TKN/TKP versus TN/TP
and New Lachat Dual TN/TP Digest Methods

Introduction:

The recent USEPA Method Update Rule (MUR), published in March 2007, has generated several questions regards Kjeldahl digestions versus other digestion methods for total nitrogen and total phosphorus.

The MUR states that **in-line, automated** sample preparation is now an equivalent sample preparation method for some parameters that are regulated for wastewater. Lachat has methods with these in-line, automated sample preparation procedures available. However, not all of these methods are applicable under the MUR and sometimes these methods are not suitable for an individual lab's reporting requirements.

For example, Total Kjeldahl Phosphorus (TKP) and Total Kjeldahl Nitrogen (TKN) are not in-line or automated methods. These digestions require lengthy digestion periods and high temperatures (380^{o}C) to complete. However, these are often preferable for an individual lab versus inline Total Nitrogen (TN) and/or Total Phosphorus (TP) methods.

Where an in-line method can be used, TP for example, particulate matter potentially present in samples must also be taken into consideration. **If SOP's or regulations require samples to be analyzed as "total" and not "dissolved", then in-line digestion methods should NOT be used.** However, a lab may opt to run side-by-side studies to determine whether particulates add significant analyte concentrations to the sample as a whole. If particulates do add significantly to the total analyte concentration, then the samples would be better suited to either Kjeldahl digestions, or to off-line total nitrogen or phosphorus methods that utilize persulfate.

Kjeldahl Digests overview:

1) The sample is decomposed by heating with sulfuric acid.
2) The boiling point of the acidic solution is raised by addition of salt (potassium sulfate).
3) Mercury or copper is used as a catalyst.
4) Nitrogen at the end is converted to ammonia (NH_3).
5) Phosphorus is converted to orthophosphorus (PO_4).

Total Kjeldahl Nitrogen (TKN):

TKN is defined as the sum of organic nitrogen, ammonia (NH3) and ammonium (NH_4^+), in biological wastewater treatment. This is the sum of free ammonia and organic nitrogen compounds, which are converted to ammonium sulfate. TKN is determined in the same manner as organic nitrogen, except that ammonia is not driven off prior to the digestion step.

It is important to note that TKN digestion may not convert some nitrogen containing compounds that may be found in industrial waste, such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.

Total Kjeldahl Phosphorus (TKP) :

Phosphorous occurs in several forms: ortho, poly and organically bound. Further classification can be made on whether the phosphorus is dissolved (passing through a 0.45 micron filter).

In a TKP digestion, polyphosphates and organic phosphorus are converted into orthophosphate.

In-Line Total Nitrogen:

Total Nitrogen is NOT an EPA parameter. Additionally, samples containing particulates may need to be digested with an off-line procedure. (Off-line procedures do NOT include UV light, but do involve pressure so that the results are very similar). Unlike the historic TKN analysis (which used mercury as a catalyst, a sulfuric acid digest, and chromium to reduce nitrate), no heavy metals are used in this digestion procedure.

To compare the TN result to a determined acid digested TKN result (using EPA method 351.2), it will be necessary to subtract the nitrate contribution from the Total Nitrogen value.

In the in-line total nitrogen methods, nitrogen compounds are oxidized in-line to nitrate using alkaline persulfate/UV digestion. In the UV digestion, oxidation of nitrogen containing compounds to nitrate is achieved by heating, with additional energy supplied by UV light.

With the alkaline persulfate, potassium persulfate in an alkaline environment converts all forms of nitrogen containing compounds to the nitrate form. This oxidation reaction is shown in Equation 1:

Eq. 1: $K_2S_2O_8 + H_2O = 2KHSO_4 + 1/2O_2$

Eq. 2: $KHSO_4 + NaOH = Na + K + SO_4 + H_2O+ + 2\ e-$

In Flow Injection Analysis, these digestions occur prior to the injection valve.

Results for wastewater samples with settleable solids may be up to 20% lower when compared with a rigorous off-line digestion. If effluent samples are acid preserved, in-line digestion results will match manual off-line digestion. Results for the samples without settleable particulates, such as surface water and seawater will match the manual off line digestion. These comparisons should be validated with a typical sample before reporting results.

After digestion, nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate) is then determined by diazotization with sulfanilamide under acidic conditions to form a diazonium ion. The diazonium ion is coupled with N- (1-naphthyl) ethylenediamine dihydrochloride. The resulting dye absorbs at 540 nm and is proportional to the total nitrogen concentration.

This is a true TOTAL nitrogen analysis. This compares in the final result to the historic Total Kjeldahl Nitrogen analysis, where all organic nitrogen was converted to ammonia nitrogen and nitrate nitrogen was NOT reduced to ammonia. (High levels of Nitrate can actually result in low recovery of TKN).

In-Line Total Phosphorus:

In an off-line TP digest, the digestion is used to convert various phosphorous forms and conversion to phosphate by acidic peroxodisulfate. This can be done in an autoclave or on a hot plate. Organic phosphorus is converted to orthophosphate by persulfate digestion. Polyphosphates are converted to orthophosphate by sulfuric acid digestion.

The Lachat in-line total phosphorus methods are based on the digestion of various phosphorous forms and the conversion to phosphate by peroxodisulfate with an in-line UV digestion. Organic phosphorus is converted to orthophosphate by UV catalyzed persulfate digestion. Polyphosphates are converted to orthophosphate by sulfuric acid digestion. In Flow Injection Analysis, the digestion process occurs prior to the sample valve. A portion of the digested sample is then injected and phosphate is determined.

When analyzing wastewater samples (that are acid preserved and filtered), in-line digestion results match the manual off-line digestion. <u>If particulate-containing samples are not filtered, in-line results can be up to 15% lower compared to off-line digestion.</u> Surface water samples may not require filtration but this should be verified with a sample containing high levels of solids.

After digestion, the orthophosphate ion (PO_4^{3-}) reacts with ammonium molybdate and antimony potassium tartrate to form a phosphomolybdate complex. This complex is reduced with ascorbic acid to form a blue complex, which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

All forms of phosphorus are converted to its ortho form in the TP procedure; in the presence of potassium persulfate and an acid background.

Lachat has methods available for Total Nitrogen and Total Phosphorus that use alkaline and acidic persulfate digestions respectively.

Comparison Table

Method	*EPA method*	*Particulates OK*	*Recovered?*	*Comments*
TKN	YES	YES	Sum of organic nitrogen: ammonia (NH3) and ammonium (NH4+).	Requires mercury or copper catalyst; chromium to handle nitrates.
TN	NO	YES for Off-Line NO for In-line methods unless validated	Same as above, plus amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.	No heavy metals. Off-line requires autoclave or block digester; in-line requires a digestion module with UV lamp.
TKP	YES	YES		Requires mercury or copper catalyst; chromium to handle nitrates.
TP	YES	YES for Off-Line NO for in-line methods unless validated		No heavy metals. Off-line requires autoclave or block digester; in-line requires a digestion module with UV lamp.

Summary of Available Lachat Methods:

TKN and TKP

Parameter	Method Number	Range	Comments
Kjeldahl Nitrogen	10-107-06-2-D	0.5-20 mg N/L	EPA accepted; Mercury catalyst
	10-107-06-2-E	0.1-5.0 mg N/L	EPA accepted; Mercury catalyst
	10-107-06-2-H	0.1-5.0 mg N/L	Equivalent under the MUR; Copper catalyst
	10-107-06-2-I	0.5-20 mg N/L	Equivalent under the MUR; Copper catalyst
	10-107-06-2-K	0.1-20 mg N/L	Equivalent under the MUR; Mercury catalyst
	10-107-06-2-M	0.25-25 mg N/L	Equivalent under the MUR; Copper Catalyst. DI carrier
	10-107-06-2-N	0.5-20 mg N/L 0.1-5.0 mg N/L	Equivalent under the MUR; Mercury catalyst, >100 samples per hour
	10-107-06-5-F	0.1-10.0 mg N/L	**Gas Diffusion** Method. Copper Catalyst. Not EPA accepted, or equivalent under the MUR
Kjeldahl Phosphorus	10-115-01-1-C	0.1-5.0 mg P/L	EPA accepted; Mercury catalyst
	10-115-01-1-D	0.05-0.5 mg P/L	EPA accepted; Mercury catalyst
	10-115-01-1-I	0.1-5.0 mg P/L	Equivalent under the MUR; Mercury catalyst, >100 samples per hour
	10-115-01-2-B	0.1-10.0 mg P/L	Equivalent under the MUR; **Copper Catalyst.** DI carrier
	10-115-01-2-C	0.1-5.0 mg P/L	Equivalent under the MUR; **Copper Catalyst.** DI carrier. >100 samples per hour

In-line TN and In-line TP:

Parameter	Method Number	Range	Comments
Total Phosphorus	10-115-01-3-A	0.1-10.0 mg P/L	Equivalent under the MUR; not suited to particulates
	10-115-01-3-B	0.1-4.0 mg P/L	Equivalent under the MUR; not suited to particulates
	10-115-01-3-C	0.05-1.0 mg P/L	Equivalent under the MUR; not suited to particulates
	10-115-01-3-D	0.1-1.0 mg P/L	Equivalent under the MUR; not suited to particulates

	10-115-01-3-E	10-500 µg P/L	Equivalent under the MUR; not suited to particulates
	10-115-01-3-F	2-100 µg P/L	Equivalent under the MUR; not suited to particulates
	31-115-01-3-D	0.05-1.0 mg P/L	Brackish water. Equivalent under the MUR; not suited to particulates
Total Nitrogen	10-107-04-3-A	200-2000 µg N/L	Not an EPA Parameter; not suited to particulates
	10-107-04-3-B	0.5-30 mg N/L	Not an EPA Parameter; not suited to particulates
	10-107-04-3-C	0.5-10.0 mg N/L	Not an EPA Parameter; not suited to particulates
	10-107-04-3-P	0.2-10.0 mg N/L	Not an EPA Parameter; not suited to particulates
	31-107-04-3-A	0.1-1.0 mg N/L	Not an EPA Parameter; not suited to particulates
	31-107-04-3-B		Not an EPA Parameter; not suited to particulates

Off-line Total Phosphorus

Parameter	Method Number	Range	Comments
Total Phosphorus	10-115-01-1-E	0.2-10.0 mg P/L	EPA accepted;
	10-115-01-1-F	0.003-0.200 mg P/L	EPA accepted;
	10-115-01-4-I	0.2-20 mg P/L	Equivalent under the MUR; can handle particulates.
	10-115-01-4-J	0.2-10.0 mg P/L	Equivalent under the MUR; can handle particulates. >100 samples per hour
	10-115-01-4-U	0.01-2.0 mg P/L	Equivalent under the MUR; can handle particulates.
	10-115-01-4-J	0.2-10.0 mg P.L	

Dual TN/TP:

Parameter	Method Number	Range	Comments
Total Nitrogen	10-107-04-4-B	0.01-5.0 mg N/L 1-40 mg N/L	Dual digestion. TN and TP are measured from the same digest. Requires 25 x 100 screw capped tubes, BD-46 or other Block Digester. With this block, can digest 46 samples/standards simultaneously.
Total Phosphorus	10-115-01-4-B	0.05-1.0 mg P/L	Dual digestion. TN and TP are measured from

		0.25-10.0 mg P/L	the same digest. Requires 25 x 100 screw capped tubes, BD-46 or other Block Digester. With this block, can digest 46 samples/standards simultaneously.