

Ammonia (Ammonium) Spectroquant[®] Test Kits Equivalency Checklist

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Introduction

The method flexibility allowed in the EPA rules 40 CFR part 136.6 [1] lay out the requirements a modified analytical method must meet to be considered equivalent to a promulgated analytical method. These requirements are explained in detail in a memo authored by Richard Redding [2]:

The March 12th Methods Update Rule promulgated 136.6 which allows the regulated community more flexibility that includes:

1. Changes in equipment operating parameters such as minor changes in the monitoring wavelength of a colorimeter
2. Adjusting sample sizes or changing extraction solvents to optimize method performance in meeting regulatory requirements
3. Minor changes in reagents used where the underlying reaction and principles remain virtually the same:
 - a. Changes in complexing reagent provided that the change does not produce interferences. The ammonia paper cited in section A provides an example of using a different complex reagent (citrate) other than either reagent specified in the EPA method (sodium potassium tartrate and EDTA) because it was found to be more effective and not interfere.
 - b. Changes in reactants provided that the change does not produce interference. The ammonia paper cited in section A gives an example and references other examples of changing the precursor to a final product that still results in the same reaction (Berthelot reaction and formation of indophenol).

This equivalency checklist will directly compare the Spectroquant[®] Ammonia-Ammonium Test Kits with the simple method modifications listed in Richard Reading's memo and allow a laboratory to establish method equivalency for their analyses and reporting to both users of the results and regulators.

Method Summary from Spectroquant[®] Equivalency Report

The report Equivalency of Ammonia (Ammonium) Spectroquant[®] Test Kits: Ammonia (Ammonium) by Indophenol Reaction and Photometry [3] provides the single laboratory equivalency data required by EPA.[2] The significant areas covered in the report that summarize the areas that equivalency must be identified are listed in Table 1 below.

Table 1: Method Equivalency Summary	
Spectroquant® Change Test Kit 1.00683, 1.14739, 1.14559, 1.14544, 1.14558, 1.14752	136.6 Requirement
Substituted phenols (2-Chlorophenol or Thymol)	<p>No change in the overall Berthelot reaction.</p> <ul style="list-style-type: none"> • Other referenced methods in 40 CFR part 136 use substituted phenols. • An indophenol was formed with the substituted compounds changing the wavelength for maximum absorbance changing. • Accuracy, Precision, MRL and MDL from the experimental data were acceptable.
Chlorine source was changed from hypochlorite to dichloroisocyanuric acid.	<p>No change in the overall Berthelot reaction.</p> <ul style="list-style-type: none"> • Other referenced methods in 40 CFR part 136 use other chlorine sources Sodium Dichloroisocyanurate, which is the acid salt of Dichloroisocyanuric Acid • An indophenol was formed with the substituted compounds changing the wavelength for maximum absorbance changing. • Accuracy, Precision, MRL and MDL from the experimental data were acceptable.
Chelation reagent was changed from trisodium citrate to 1 Hydroxy Ethylidene 1,1 Diphosphonic Acid	<p>No change in the overall Berthelot reaction.</p> <ul style="list-style-type: none"> • Cations were chelated in the MS/MSD and did not affect Accuracy or Precision
Sorbitol was added to the dry Spectroquant® reagent to prevent caking.	<p>No change in the overall Berthelot reaction.</p>

The Equivalency of Ammonia (Ammonium) Spectroquant® Test Kits: Ammonia (Ammonium) by Indophenol Reaction and Photometry report has provided the literature review information, EPA 40 CFR part 136.6 requirements and experimental data to support the equivalency of the current Spectroquant® ammonium test kits with the EPA current promulgated ammonia phenate methods listed in the 40 CFR part 136.

Conclusion

In conclusion, these changes in the Spectroquant® Test Kits (or future test kits with the same equivalent chemistry) produce an equivalent set of tests to the current EPA promulgated ammonia phenate methods listed in the 40 CFR part 136.

Current Spectroquant® Ammonium Test Kits of Merck KGaA, Darmstadt, Germany listed in this report are:

- A. 1.00683
- B. 1.14739
- C. 1.14559
- D. 1.14544
- E. 1.14558
- F. 1.14752

In Table 2 below, “*Method Equivalency of Standard Methods for the Examination of Water and Wastewater Ammonia Method to Spectroquant® Ammonium Test Kits of Merck KGaA, Darmstadt, Germany*”, each approved Standard Methods for the Examination of Water and Wastewater ammonia phenate method requirement listed in the Reding memo and 40 CFR part 136.7 is compared to the Spectroquant® test kits. This checklist should be kept onsite at the laboratory so as to be provided to any user of the laboratory results or as needed for regulatory audits/requirements.

Copies of the “*Equivalency of Ammonia (Ammonium) Spectroquant® Test Kits: Ammonia (Ammonium) by Indophenol Reaction and Photometry*” report can be obtained from <http://www.emdmillipore.com/USEPA>

Table 2: Method Equivalency of Standard Methods for the Examination of Water and Wastewater Ammonia Method to Spectroquant® Ammonium Test Kits of Merck KGaA, Darmstadt, Germany

Method or Quality Control Requirement	Standard Methods for the Examination of Water and Wastewater 4500-NH₃ (F) 1997,2011 Phenate Method 4500-NH₃ (G) 1997,2011 Automated Phenate Method 4500-NH₃ (H) 1997,2011 Flow Injection Analyses Method	Spectroquant® Ammonium Test Kits 1.00683 1.14739 1.14559 1.14544 1.14558 1.14752
1. Analyte Detected	NH ₃ or NH ₃ -N	NH ₃ or NH ₃ -N
2. Matrix Tested	Water	Water
3. Detection Method	Visible Absorbance Maxima	Visible Absorbance Maxima
4. Wavelength Maxima (nm)	F. 640 G. 630-660 H. 630	690-710
Analytical Reagents Required		
1. pH Adjustment Chemical to Convert Ammonium to Ammonia	F. NaOH G. NaOH H. NaOH	NaOH

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2. Catalyst	F. Sodium Nitroprusside G. Sodium Nitroprusside H. Sodium Nitroprusside	Sodium Nitroprusside
3. Chlorine Reagent	F. Sodium Hypochlorite G. Sodium Hypochlorite H. Sodium Hypochlorite	Sodium Dichloroisocyanurate
4. Phenol Reagent	F. Phenol G. Phenol H. Phenol	2 Chlorophenol or Thymol
5. Magnesium and Calcium Chelation Reagent	F. Trisodium Citrate G. Disodium Ethylenediamineteraacetate H. Disodium Ethylenediamineteraacetate	1 Hydroxy Ethylidene 1,1 Diphosphonic Acid

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6. Anticaking Reagent	Not Required	Sorbitol
Quality Control Requirements from 40 CFR part 136.7		
1. Demonstration of Capability (DOC),	Required in 4020	Required in Spectroquant® Ammonia Method
2. Method Detection Limit (MDL),	Required in 4020	Required in Spectroquant® Ammonia Method Single Laboratory Results in: Spectroquant® Ammonia Equivalency Report
3. Reagent blank (also referred to as method blank),	Required in 4020	Required in Spectroquant® Ammonia Method Single Laboratory Results in: Spectroquant® Ammonia Equivalency Report

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4. Laboratory fortified blank (LFB, also referred to as a spiked blank, or laboratory control sample (LCS)),	Required in 4020	Required in Spectroquant® Ammonia Method Single Laboratory Results in: Spectroquant® Ammonia Equivalency Report
5. Matrix spike (MS), matrix spike duplicate (MSD), or laboratory fortified blank duplicate (LFBD) for suspected difficult matrices,	Required in 4020	Required in Spectroquant® Ammonia Method Single Laboratory Results in: Spectroquant® Ammonia Equivalency Report
6. Internal standard/s, surrogate standard/s (for organic analysis) or tracer (for radiochemistry),	Not Required	Not Required

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7. Calibration (initial and continuing),	Required in 4020	Required in Spectroquant® Ammonia Method Single Laboratory Results in: Spectroquant® Ammonia Equivalency Report
8. Control charts (or other trend analyses of quality control results), and	Required in 4020	Required in Spectroquant® Ammonia Method
9. Corrective action (root cause analyses),	Required in 4020	Required in Spectroquant® Ammonia Method
10. Specific frequency of QC checks,	Required in 4020	Required in Spectroquant® Ammonia Method
11. QC acceptance criteria,	Required in 4020	Required in Spectroquant® Ammonia Method

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12. Definitions of a batch (preparation and analytical)	Required in 4020	Required in Spectroquant® Ammonia Method

References

1. EPA, *Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures*. 2012. p. 29758-29846.
2. Reding, R., *Flexibility to Modify CWA Methods*, E. Engineering & Analytical Support Branch, OST, Editor. 2007, EPA.
3. Askew, E.F., *Equivalency of Ammonia (Ammonium) Spectroquant® Test Kits: Ammonia (Ammonium) by Indophenol Reaction and Photometry*. 2016.