Designation: ~~D7742 – 11~~ D7742 – 17

Standard Practice for Determination of Nonylphenol Polyethoxylates (NPnEO, 3 ≤ n ≤ 18) and Octylphenol Polyethoxylates (OPnEO, 2 ≤ n ≤ 12) in Water by Single Reaction Monitoring (SRM) Liquid Chromatography/ Tandem Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation D7742; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This ~~procedure~~practice covers the determination of nonylphenol polyethoxylates (NPnEO, 3 ≤ n ≤ 18) and octylphenol polyethoxylates (OPnEO, 2 ≤ n ≤ 12) in water by Single Reaction Monitoring (SRM) Liquid Chromatography/ Tandem Mass Spectrometry (LC/MS/MS) using direct injection liquid chromatography (LC) and detected with tandem mass spectrometry (MS/MS) detection. This is a screening practice with qualified quantitative data to check for the presence of longer chain ethoxylates in a water sample.

1.1.1 All data are qualified because neat standards of each alkylphenol ethoxylate (APEO) are not available and the synthesis and characterization of these neat standards would be very expensive. The ~~Igepal®~~Igepal[2] ~~Brand~~brand standards, which contain a mixture of various chain lengths of the alkylphenol ethoxylates (APEOs), were used. The mixture was characterized in-house assuming the instrument response at an optimum electrospray ionization cone and collision voltage for each APEO was the same. This assumption, which may not be accurate, is used to determine qualified amounts of each ethoxylate in the standards. The n-Nonylphenol diethoxylate ~~(n- NP2EO)~~ (n-NP2EO) surrogate was available as a neat characterized standard, therefore, this concentration and recovery data was not estimated. APEOs are not regulated by the EPA, but nonylphenol, a breakdown product of NPnEOs, is regulated for fresh and saltwater dischargers. A request by a sewage treatment plant (STP) was made to make this practice available through ASTM in order to screen for the influent or effluent from sources of APEOs coming into the STP. The interest lies in stopping the source of the longer chain APEOs from entering the STP in order to meet effluent guidelines. Based upon the above, this is a practice rather than a ~~Standard Method.~~test method. A comparison between samples is possible using this practice to determine which has a higher concentration of APEOs.

1.2 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this practice.

1.3 The estimated screening range shown in Table 1 was calculated from the concentration of the Level 1 and 7 calibration standards shown in Table 4. These numbers are qualified, as explained in Section 1~~1,~~, and must be reported as such. Figs. 1-5 show the SRM chromatograms of each analyte at the Level 1 concentration with the signal to noise (S/N) ratio. This is a screening practice and method detection limits are not given. The S/N ratio for each analyte at the Level 1 concentration must be at least 5:1 for adequate sensitivity. If the instrument can not meet the criteria, the screening limit must be raised to an acceptable level.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate ~~safety~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

[1] This practice is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

Current edition approved ~~June 15, 2011~~Dec. 15, 2017. Published ~~July 2011~~January 2018. Originally approved in 2011. Last previous edition approved in 2011 as D7742 – 11. DOI: ~~10.1520/D7742-11.~~10.1520/D7742-17.

[2] Igepal is a trademark of Rhodia Operations, Aubervilliers, CA.

TABLE 1 Estimated Screening Range

Analyte	Estimated Screening Range (µg/L)
~~Nonylphenol triethoxylate (NP3EO)~~	~~0.73–11.6~~
Nonylphenol triethoxylate (NP3EO)	0.73–11.6
Nonylphenol tetraethoxylate (NP4EO)	1.1–18.3
Nonylphenol pentaethoxylate (NP5EO)	1.4–22.1
~~Nonylphenol hexaethoxylate (NP6EO)~~	~~1.8–28.2~~
Nonylphenol hexaethoxylate (NP6EO)	1.8–28.2
~~Nonylphenol heptaethoxylate (NP7EO)~~	~~1.9–30.1~~
Nonylphenol heptaethoxylate (NP7EO)	1.9–30.1
~~Nonylphenol octaethoxylate (NP8EO)~~	~~1.8–29.2~~
Nonylphenol octaethoxylate (NP8EO)	1.8–29.2
~~Nonylphenol nonaethoxylate (NP9EO)~~	~~1.6–26.3~~
Nonylphenol nonaethoxylate (NP9EO)	1.6–26.3
~~Nonylphenol decaethoxylate (NP10EO)~~	~~1.5–24.1~~
Nonylphenol decaethoxylate (NP10EO)	1.5–24.1
~~Nonylphenol undecaethoxylate (NP11EO)~~	~~1.3–21.3~~
Nonylphenol undecaethoxylate (NP11EO)	1.3–21.3
~~Nonylphenol dodecaethoxylate (NP12EO)~~	~~1.0–15.7~~
Nonylphenol dodecaethoxylate (NP12EO)	1.0–15.7
~~Nonylphenol tridecaethoxylate (NP13EO)~~	~~0.64–10.3~~
Nonylphenol tridecaethoxylate (NP13EO)	0.64–10.3
~~Nonylphenol tetradecaethoxylate (NP14EO)~~	~~0.41–6.5~~
Nonylphenol tetradecaethoxylate (NP14EO)	0.41–6.5
~~Nonylphenol pendecaethoxylate (NP15EO)~~	~~0.21–3.4~~
Nonylphenol pendecaethoxylate (NP15EO)	0.21–3.4
~~Nonylphenol hexadecaethoxylate (NP16EO)~~	~~0.11–1.7~~
Nonylphenol hexadecaethoxylate (NP16EO)	0.11–1.7
~~Nonylphenol heptadecaethoxylate (NP17EO)~~	~~0.05–0.80~~
Nonylphenol heptadecaethoxylate (NP17EO)	0.05–0.80
~~Nonylphenol octodecaethoxylate (NP18EO)~~	~~0.023–0.4~~
Nonylphenol octodecaethoxylate (NP18EO)	0.023–0.4
Total NPnEO	16–250
~~Octylphenol diethoxylate (OP2EO)~~	~~0.14–2.3~~
Octylphenol diethoxylate (OP2EO)	0.14–2.3
Octylphenol triethoxylate (OP3EO)	1.4–22.2
Octylphenol tetraethoxylate (OP4EO)	2.2–35.2
Octylphenol pentaethoxylate (OP5EO)	2.9–45.8
~~Octylphenol hexaethoxylate (OP6EO)~~	~~2.6–41.9~~
Octylphenol hexaethoxylate (OP6EO)	2.6–41.9

Analyte	Estimated Screening Range (µg/L)
~~Octylphenol heptaethoxylate (OP7EO)~~	~~2.5–40.4~~
Octylphenol heptaethoxylate (OP7EO)	2.5–40.4
~~Octylphenol octaethoxylate (OP8EO)~~	~~1.8–28.8~~
Octylphenol octaethoxylate (OP8EO)	1.8–28.8
Octylphenol nonaethoxylate (OP9EO)	1.1–17.6
~~Octylphenol decaethoxylate (OP10EO)~~	~~0.62–9.9~~
Octylphenol decaethoxylate (OP10EO)	0.62–9.9
~~Octylphenol undecaethoxylate (OP11EO)~~	~~0.26–4.2~~
Octylphenol undecaethoxylate (OP11EO)	0.26–4.2
Octylphenol dodecaethoxylate (OP12EO)	0.11–1.8
Total OPnEO	16–250
~~n-Nonylphenol diethoxylate (n-NP2EO)~~	~~15.6–250 (Not Estimated)~~
n-Nonylphenol diethoxylate (n-NP2EO)	15.6–250 (Not Estimated)

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water

D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

E2554 Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques

2.2 *Other Standard:*[4]

EPA Publication SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Available from National Technical Information Service (NTIS), ~~U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA, 22161 or at http://www.epa.gov/epawaste/hazard/testmethods/index.htm~~5301 Shawnee Rd., Alexandria, VA 22312, http://www.ntis.gov.

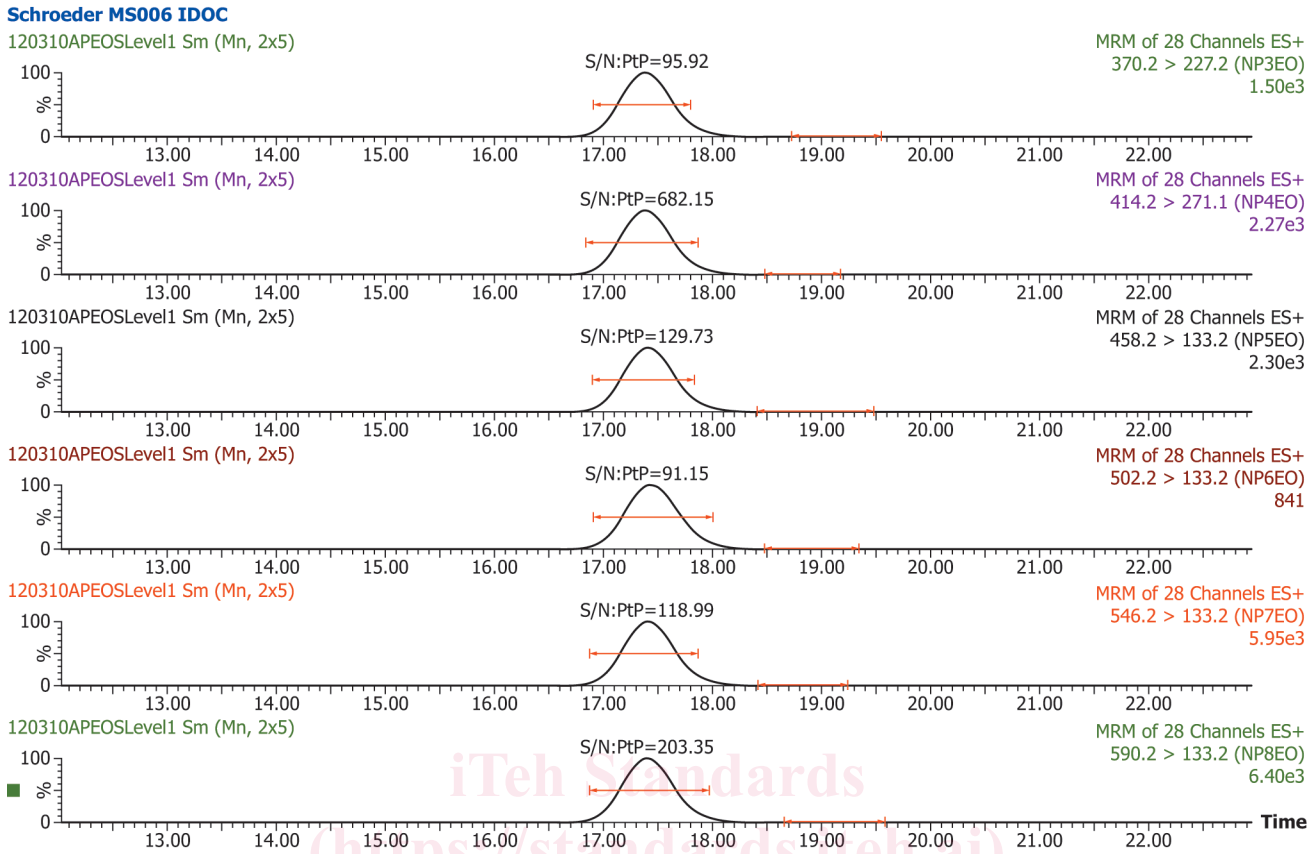

FIG. 1 SRM Chromatograms NP3EO-NP8EO

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 ~~*Definitions:*~~*Definitions of Terms Specific to This Standard:*

~~3.1.1 *Screening Limit, SL, n*—the estimated concentration of the lowest-level calibration standard used for quantification accounting for the sample dilution.~~

3.2.1 ~~*Alkylphenol Ethoxylates,*~~*alkylphenol ethoxylates, n—in this practice*, nonylphenol polyethoxylates (NPnEO, $3 \leq n \leq 18$) and octylphenol polyethoxylates (OPnEO, $2 \leq n \leq 12$) collectively.

3.2.2 *screening limit, SL, n*—the estimated concentration of the lowest-level calibration standard used for quantification accounting for the sample dilution.

3.3 *Abbreviations:*

~~3.2.1 *ppt*—parts per trillion, ng/L~~

3.3.1 *mM*—millimolar, 1×10^{-3} moles/L

3.3.2 *ND*—non-detect

3.3.3 *ppt*—parts per trillion, ng/L

4. Summary of Practice

4.1 This is a performance-based practice and modifications are allowed to improve performance.

4.2 For APEOs analysis, samples are shipped to the lab between 0°C and 6°C containing 1 % formaldehyde and analyzed within 7 days of collection. In the lab, an aliquot of the sample is filtered, spiked with surrogate, and analyzed directly by LC/MS/MS.

4.2.1 Field samples from sewage systems propose a challenging analysis. Since this is a screening technique to determine if APEOs are present, a 10–25 mL aliquot of the sample is filtered through a PVDF syringe driven filter unit before spiking with surrogate. It was demonstrated that similar recoveries of the APEOs are achieved filtered and unfiltered using PVDF filters. Filtering using PTFE filters produced much lower recoveries. This practice does not account for the APEOs adhered to particulates or the sample bottle.

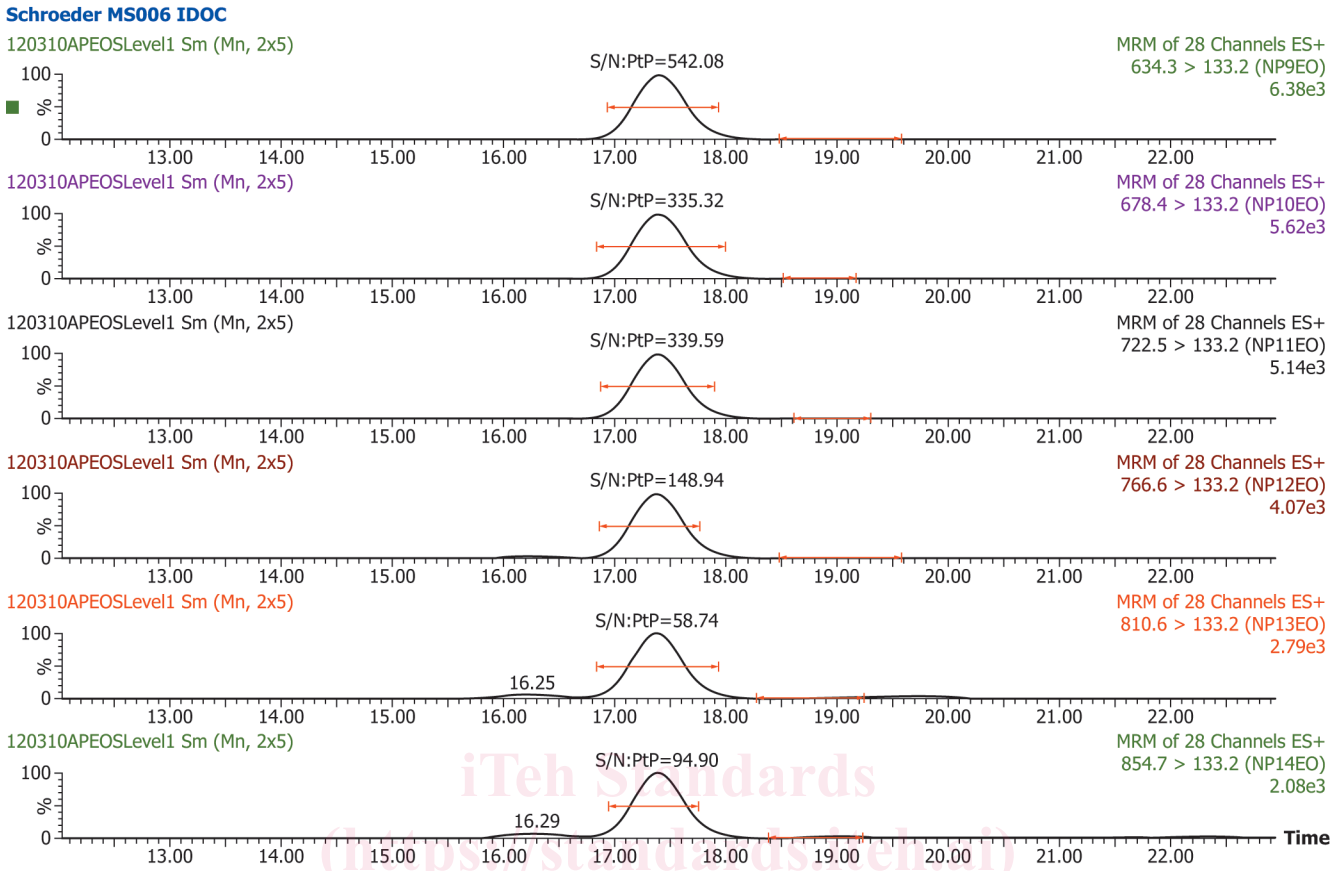

FIG. 2 SRM Chromatograms NP9EO-NP14EO

4.3 Nonylphenol polyethoxylates (NPnEO, $3 \leq n \leq 18$), octylphenol polyethoxylates (OPnEO, $2 \leq n \leq 12$), and n-nonylphenol diethoxylate (n-NP2EO, surrogate) are identified by retention time and one SRM transition. The target analytes and surrogates are quantitated using the SRM transition by external calibration. The final report issued for each sample lists their qualified concentration and the surrogate recovery.

5. Significance and Use

5.1 This practice has been developed in support of the ~~US~~U.S. EPA Office of Water, Office of Science and Technology by the Chicago Regional Laboratory (CRL).

5.2 Nonylphenol (NP) and Octylphenol (OP) have been shown to have toxic effects in aquatic organisms. The prominent source of NP and OP is from common commercial surfactants which are longer chain APEOs. The most widely used surfactant is nonylphenol polyethoxylate (NPnEO) which has an average ethoxylate chain length of nine. The APEOs are readily biodegraded to form NP1EO, NP2EO, nonylphenol carboxylate (NPEC) and NP. NP will also biodegrade, but may be released into environmental waters directly at trace levels. This practice screens for the longer chain APEOs which may enter the STP at elevated levels and may cause a STP to violate its permitted discharge concentration of nonylphenol.

6. Interferences

6.1 Practice interferences may be caused by contaminants in solvents, reagents, glassware and other apparatus producing discrete artifacts or elevated baselines. All of these materials are routinely demonstrated to be free from interferences by analyzing laboratory reagent blanks under the same conditions as the samples.

6.2 All glassware is washed in hot water with detergent such as powdered Alconox, ~~Deto-Jet,~~Det-o-Jet, Luminox, or ~~Citrojet,~~Citrajet,[5] rinsed in hot water, and rinsed with distilled water. The glassware is then dried and heated in an oven at 250ºC for 15 to 30 minutes. All glassware is subsequently cleaned with acetone and methanol. Detergents containing alkylphenolic compounds must not be used.

6.3 All reagents and solvents should be of pesticide residue purity or higher to minimize interference problems.

[5] Alconox, Det-o-Jet, Luminox, and Citrajet are trademarks of Alconox, Inc., White Plains, NY.

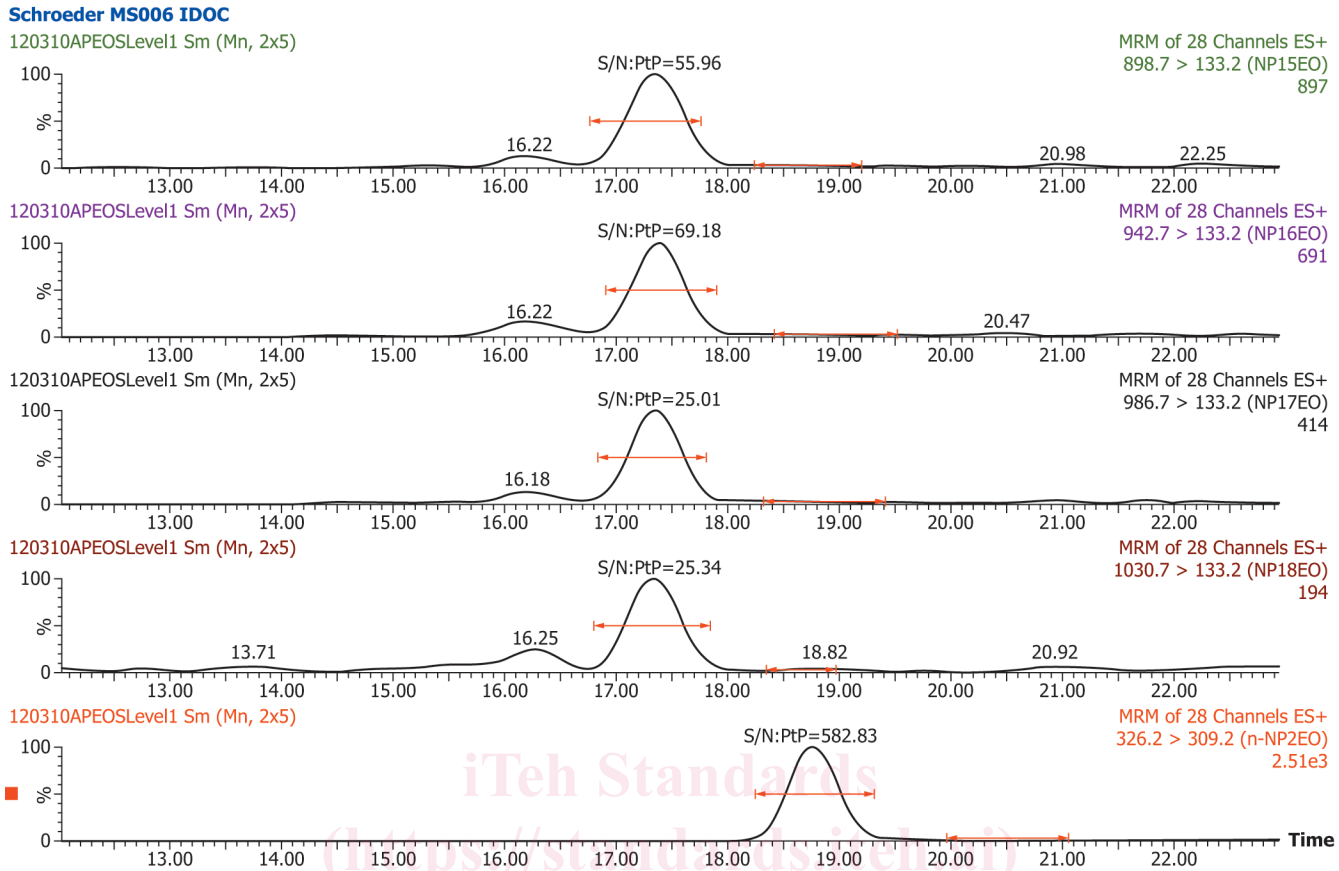

FIG. 3 SRM Chromatograms NP15EO-NP18EO and n-NP2EO

6.4 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences can vary considerably from sample source to sample source, depending on variations of the sample matrix.