (or 3-month period). That will allow labs to generate at least 8 data points to establish a new "initial" LOD using the new LOD protocol.

We will have more information available (e.g., benchsheets) as we develop them and will post links to them on the Lab Certification web site (http://dnr.wi.gov/regulations/labcert/).

Notes regarding HEM and SGT-HEM

We now offer accreditation for SGT-HEM. Know what PT analyte codes and method codes are required for your PT results to be acceptable!

The basic dilemma/confusion is that available "WP" (Water Pollution) PT samples for SGT-HEM are associated with "product names" generally labelled TPH, or "Total Petroleum Hydrocarbons," which is a parameter that does not link to any covered under the Clean Water Act. The regulated parameter is Oil&Grease. And under that parameter, the SGT option is discussed as an approved protocol.

Background

The Clean Water Act (NR 219, Wis. Admin. Code) establishes "Oil&Grease" as a water quality parameter. Initially, Oil&Grease was measured using a Freon extraction, followed by a gravimetric measurement of the residue. Over the past 10 years, the use of Freon was banned, and hexane was promulgated as a replacement solvent. Enter hexane and the switchover to calling the parameter "Hexane Extractable Material" (HEM) rather than "Oil&Grease" (despite the fact that Table B of 40 CFR 136.3 still refers to the parameter as "Oil and Grease."

The hexane extraction, followed by gravimetric determination, yields HEM. HEM contains both polar animal and vegetable fats, oils, and greases (once known as F.O.G.) and non-polar mineral/petroleum oils. Animal and vegetable "grease" is largely the source of grease blockages within wastewater collection systems. These materials are usually associated with food preparation waste (kitchens, restaurants).

There is also a parameter, for which we will now offer accreditation, called "Silica Gel-Treated HEM," or SGT-HEM. The addition of silica gel to a hexane extract will adsorb any polar materials, leaving us with just mineral or petroleum based oils. SGT-HEM usually involves things like gasoline, engine and heating oils.

It's important to note that while many facilities have permit limits for HEM, only a handful of facilities are testing for SGT-HEM, and most of those are related to pre-treatment rather than discharge monitoring. In the past several years, we've seen increasing numbers of unacceptable PTs due to inappropriately reporting a PT as SGT-HEM, or analyzing an HEM PT but reporting results with a method code for SGT-HEM.

To further complicate matters, there are a significant number of analyte code/method code combinations out there, not all of which are acceptable. And each PT Provider seems to have their own preference for each. This has culminated in a number of labs having to scramble to obtain and report acceptable results for a PT each year. So, we decided to put together a comprehensive packet of information related to HEM/SGT-HEM.

What analytical methods should be used?

Based on the approved methods listed in NR 219, the following methods can be used to report data for these two parameters:

Table B
List of Approved Inorganic Test Procedures For Wastewater

Parameter, Units	Analytical Technology	EPA	Standard methods
41. Oil and grease—Total recoverable, mg/L	Hexane extractable material (HEM): n-Hexane extraction and gravimetry	1664 Rev. A; 1664 Rev. B	5520 B-2001
	Silica gel treated HEM (SGT-HEM): Silica gel treatment and gravimetry	1664 Rev. A; 1664 Rev. B	5520 B-2001 and 5520 F-2001

What TNI PT analyte codes should be reported?

The most generally used codes (by PT Providers) are highlighted below. Note that there are several options. The table above shows the analyte codes reported by PT Providers based on the catalog numbers you choose.

Analyte Codes for HEM

TNI#	Analyte
1803	n-Hexane Extractable Material (O&G)
1860	Oil & Grease
6143	Hexane Extractable Material (HEM)

Analyte Codes for SGT-HEM

TNI#	Analyte
1853	Non-Polar Extractable Material (TPH)
~~1935~~	~~Total Recoverable Petroleum Hydrocarbons (TRPH)~~
6142	Hexane Extractable Material - Silica Gel Treated (HEM-SGT)

Note: *We recently learned that TNI is discontinuing the use of analyte code 1935 and replacing it with analyte code 1853 While it seems more logical to apply analyte code 6142 to a sample to be analyzed for SGT-HEM, only one of the PT Providers appears to be using it.*

TNI PT Method Codes should be reported?

Method codes for HEM

Method Code	Method
10127807	EPA 1664A (1999)
10261617	EPA 1664B (2010)
20141406	SM 5520 B 21st (2001)
20141417	SM 5520 B 22nd (2011)
20141655	SM 5520 B-2001
20141666	SM 5520 B-2011

Method codes for SGT-HEM

Method Code	Method
10261606	EPA 1664A 1999
10260628	EPA 1664B 2010
20143015	SM 5520 F 22nd ed.
20143004	SM 5520 F 21st ed.
20143208	SM 5520 F-2001
20143413	SM 5520 F-2011

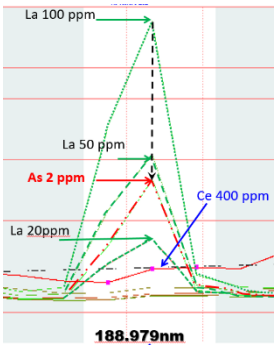
NOTEs: *NR219 indicates that for SGT-HEM, when using Standard Methods procedures, labs are to follow method SM 5520 B and then SM 5520 F (for the silica gel portion).*

Because there are no TNI method codes for the combination procedure (5520B + F), use the method codes for SM 5520 F, the determinative step.

Impact of Phosphorus Removal Products on Metals in Biosolids

Rare earth metals used to complex phosphorus work quite well. Labs subsequently analyzing metals in biosolids, however, must correct interferences.

Summary of problem



During the spring and summer of 2017, the LabCert Program worked with the Wisconsin State Lab of Hygiene to better evaluate the impact of using Rare Earth (RE) element-based products, deigned to remove phosphorus from wastewater, on metals in biosolids.

It has been documented that RE metals, particularly Cerium (Ce) and Lanthanum (La) pose spectral overlap problems in conventional ICP when analyzing arsenic. In addition, there are secondary RE elements that can interfere with arsenic using ICP/MS due to isobaric interferences. Our goal was to better categorize the potential interferences in Neo Materials' RE-100 and RE-300 products. [It is important to note that these products are approved for use in phosphorus removal and have documented ability to remove significant levels of phosphorus. The issue at hand is how labs should deal with spectral interferences from high levels of elements not routinely encountered.]

About 2 years ago we learned that products were available that contained over 30% Cerium (Ce). In late summer 2016, the village of Kewaskum requested assistance as they were having trouble landspreading their biosolids. Lab results indicated that the biosolids exceeded the standard for arsenic, despite the fact that arsenic had never been an issue previously. The village submitted samples to 3 different labs; all reported that either the arsenic (As) levels exceeded standards or that results indicated the presence of an interferent. The only difference from past results was that Kewaskum had been taking in a waste source which had been using SorbX-100 to remove/reduce phosphorus levels.

After checking with the labs, we learned that no spectral interference correction for Ce (or other REEs) on As had been applied. Upon application of appropriate correction factors, the As exceedance disappeared.

Do SorbX-110/RE-100/RE-300 products work?

The City of Watertown performed a test of RE-300's effectiveness during the summer of 2017. Results demonstrated that significant reductions in total phosphorus and orthophosphate in the final effluent could be achieved with the product. It was clear that as the dosage level decreased, the benefits of the product's phosphorus removing capacity were similarly reduced.

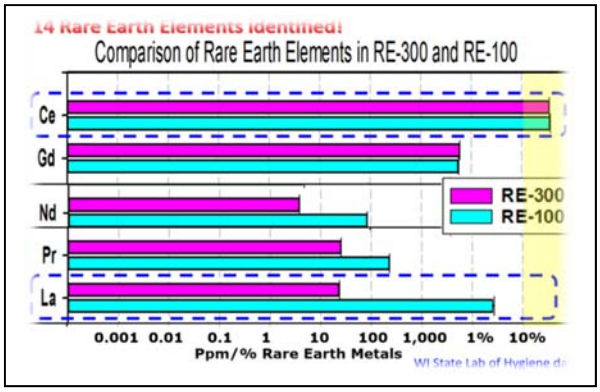
	Pre RE-300	RE-300 200 gpd	RE-300 135 gpd	RE-300 94 gpd
Influent TP	4.00	4.04	2.97	4.86
Effluent TP	0.510	0.133	0.172	0.291
Removal	*88%*	*97%*	*94%*	*94%*
Eff. PO4 (grab)	0.300	0.043	0.068	0.241
PO4 % of TP	60%	32%	40%	82%

What is the composition of NeoMaterials' products?

The Wisconsin State Lab of Hygiene performed detailed testing of the neat product using high resolution ICP-MS. A total of 14 rare earth elements (REE) were identified. The graphic below shows the

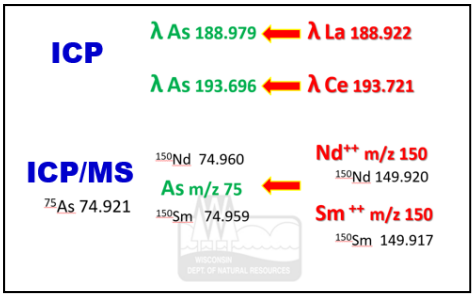
relative amounts of the 5 most prevalent elements in RE-100 and RE-300.

As the figure shows, significant reductions in the concentrations of Lanthanum, Neodymium (Nd), and Praesodymium (Pr) were achieved with the move from RE-100 to RE-300. Cerium (Ce) levels, however, stayed fairly constant at over 10% (10,000 ppm) of the product.



What interferences were identified?

We determined that Lanthanum (La) has a very strong peak with nearly a direct overlap on the Arsenic (As) 188.979 nm wavelength, which will cause high bias in arsenic data. Direct overlaps are very difficult to correct for; therefore, the 193.696 wavelength is recommended for As quantitation in these situations. The As 193.696 line, however, is significantly impacted by an adjacent Cerium (Ce) wavelength and requires correction.



In ICP/MS determinations, we identified Neodymium as an interferent on As. Neodymium has an isotope with a mass-to-charge (m/z) ratio of 150. It is a doubly-charged species and therefore the mass spectrometer will "see" response at m/z= 75, which is also used for arsenic quantitation. Note that the actual m/z values are not identical and this interference can be resolved using high-resolution ICP/MS. Most labs however, use low resolution ICP/MS units typically used in labs, and the lower resolving power will read Neodymium as Arsenic.

Preliminary Biosolids results

The table below clearly shows a significant bias in results when inter-element correction (IEC) factors are not applied (w/o IEC column). For the 188.979 wavelength, which has direct overlap (high bias) from Lanthanum on Arsenic, results were biased at least 10 times high for each of the 4 facilities tested, and arsenic levels ranged from 127 to 849 mg/kg, each of which is well in excess of the 75 mg/kg arsenic ceiling standard for land-spreading biosolids.

Note that, for the preferred 193.696 wavelength, results without IEC correction factors applied were significantly negative, indicating a low bias. This occurred because of over-correction stemming from inappropriate placement of the default background correction points. Many labs incorrectly use two background correction points for ICP, one on either side, in close proximity to, the target peak. The use of two background correction points would be reserved for elements whose wavelengths are in regions of sloping background, such as potassium. These are generally elements with wavelengths greater than 500 nm.

Preliminary biosolids data (with and without correction), mg/kg

Element	Norway	*Norway (w/o IEC)*	Sussex	*(w/o IEC)*	Watertown	*Watertown (w/o IEC)*	Juneau	*(w/o IEC)*
As 188.979	4.3	*127.2*	(8.6)	*196.2*	(32.2)	*466.4*	(50.9)	*848.7*
As 193.696	61.0	*(675.4)*	12.6	*(265.4)*	28.0	*(324.4)*	18.6	*(276.1)*
Pb 220.353	10.3	*128.1*	15.2	*54.9*	31.4	*49.5*	25.7	*64.2*
Pb 217.000	7.0	*319.1*	17.8	*132.3*	36.2	*136.0*	13.7	*148.7*
P 213.617	40,328.6	*40,518.2*	35,126.7	*35,492.5*	37,613.4	*37,708.0*	17,017.1	*17,059.8*
P 178.221	36,926.9	*36,845.5*	32,801.6	*32,774.3*	34,885.5	*34,857.5*	17,137.4	*17,100.7*
Sr 407.771 R	314.0	*258.7*	3,100.0	*???*	225.2	*101.5*	787.9	*553.7*
S 181.975	5,807.6	*6,612.7*	5,690.2	*6,704.6*	5,338.2	*10,154.5*	3,584.3	*924.1*
Y (IS)	272.6	*(509.1)*	255.1	*(185.5)*	274.4	*(119.5)*	94.1	*(234.2)*
Y (IS) R	237.3	*(445.3)*	217.4	*(167.5)*	237.4	*(106.6)*	82.0	*(204.7)*
Ce 413.764 R	76,871.3	*76,809.4*	28,252.0	*28,249.7*	18,005.4	*18,039.8*	34,721.2	*34,788.1*
La 408.672 R	3,437.7	*2,610.6*	4,166.6	*3,860.8*	8,979.8	*8,781.4*	16,860.6	*16,478.8*
Nd 406.109 R	4,218.4	*2,959.3*	1,216.1	*749.9*	118.2	*(172.7)*	208.4	*(350.4)*

The table below represents final results for each of the 4 facilities after initially applying appropriate spectral corrections, and then using only single background correction point and ensuring proper placement of it. Negative values with an absolute value greater than the LOD should be assessed for potential over-correction of spectral interferences or a need to adjust the position of the background correction point.

FINAL results …after re-adjustment of BGC:

EHD-Metals ICP-OES Data of WWTP Biosolids for As using individual IEC tables					
Element	Norway	Sussex	Watertown	Juneau	units
As 188.979 axial	14.0	1.4	4.6	-23.0	mg/kg
As 193.696 axial	-1.6	-10.0	3.2	0.0	mg/kg

These results were generated using a single point for background correction for both wavelengths. 193.696 nm is the preferred wavelength due to direct spectral overlap interference from Lanthanum (La). In addition, the State Lab of Hygiene found that best results could only be achieved by developing a unique IEC table for each biosolid, based on the composition and concentrations of elements identified in that biosolid.

Wait…what about Kewaskum?

So…what happened with the original facility that raised the issue? Kewaskum had 3 different labs test their biosolids. At least one lab used ICP/MS rather than conventional ICP; two different ICP wavelengths were used as well. The three labs submitted widely varying results ranging from not detected to well over the maximum limit for arsenic. As shown in the figure below, results appeared to be acceptable when using the 193.696 line, but were significantly biased high using the 188.979 line.

Kewaskum's Biosolids Data

Initial results

NR 204 limit 75 mg/kg

As 188.979 (mg/kg)	As 193.696 (mg/kg)
118	ND
120.5	ND
123.4	7.9

Follow-up results (line 193.696)

	Uncorrected	After correction
Outfall 002-1G	84.9	9.58
Outfall 002-2G	90.2	8.77
Outfall 002-3G	88.9	9.99
Average	***88***	***9.11***

Checklist: Contracting out biosolids samples

- TELL the lab if you use(d) RE100 or RE300.
- ASK if they plan to use ICP (or GFAA or ICP/MS).
- Verify that they understand and correct for interferences due to REE.
- If results for Arsenic appear to be biased high, verify that the lab applied corrections for REEs.
- The lab should understand. If they do not, you may want to consider using a different lab.

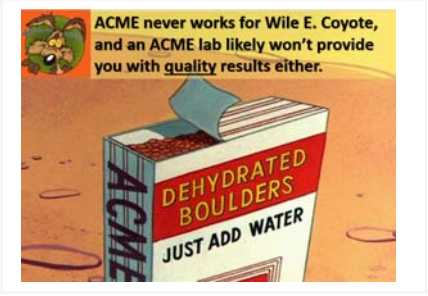
Checklist: If you receive biosolids samples:

ASK if any phosphorus-complexing chemicals were used (and which ones), or if the facility received flow/solids from another facility that used these products. If SorbX100, RE100, or RE300 were used:

- Review pre-RE100/300 data for the facility's samples (if you have it).
- Review historical levels & dosage rate vs. flow.
- Arsenic: Use the 193.696 nm line vs. 188.979 nm
- Use only a single background correction point.
- Ensure proper corrections are in place. For best results, each facility's biosolids should be treated uniquely to design a correction algorithm for that specific matrix.
- Create a special interference check standard (ICS), designed at levels equal to those found, to assess effectiveness of inter-element correction (IEC) factors.
- Verify that arsenic (and other elements that are not contained in the ICS) is not present.

Conclusions

- RE100/RE300 products DO effectively remove phosphorus.
- These products DO pose challenges for ICP & ICP/MS
- But…. The challenges can be overcome …
- …as long as you know to address them
- GFAA= slow (8 elements = 8 runs)
- ICP =faster; less matrix interferences than GFAA
- ICP/MS, while a viable option, is overkill



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