Designation: D7993 – 15

Standard Guide for Analyzing Complex Phthalates[1]

This standard is issued under the fixed designation D7993; 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 guide is established in response to regulatory requirements for the determination of complex branched phthalates by CAS numbers. This guide is intended to provide information on how to interpret and analyze data from a chromatographic analysis involving complex phthalates with defined CAS numbers.

1.2 This guide provides a logical approach to determine levels of complex branched phthalates meeting regulatory and CAS number requirements.

1.3 The specific complex phthalates covered within this guide are DINP and DIDP.

1.4 *Limitations*—This guide does not recommend any specific test method. In some cases, it is necessary to deduce the quantity of substance present through the analysis and quantification of its components. Although this approach is routinely used some degree of uncertainty exists in the final result due to the reduced accuracy of the method.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

D1600 Terminology for Abbreviated Terms Relating to Plastics

D3465 Test Method for Purity of Monomeric Plasticizers by Gas Chromatography

D7083 Practice for Determination of Monomeric Plasticizers in Poly (Vinyl Chloride) (PVC) by Gas Chromatography

D7823 Test Method for Determination of Low Level, Regulated Phthalates in Poly (Vinyl Chloride) Plastics by Thermal Desorption—Gas Chromatography/Mass Spectrometry

E355 Practice for Gas Chromatography Terms and Relationships

E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

IEEE/ASTM SI-10 Practice for Use of the International System of Units (SI), the Modernized Metric System

2.2 *Spectral Library:*

NIST/EPA/NIH Mass Spectral Library

2.3 *SPI Association Publication:*

"Analytical Challenges in Detecting regulated Phthalates in Flexible PVC products" SPI Flexible Vinyl Products Division 23rd Annual Compounding Conference, July 17, 2012

3. Terminology

3.1 *Definitions*—For definition of plastic terms used in this test method, see Terminologies D883 and D1600.

3.2 For units, symbols, and abbreviations used in this test method refer to Practices E355, E594, or IEEE/ASTM SI-10.

3.3 *Acronyms:*

3.3.1 *CAS*—Chemical Abstract Services

3.4 *Compounds and Instrumentation:*

3.4.1 *(DINP) 1,2-Benzenedicarboxylicacid, di-C_{8-10}-branched alkyl esters, C_9-rich* CAS #68515-48-0

3.4.2 *(DINP) 1,2-Benzenedicarboxylicacid, 1,2-diisononyl* CAS #28553-12-0

3.4.3 *(DIDP) 1,2-Benzenedicarboxylicacid, di-C_{9-11}-branched alkyl esters, C_{10}-rich* CAS #68515-49-1

3.4.4 *(DIDP) 1,2-Benzenedicarboxylicacid, 1,2-diisodecyl* CAS #26761-40-0

3.4.5 *GC Gas Chromatography*

3.4.6 *GC-MS Gas Chromatography-Mass Spectrometry*

3.4.7 *LC-MS Liquid Chromatography-Mass Spectrometry*

3.4.8 *PVC Poly(Vinyl Chloride)*

3.4.9 Complex branched phthalates are phthalate diesters/coesters based on alcohols with a variety of branched isomers.

[1] This guide is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.

Current edition approved April 1, 2015. Published April 2015. DOI: 10.1520/D7993-15

[2] 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.

NOTE 1—DINP and DIDP, used in various PVC or formulations in other matrix are technical mixtures. When preparing the phthalate calibration standard, technical grade material shall be used. Specific information on examples of technical grade DINP and DIDP can be located on the internet search engine.

NOTE 2—Branched phthalates have ranges of degrees and positions in branching. Example: Branched C_9 phthalates have ranges of Slightly Branched (primarily monomethyl-1-octyl- and dimethyl-1-heptyl-), Moderately Branched (primarily dimethyl-1-heptyl), and Highly Branched (3,5,5-trimethyl-1-hexyl-).[3]

4. Summary of Guide

4.1 This guide provides a schematic flow diagram, illustrating how to identify and quantify either one or both DINP and DIDP, either in neat chemical form or as extract from a polymer matrix.

4.2 This guide provides identifier for each substance by CAS number and the chemical name that defines that CAS number. Two CAS numbers and two associated chemical names for DINP, and two CAS number and two associated chemical names for DIDP are in Section 3.

4.3 This guide does not specify analytical method or procedure used for speciation. GC-MS and LC-MS are typically used to identify chemical components in a substance.

5. Significance and Use

5.1 The regulatory candidate list classifies substances by CAS number. Complex branched phthalates, such as DINP or DIDP, manufactured with a defined alcohol distribution and registered by CAS number with a chemical description of the composition, shall be considered a single substance with that composition as described.

5.2 It is possible for the alcohols used in the manufacture of complex branched phthalates to vary in isomer composition. Care must be used to ensure a representative standard is used to the quantitation of the level of a complex branched phthalate.

[3] Handbook of PVC Formulating. Edward Wickson, John Wiley & Sons, 1993.

5.3 This guide is intended to provide a method on how to interpret and determine data from an analysis involving complex branched phthalates with defined CAS numbers. The test procedure employed shall be used to provide speciation information to assist use of the schematic flow diagram.

NOTE 3—A discussion on analytical challenges in complex branched phthalate analysis is found in: "Analytical Challenges in Detecting Regulated Phthalates in Flexible PVC Products," SPI Flexible Vinyl Products Division, 23rd Annual Compounding Conference, July 17, 2012.

6. Substance List

6.1 Each of the four substances listed in Table 1 is a unique substance by manufacture defined by its CAS number. Its unique chemical name defines its specific chemical composition as shown in Table 2. Since the same diesters and coesters can be found in each of the four substances, care must be taken to allocate the components to the correct CAS number.

6.2 The schematic flow diagram is designed to aid in the correct allocation as described in 6.1.

7. Scheme Diagram

7.1 Quantification of DINP (1) (2) and DIDP (1) (2) by CAS number shall include the entire distribution profile identified following the flow diagram (see Fig. 1). Distribution profile of DINP (1) or DIDP (1) is sample specific and shall not be defined by controls, which are not from the same sample source.

NOTE 4—Commercially purchased control samples that are not representative of DINP (1), and DIDP (1) can introduce significant error in both qualitative and quantitative analysis. Examples are shown in the publication referenced in Note 3.

7.2 Some other complex substances with different CAS numbers, which share similar components as DINP and DIDP must not be mistaken as containing DINP or DIDP. Care must be used to properly identify correctly. Some of such substances are provided in the reference library list in Practice D7083.

7.3 A second set of scheme diagram is provided in Annex A1, using m/z mass ions in the flow cells as reference.

TABLE 1 DINP and DIDP Substances CAS Number and Their Corresponding Registered Chemical Names

Substance Name	CAS Number	Chemical Names
DINP (1)	68515-48-0	1,2-Benzenedicarboxylicacid, di-C_{8-10}-branched alkyl esters, C_9-rich
DINP (2)	28553-12-0	1,2-Benzenedicarboxylicacid, 1,2-diisononyl
DIDP (1)	68515-49-1	1,2-Benzenedicarboxylicacid, di-C_{9-11}-branched alkyl esters, C_{10}-rich
DIDP (2)	26761-40-0	1,2-Benzenedicarboxylicacid, 1,2-diisodecyl

TABLE 2 DINP and DIDP Substances CAS Number and Their Chemical Compositions

Substance Name	CAS Number	C_n/C_m- Chemical Composition of 1,2-C_n/C_m-phthalate (C_n and C_m are groups of branched isomers)
DINP (1)	68515-48-0	$C_8/C_8 < C_8/C_9 < C_9/C_9 > C_9/C_{10} > C_{10}/C_{10}$ (plus C_8/C_{10})
DINP (2)	28553-12-0	C_9/C_9
DIDP (1)	68515-49-1	$C_9/C_9 < C_9/C_{10} < C_{10}/C_{10} > C_{10}/C_{11} > C_{11}/C_{11}$ (plus C_9/C_{11})
DIDP (2)	26761-40-0	C_{10}/C_{10}

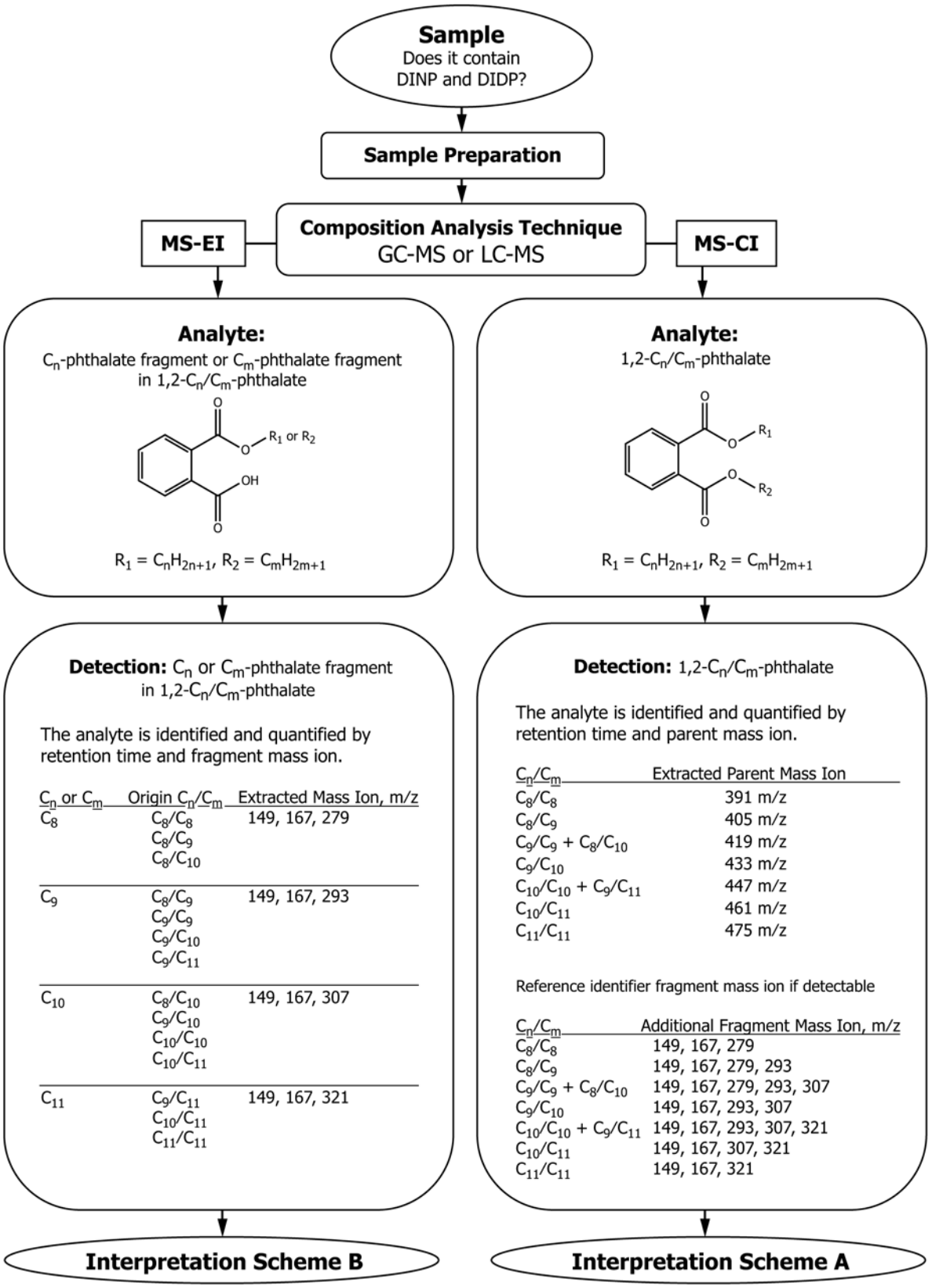

FIG. 1 Scheme Diagram

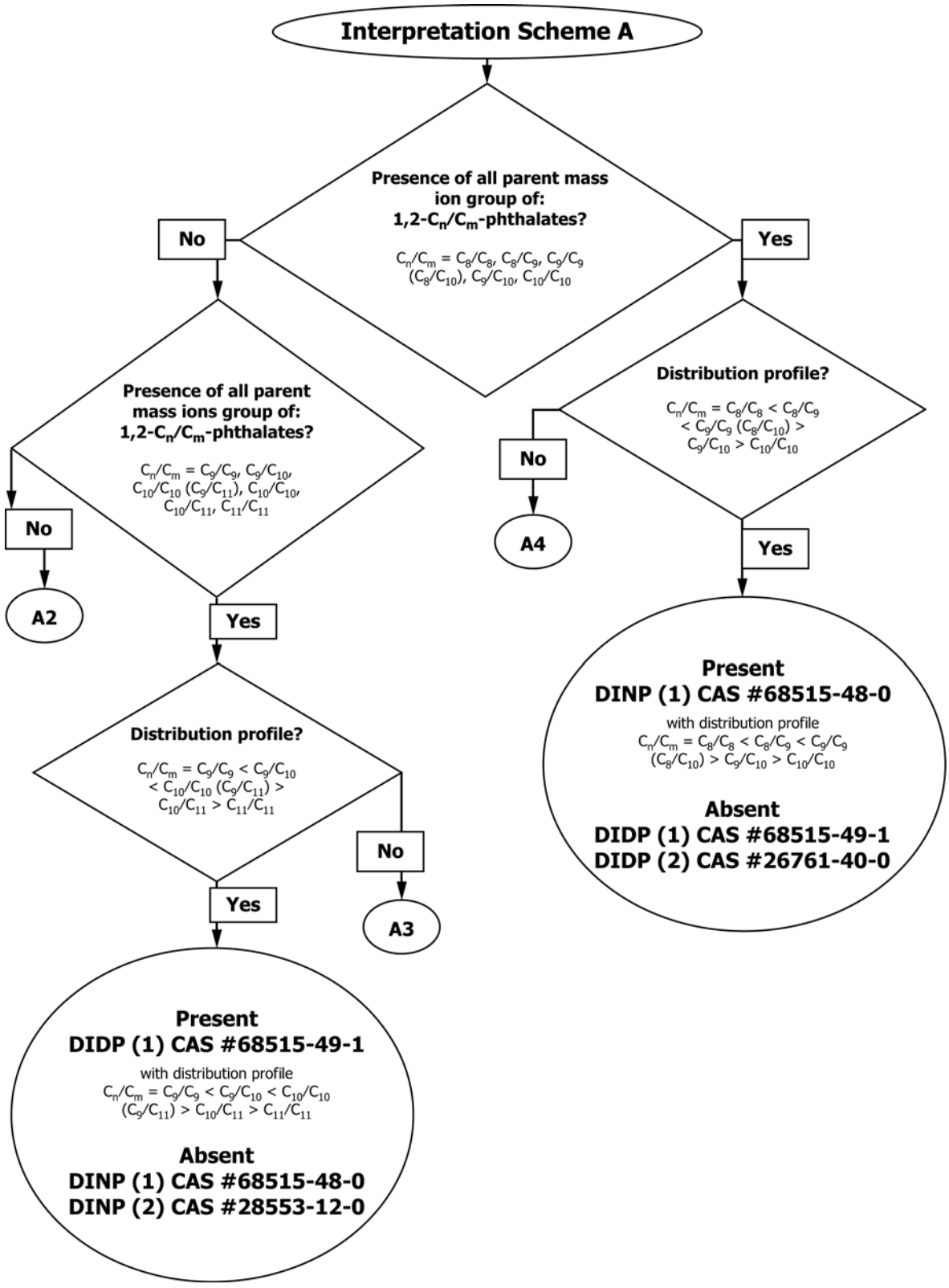

FIG. 1 *(continued)*

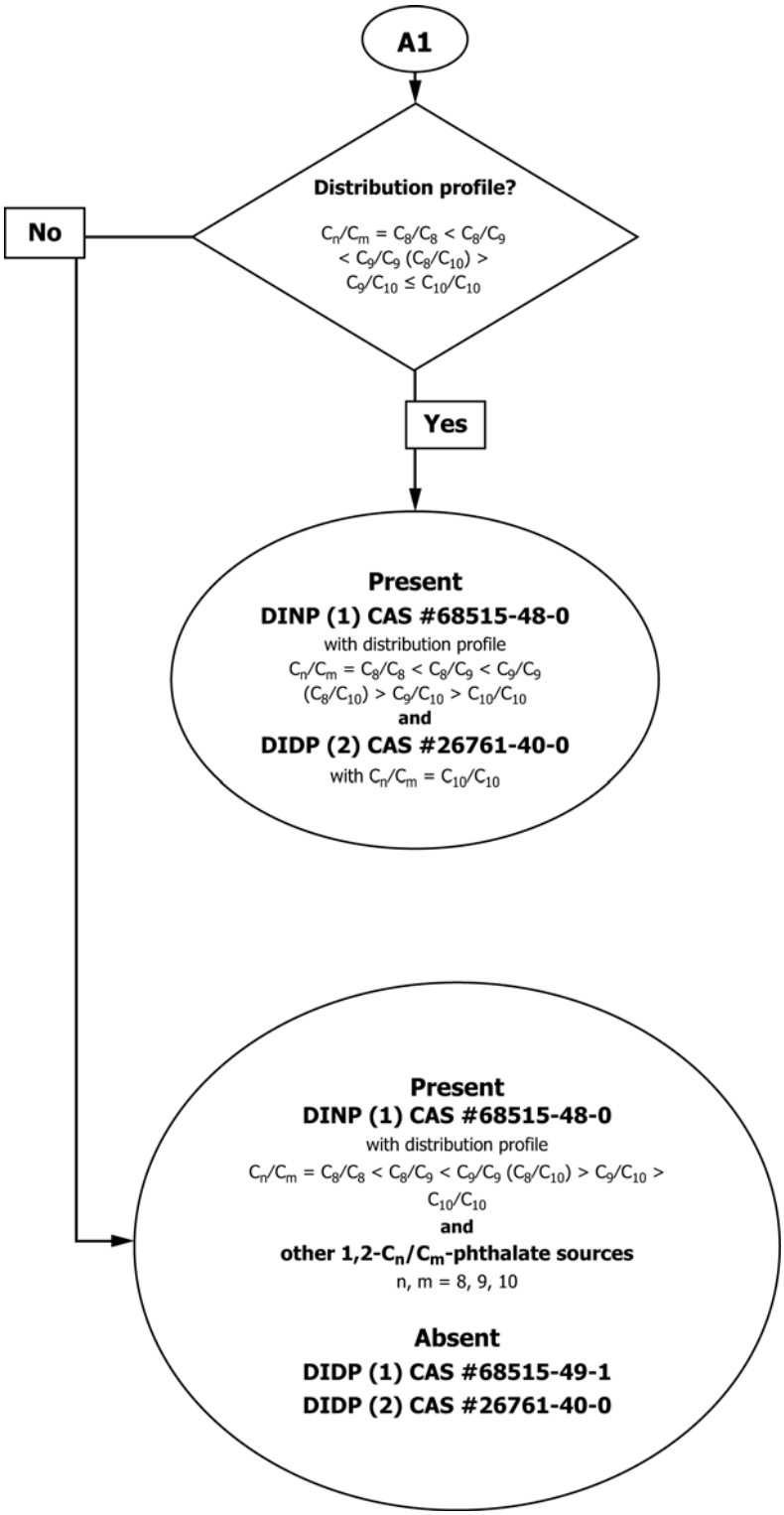

FIG. 1 *(continued)*

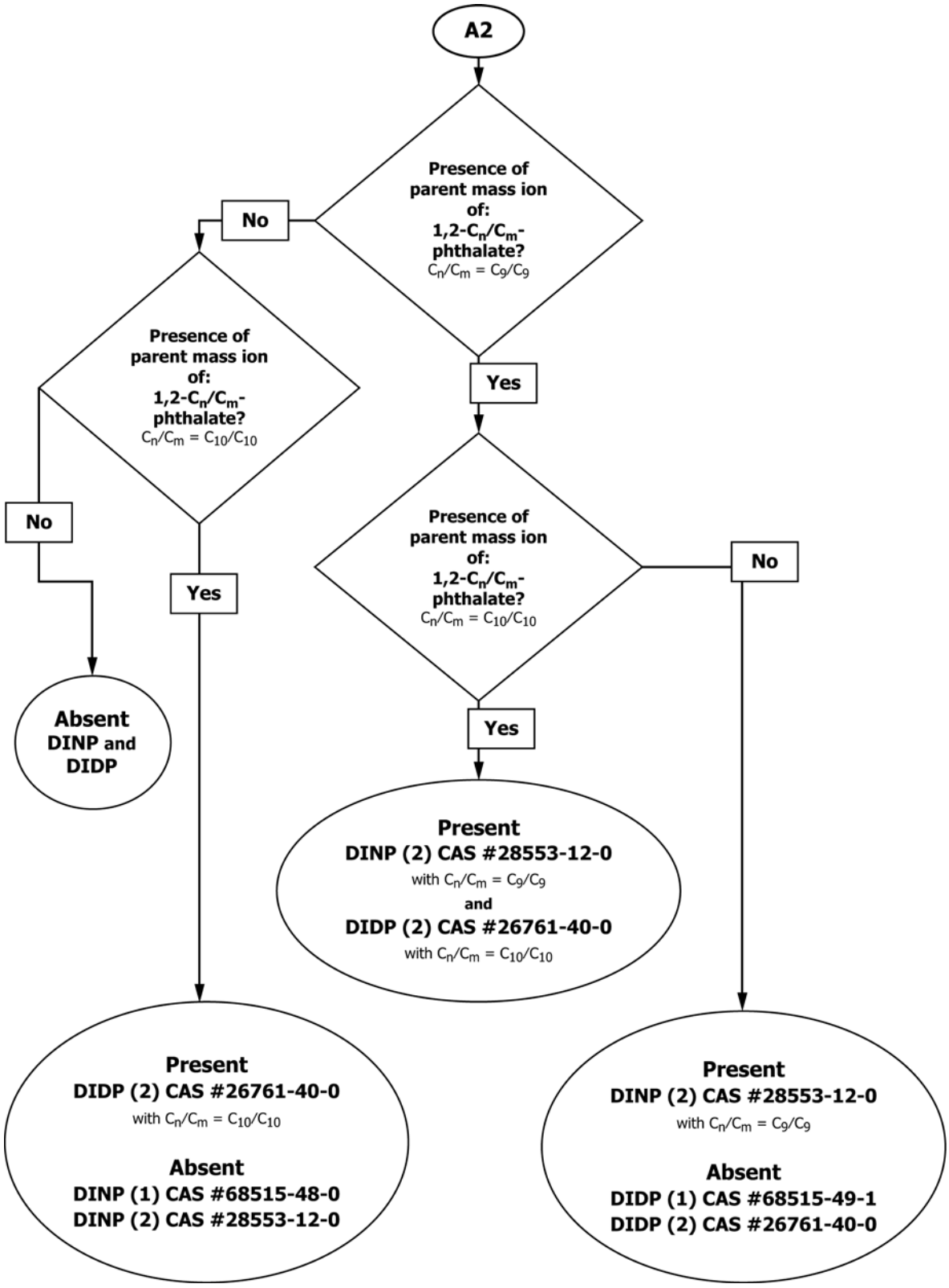

FIG. 1 *(continued)*

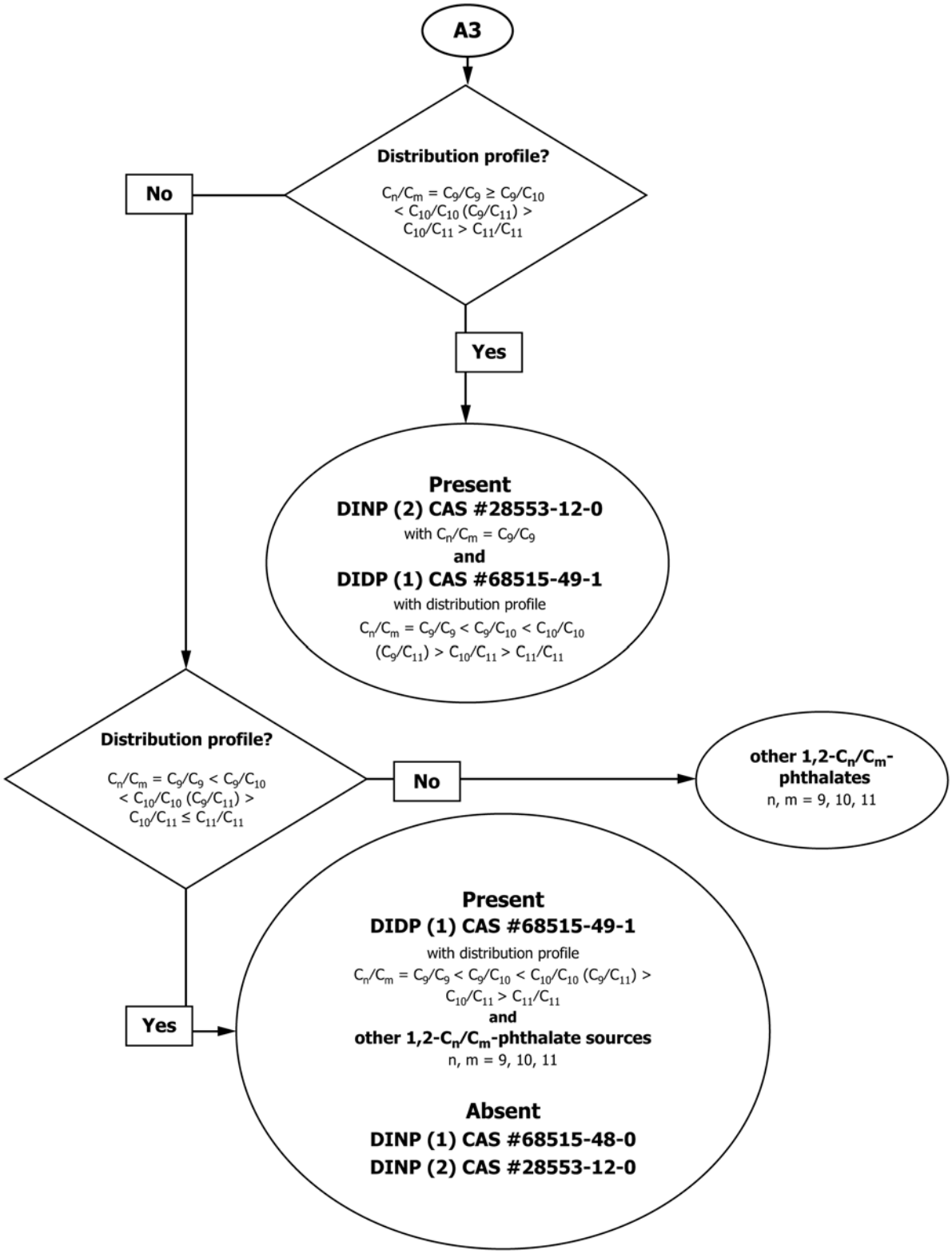

FIG. 1 *(continued)*

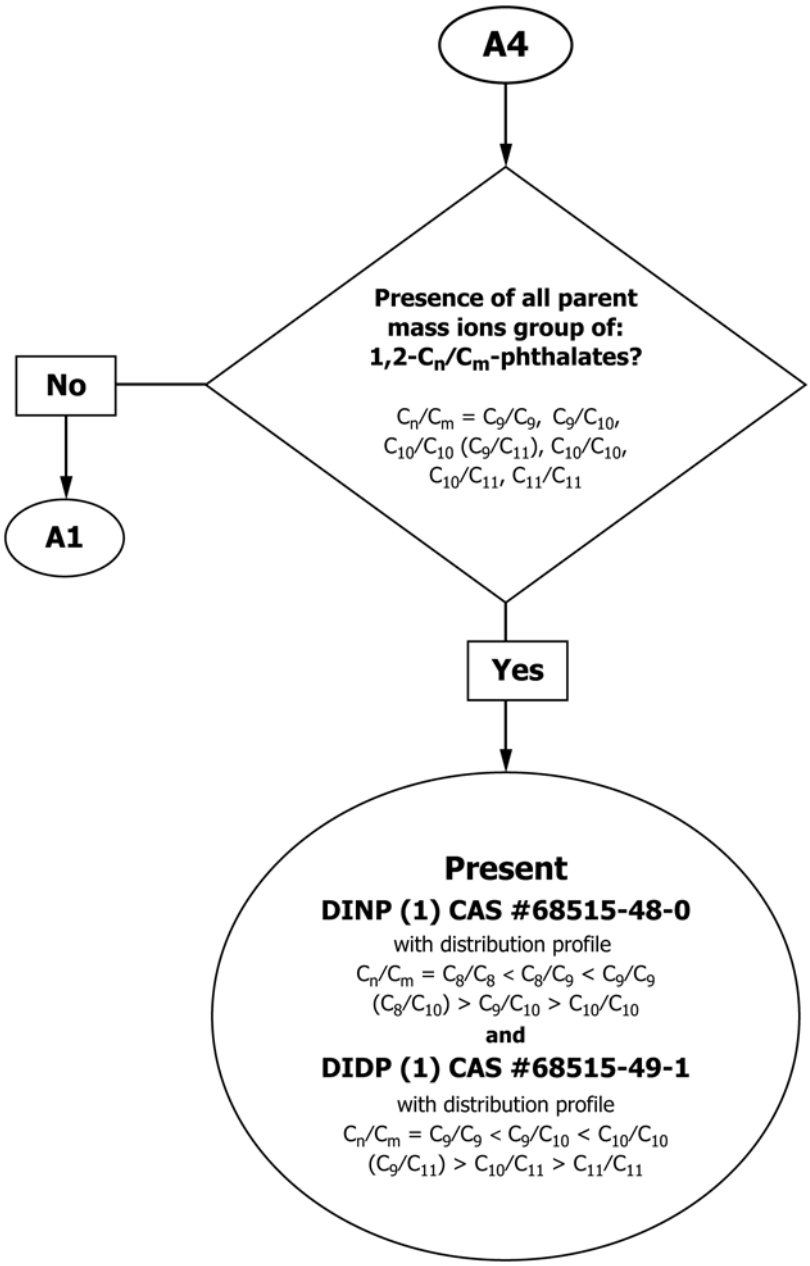

FIG. 1 *(continued)*

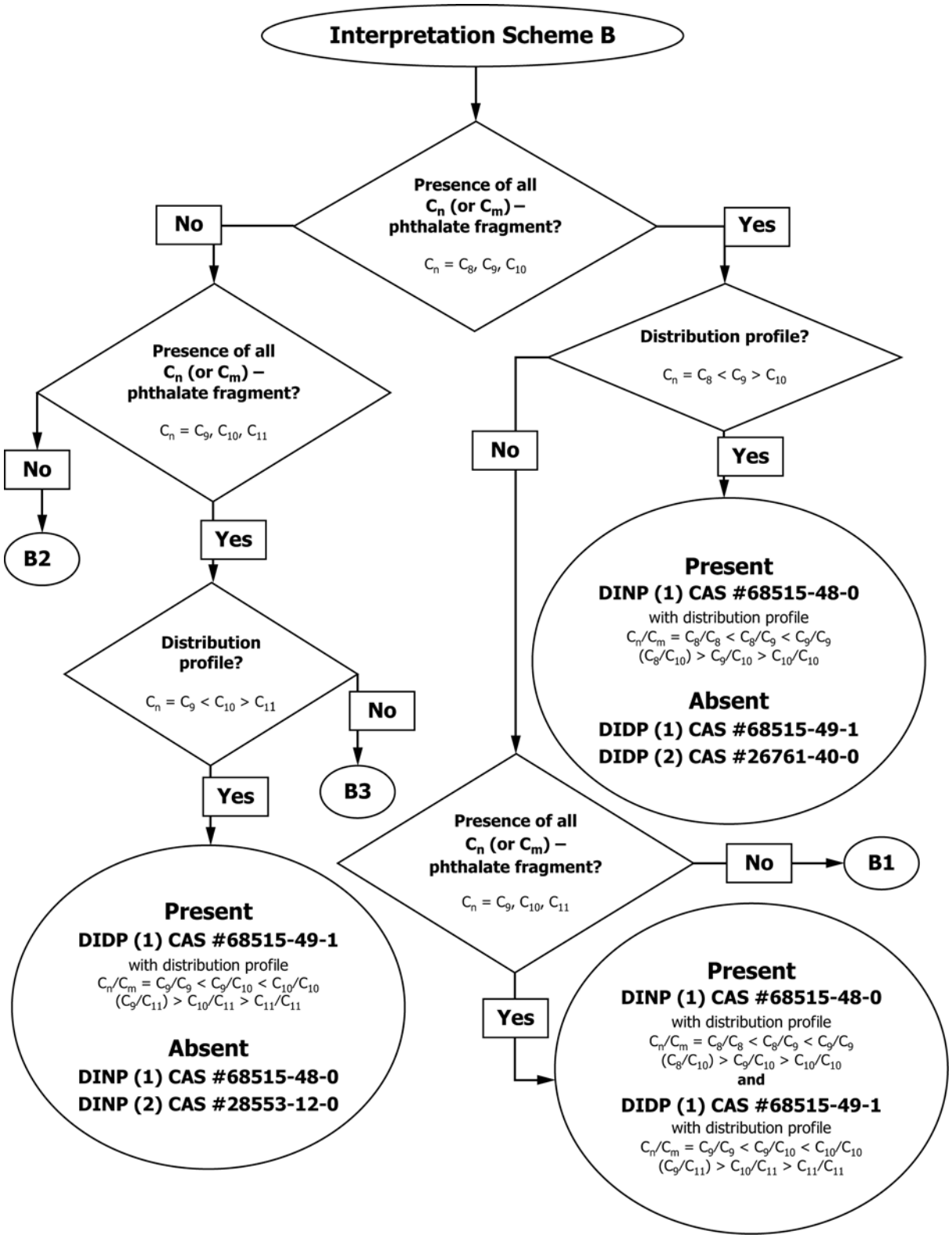

FIG. 1 *(continued)*

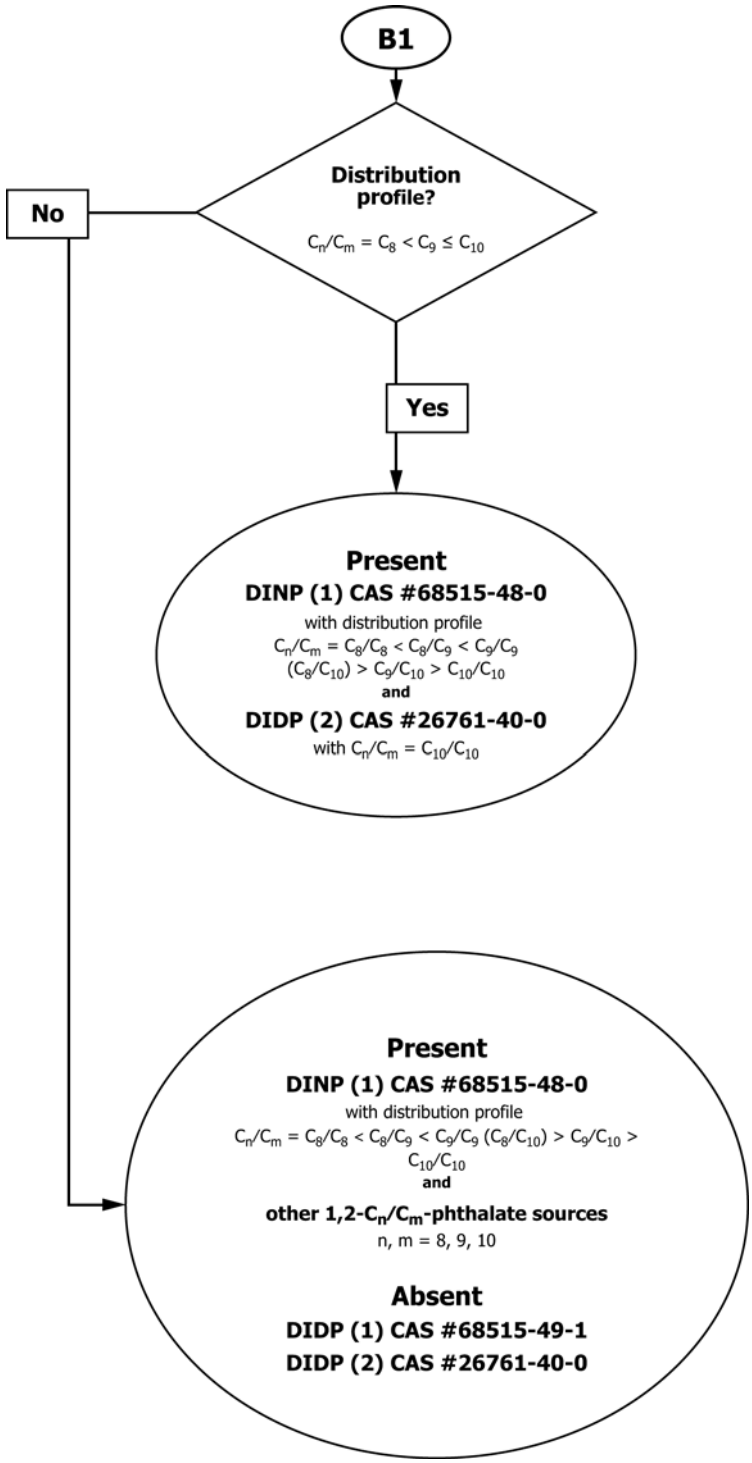

FIG. 1 *(continued)*

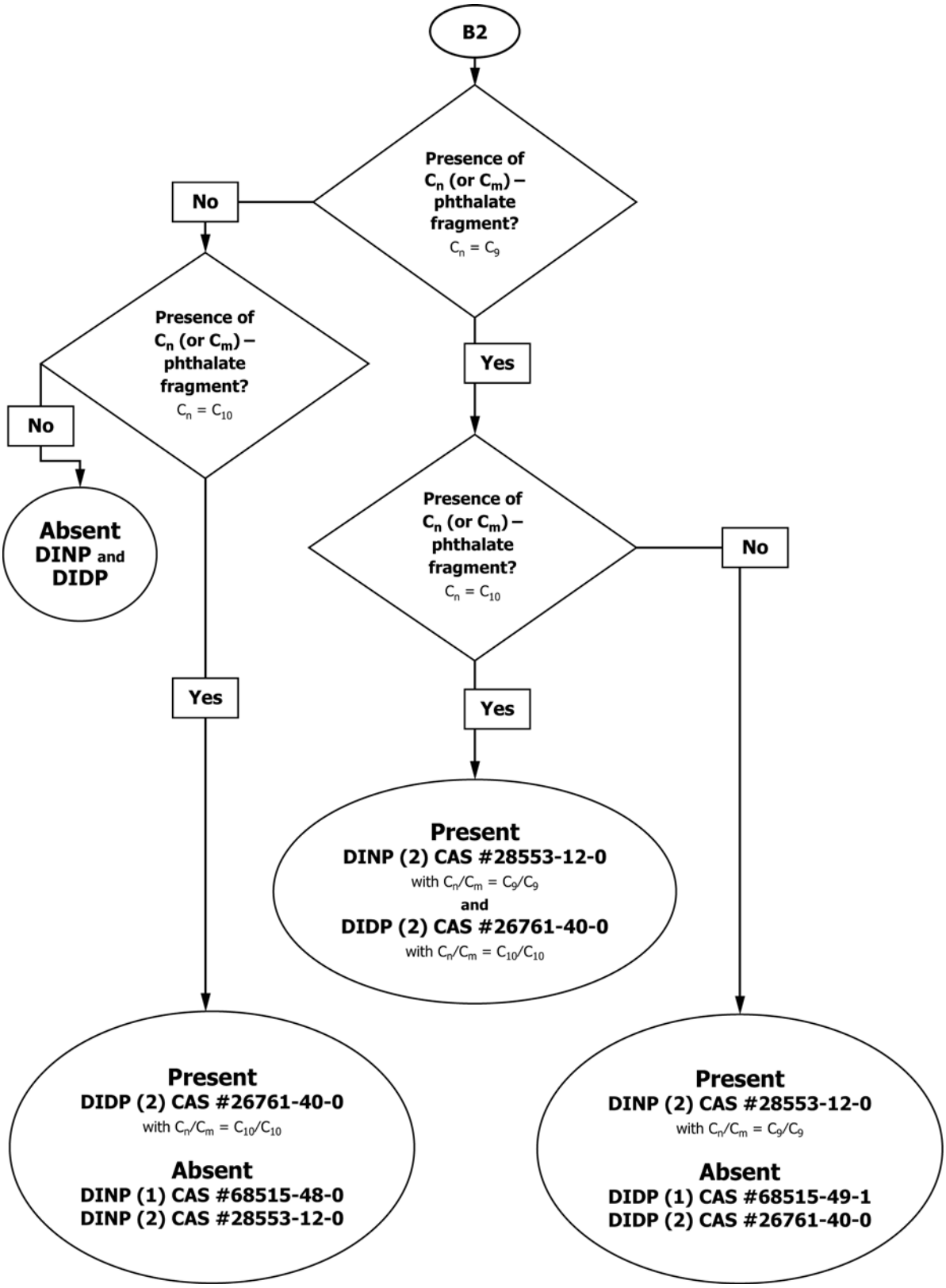

FIG. 1 *(continued)*

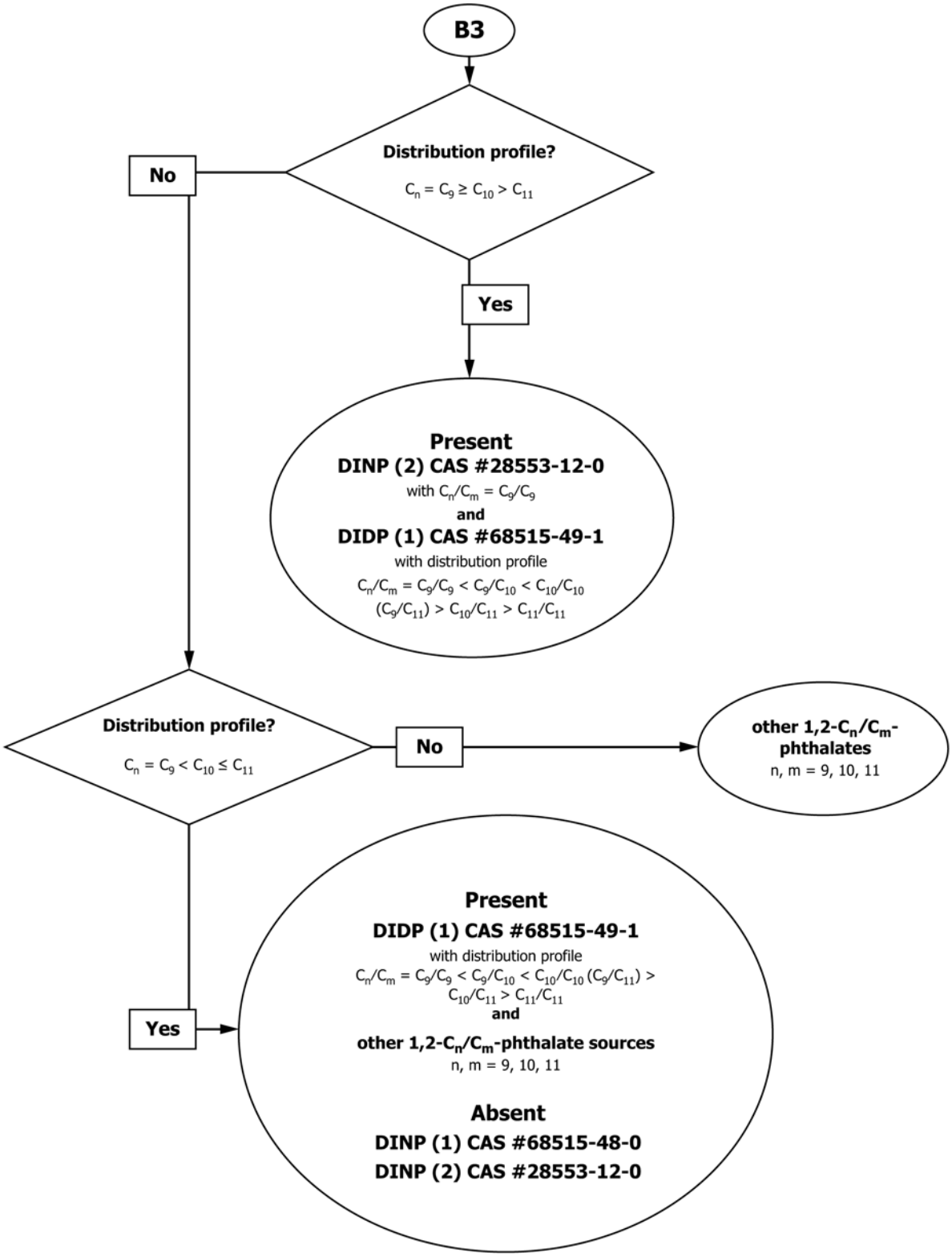

FIG. 1 *(continued)*

ANNEX

(Mandatory Information)

A1. SCHEME DIAGRAM USING m/z MASS IONS IN THE FLOW CELLS AS REFERENCE

A1.1 See Fig. A1.1.

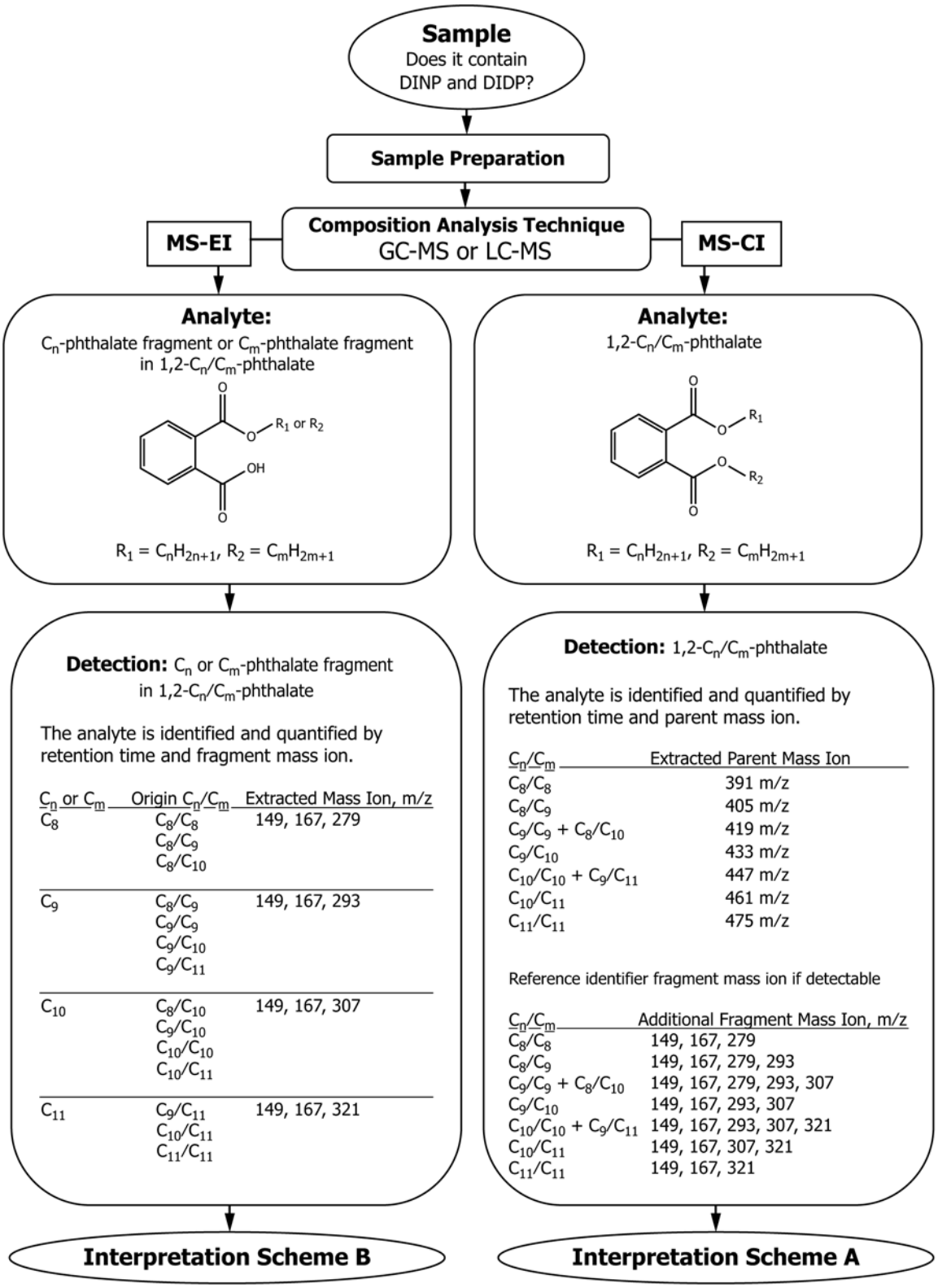

FIG. A1.1 Scheme Diagram

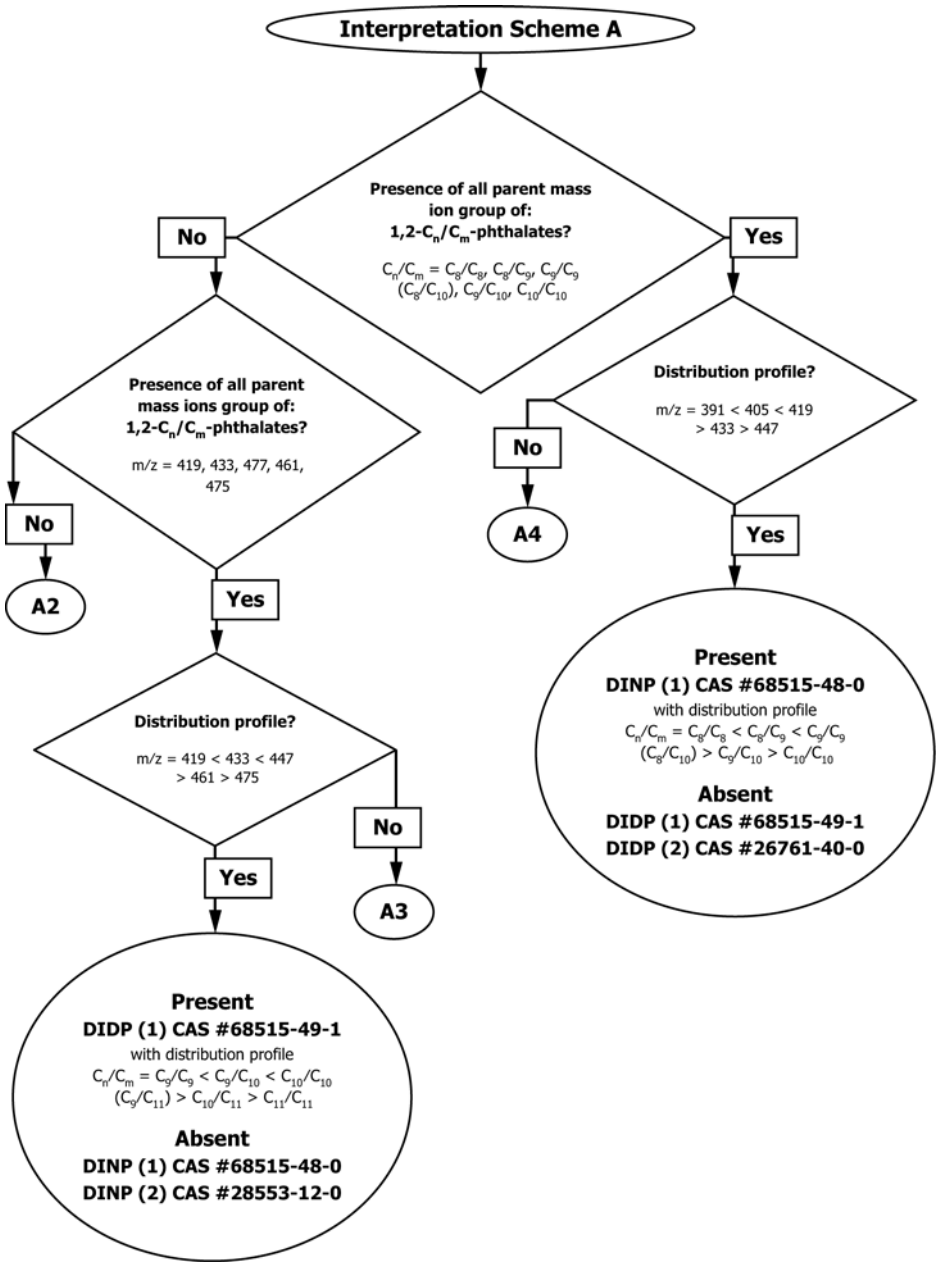

FIG. A1.1 *(continued)*

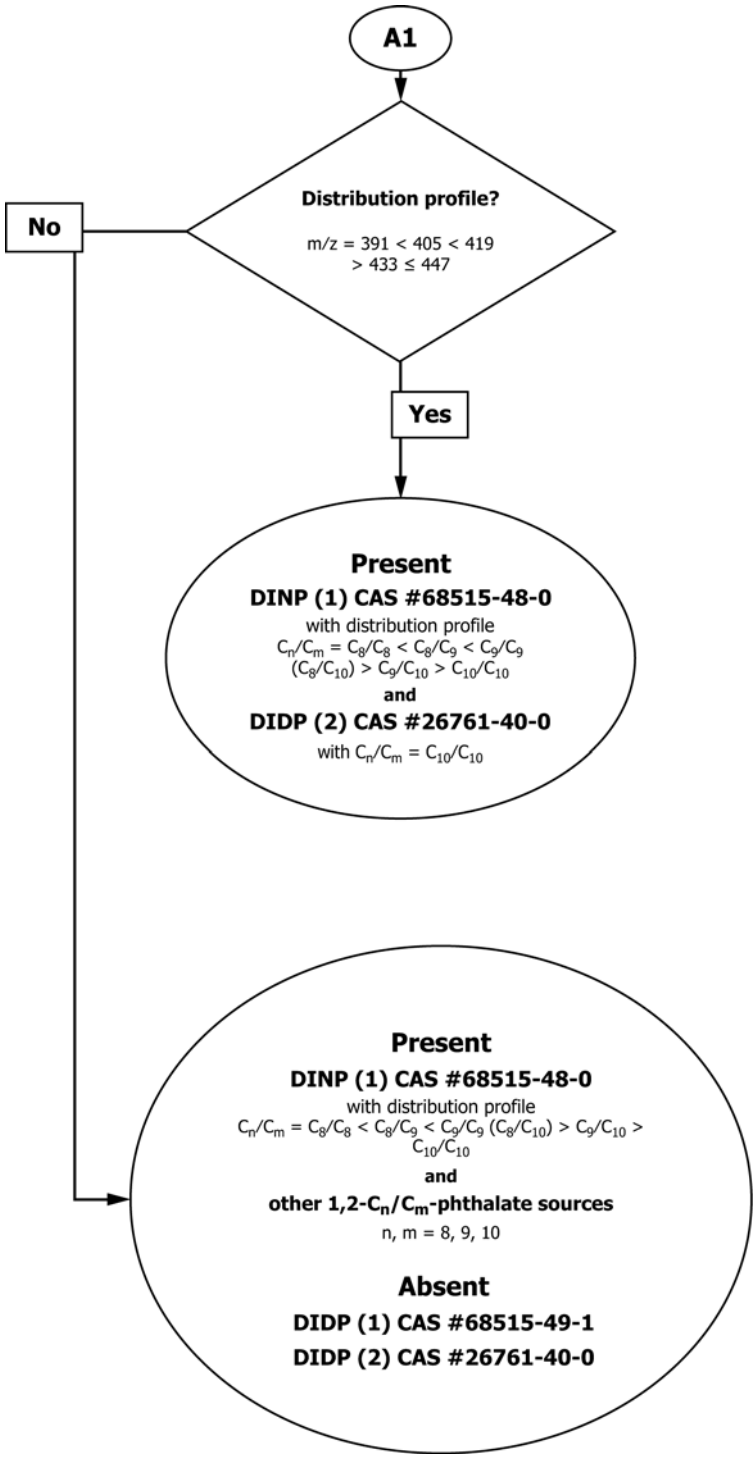

FIG. A1.1 *(continued)*

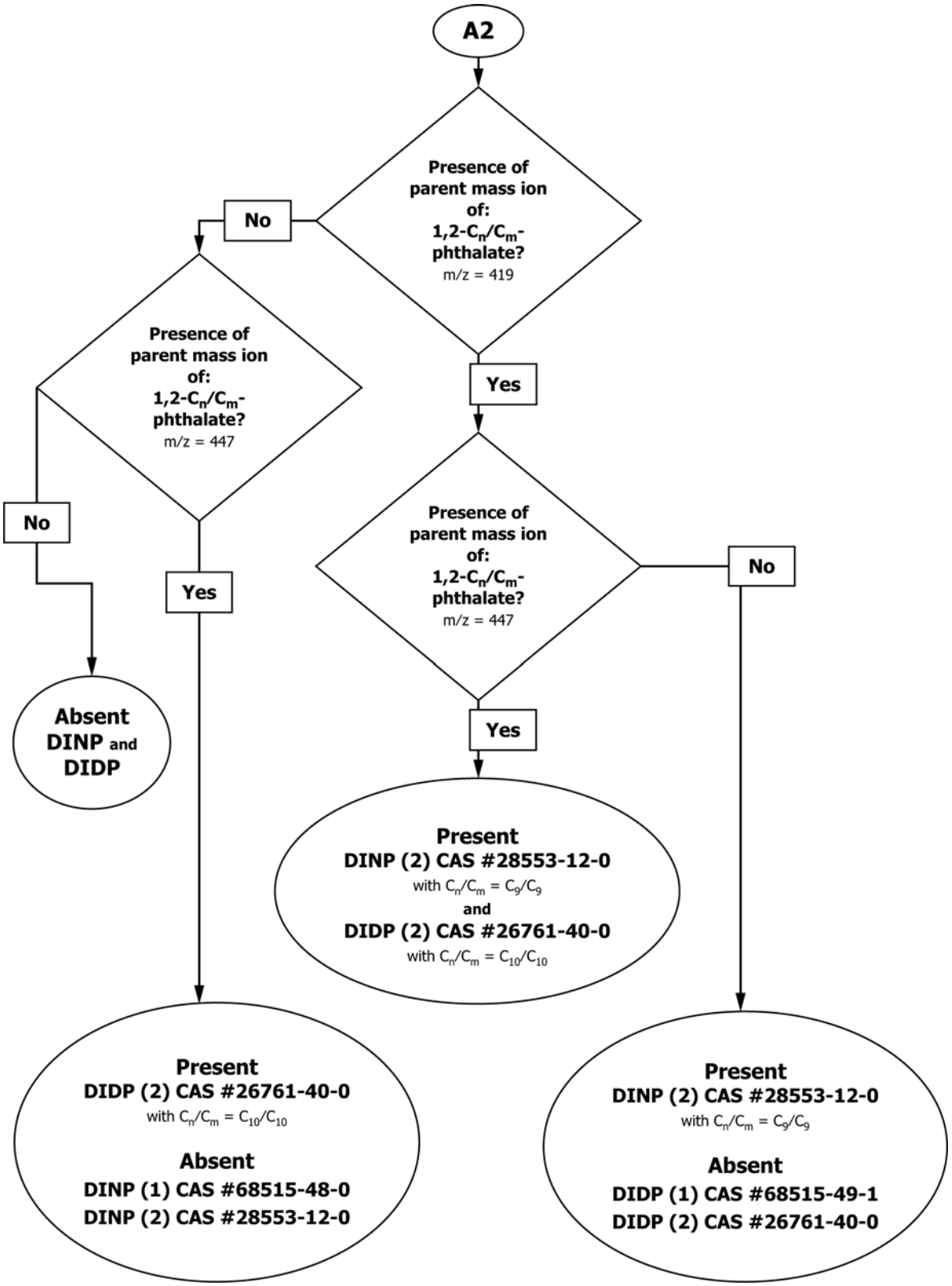

FIG. A1.1 *(continued)*

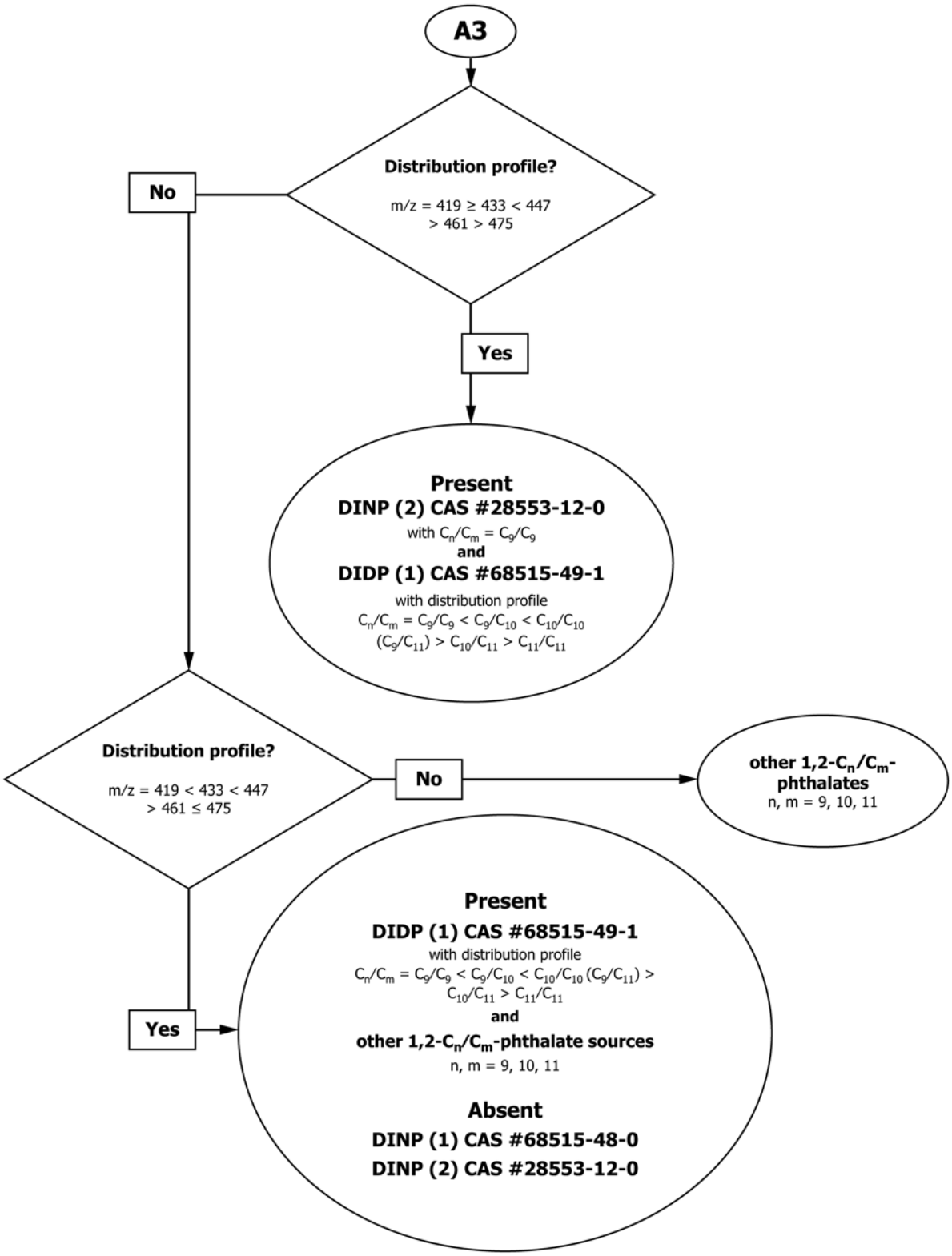

FIG. A1.1 *(continued)*

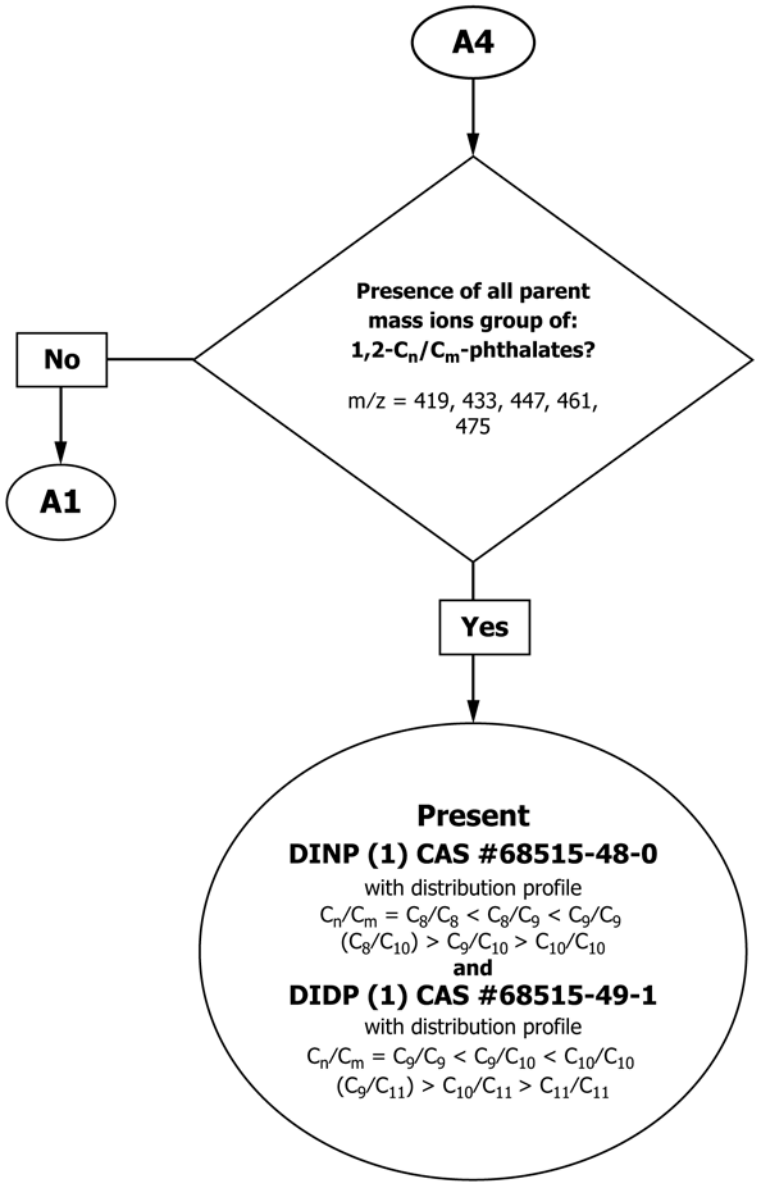

FIG. A1.1 *(continued)*

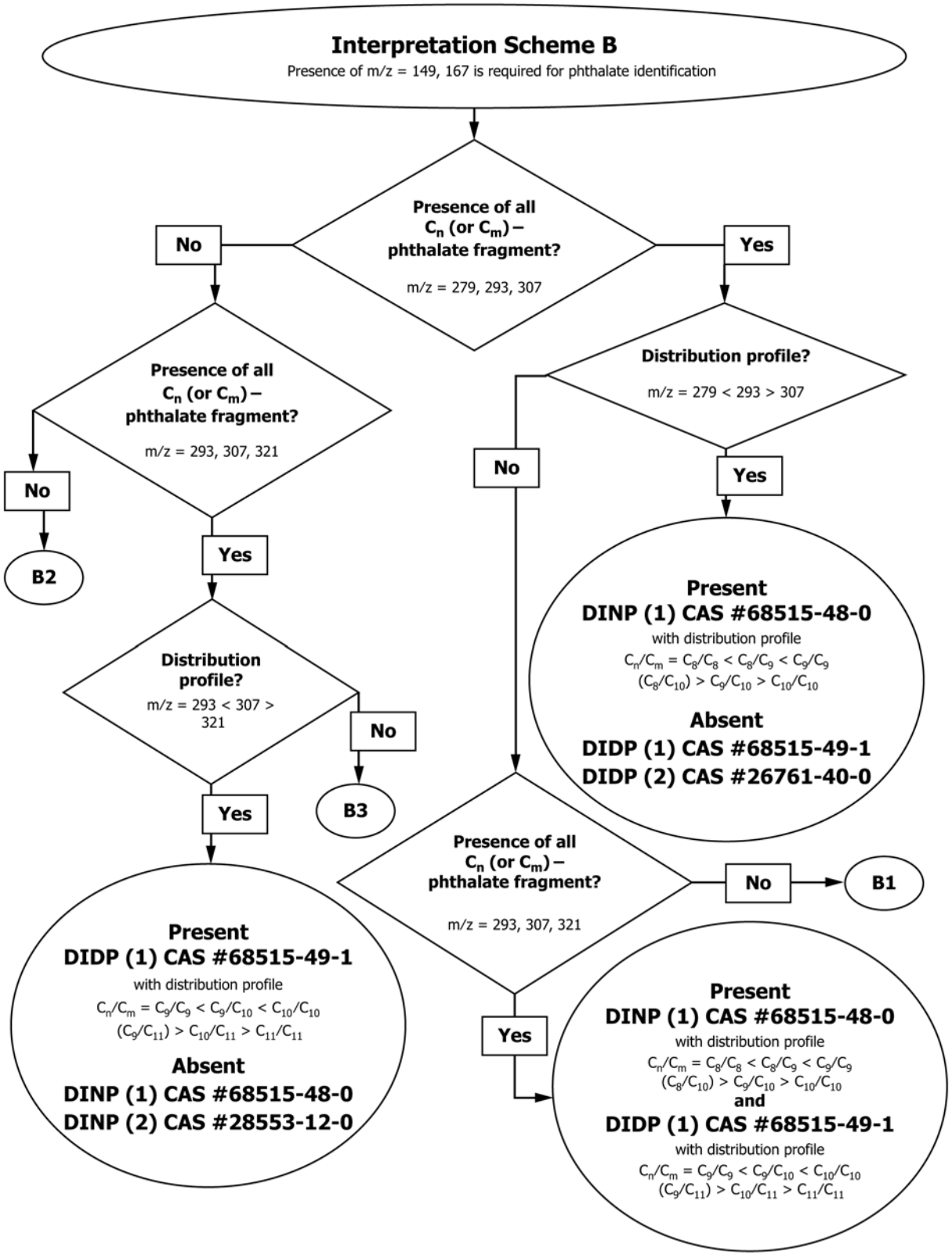

FIG. A1.1 *(continued)*

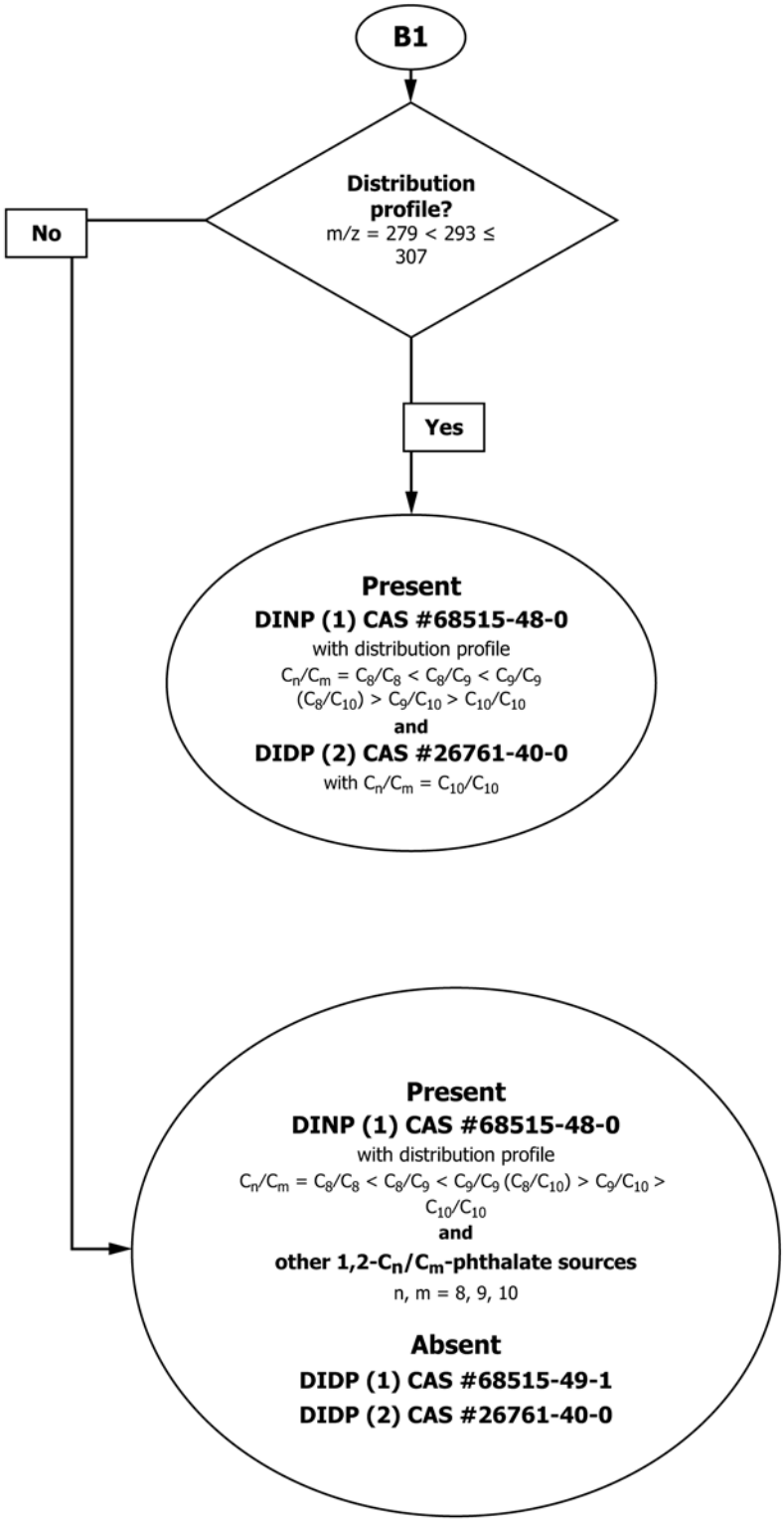

FIG. A1.1 *(continued)*

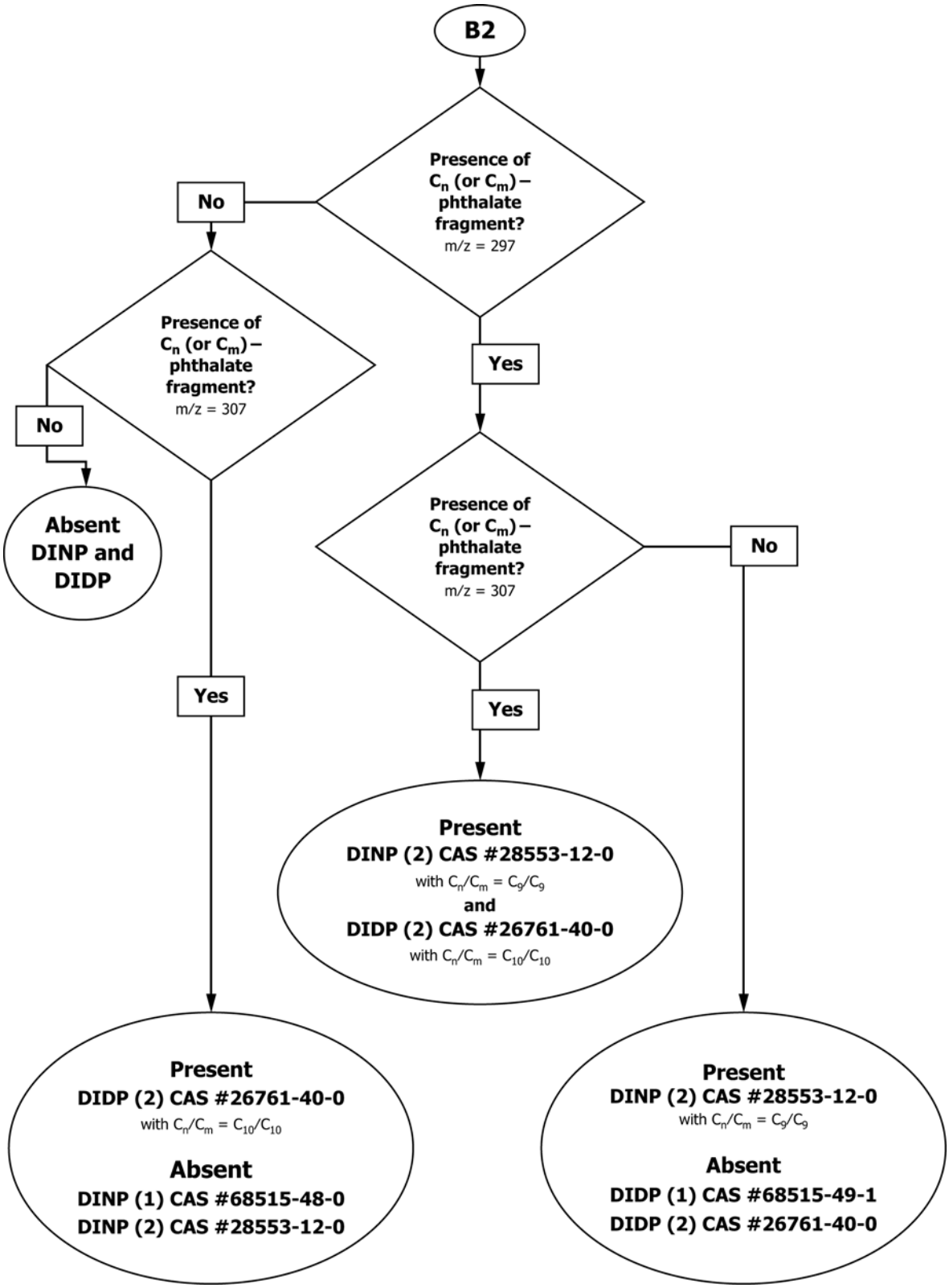

FIG. A1.1 *(continued)*

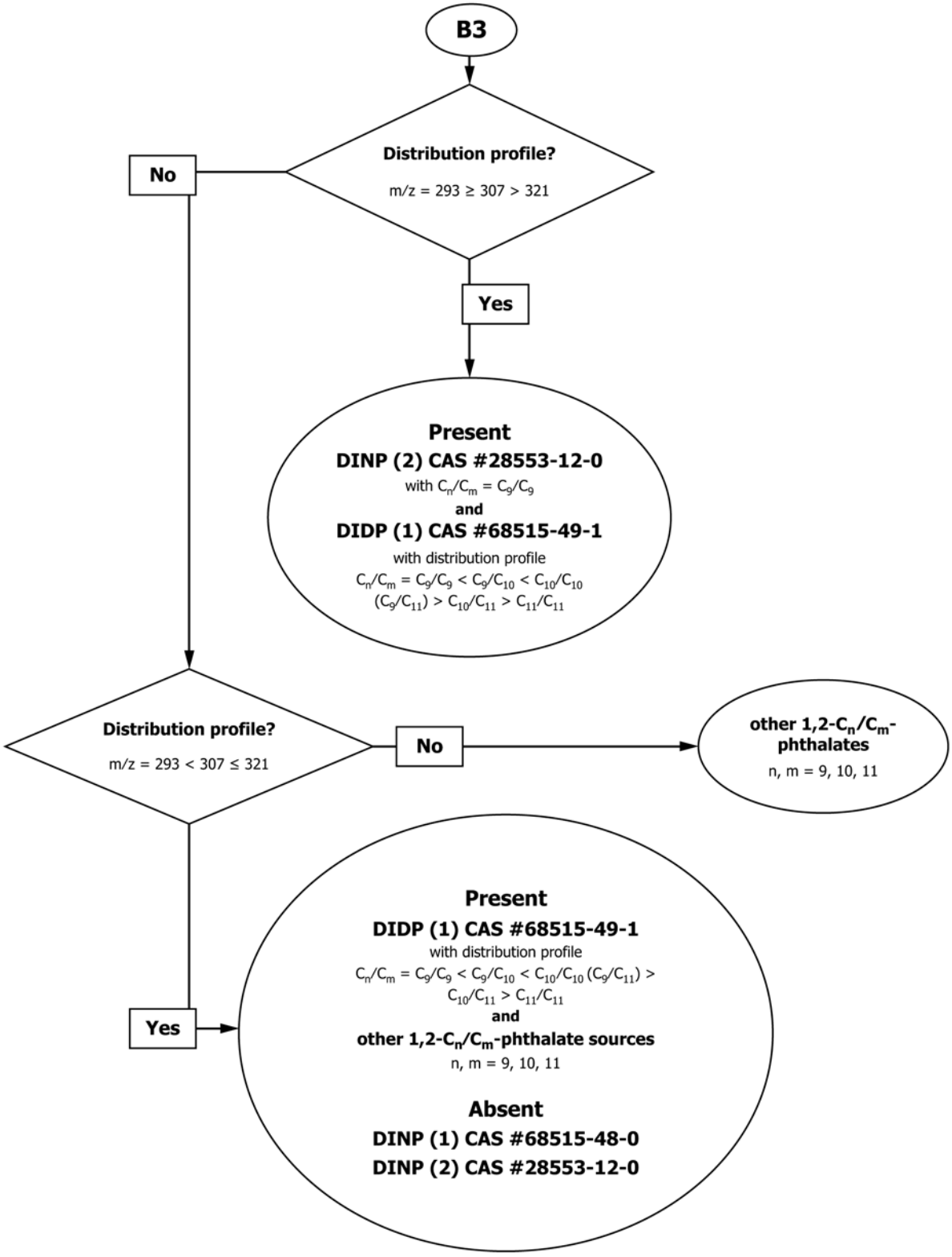

FIG. A1.1 *(continued)*