



**OPCW**

**Technical Secretariat**

---

S/1686/2018  
13 November 2018  
ENGLISH only

**NOTE BY THE TECHNICAL SECRETARIAT**

**PROCEDURES FOR THE EVALUATION OF DATA TO BE INCLUDED IN  
THE OPCW CENTRAL ANALYTICAL DATABASE**

At its forty-seventh meeting, held on 25 and 26 September 2018, the Validation Group reviewed the document entitled “Procedures for the Evaluation of Data to Be Included in the OPCW Central Analytical Database” (S/1519/2017, dated 21 July 2017). This current Note by the Technical Secretariat (hereinafter “the Secretariat”) supersedes S/1519/2017.

Annex: Procedures for the Evaluation of Data to be Included in the OPCW Central Analytical Database



## **Annex**

### **PROCEDURES FOR THE EVALUATION OF DATA TO BE INCLUDED IN THE OPCW CENTRAL ANALYTICAL DATABASE**

#### **1. Introduction**

The evaluation of analytical data to be included in the OPCW Central Analytical Database (OCAD) is carried out by the Validation Group (hereinafter “the Group”) in close association with the Scientific Advisory Board (SAB). The work of the Group is reviewed from time to time by the Executive Council (hereinafter “the Council”) in accordance with the procedure, “Proposed Mechanism for Updating the OPCW Central Analytical Database” (EC-IV/DEC.2, dated 5 September 1997), which was adopted by the Council at its Fourth Session and was approved by the Conference of the States Parties at its Second Session (subparagraph 11.2(c) of C-II/8, dated 5 December 1997). The Group consists of specialists experienced in one or more analytical techniques. This paper describes the various steps in the evaluation process that the Group applies.

#### **2. Documentation provided with the analytical data**

Any of the data a contributor submits must be accompanied by the information items not marked “optional” in Appendix 1. Contributors should try to provide as much information as possible on those items the relevant appendix indicates are optional. They may produce a single list for items common to a series of measurements.

#### **3. Documentation of the evaluation process**

3.1 The following requirements and recommendations govern the approval of analytical data:

- (a) The information specified in Appendix 1 must be present, in addition to the analytical data.
- (b) The analytical data must be reviewed by at least three evaluators experienced in the particular analytical technique used.
- (c) The analytical data must be reviewed in accordance with the evaluation criteria for each analytical technique (see Appendix 2).
- (d) The following designations should be used for decisions by individual evaluators:

A = accepted;

B = accepted subject to the minor corrections<sup>1</sup> indicated; data does not have to be presented to the Group again, and there is no change to the OPCW Code;

C = accepted in principle, but subject to the major corrections indicated; corrected data must be resubmitted to the Group (with an “r” for “resubmitted data” in the OPCW Code);

DIS = to be discussed;

N = not accepted; and

P = evaluation postponed.

- (e) The evaluators must present their written comments to the coordinator for each analytical technique before the meeting of the Group at which the data will be discussed. On the basis of these comments, which are included in a checklist (as indicated in Appendix 2), the coordinators prepare a summary report.
- (f) The evaluators must discuss the summary report at a meeting of the Group. Technical approval of the analytical data can be granted only if three or more evaluators for a particular technique have given their written approval. If fewer than three evaluators for a particular technique can attend the meeting, the data can be approved if all the evaluators provide their written approval to the coordinator before the meeting. If fewer than three evaluators for a particular analytical technique can attend the meeting and if the evaluators have not presented their unanimous approval in writing to the coordinator in advance, the summary report shall be discussed at a later meeting of the Group.
- (g) The evaluators should discuss all the differences in the individual evaluations and must reach a consensus on a decision. The result must be provided to the Group and to the Secretariat in a table that lists the OPCW Code, the chemical name, the schedule number, and the evaluation result coded as “A”, “B”, “C”, “P”, or “N”. (See subparagraph 3.1(d) above for the definitions of these designations. “DIS”, which does not refer to a result, is used only within subgroups.)
- (h) The coordinator for each analytical technique must provide the Group with a list of approved analytical data, coded as “A” or “B” only, to be included in a report of the Group.
- (i) The Validation Group shall propose the acceptance of technically valid spectra to the Director-General, who shall propose that the Council approve their inclusion in the OCAD in accordance with the mechanism specified in EC-IV/DEC.2 and subparagraph 11.2(c) of C-II/8.

---

<sup>1</sup>

Minor corrections can be made by the Group, the Secretariat, or the contributor of the analytical data.

- 3.2 All validated analytical data must be accompanied by a summary evaluation report, by which the evaluators of a particular technique indicate that the evaluation criteria have been fulfilled. The final evaluation reports do not give complete instructions on what follow-up actions are required on the evaluated data that—subject to minor or major corrections—has been accepted. Within one month after the Group meets, the coordinators will send a list of the corrections that are needed to the contributors, together with a copy to the Secretariat.
- 3.3 The chemical names provided by the contributors are considered acceptable for identification if they are unambiguous and correspond to the chemical structure. These names are frequently altered as a consequence of the Group's naming rules, and the Group has authorised the Secretariat to make these name changes in the forms that accompany the analytical data. An evaluation that has resulted in a name change must be marked with a "B".

#### **4. Documentation of remedial actions**

- 4.1 If new analytical data that differs significantly from the data that is either already present in the OCAD or that has been approved for inclusion for a chemical becomes available, the data must be re-evaluated in accordance with the rules applied to new data. The replacement of data that has already been accepted must be documented, and the Group shall propose to the Director-General any further additions or replacements, in accordance with the mechanism established in EC-IV/DEC.2 and approved by the Council (see subparagraph 11.2(c) of C-II/8). However, the Secretariat can correct misprints or minor errors in the approved data in the OCAD in accordance with standard operating procedures.
- 4.2 If there is evidence of the presence of incorrect or low-quality data in the OCAD, the Group should be notified. The data and the evidence will be evaluated in accordance with the regular procedure. In the case of multiple entries, data of a lower quality can readily be removed, whereas in the case of a single entry, the data should be re-measured as a priority and submitted for evaluation to the Group.
- 4.3 When necessary, analytical data can be accepted during the Group's meetings, after evaluators who are present at the meeting have made minor modifications to the accompanying information (see Appendix 1). These modifications must be documented and brought to the attention of the Secretariat when the data is resubmitted in electronic form.

#### **5. Submission of EI mass spectra**

- 5.1 Mass spectra submitted for inclusion in the OCAD must meet specific criteria if they are to be evaluated by the Group. In addition, the spectra must be provided to the Secretariat in specified formats.

- 5.2 The following requirements and recommendations govern the submission of data:
- (a) Spectra must be accompanied by the information specified in Appendix 1 and must satisfy the minimum requirements listed there. The accompanying information must be in electronic form.
  - (b) Spectra that have been obtained on ion-trap instruments will not be accepted.
  - (c) It is recommended either that spectra acquired by GC-MS be extracted with the automated mass spectral deconvolution and identification system (AMDIS), or that they be averaged across the GC peak and an appropriate background be subtracted.
  - (d) The Secretariat requires that electronic spectra be submitted in NIST MS database format. Contributing laboratories are requested to place the OPCW Code and the schedule number in the Synonym field of the database and include the RI field. The file may be transmitted to the Secretariat either as a NIST MS user database or in the form of the corresponding set of text files representing the .MSP (spectral) and .MOL (structure) information.
  - (e) MS data will not be accepted without the corresponding GC(RI) data if it can be acquired.
  - (f) Laboratories are strongly encouraged to provide a table linking the OPCW codes for the MS and corresponding GC(RI) data.
- 5.3 The Secretariat must provide the spectra and the accompanying information to the Group as a NIST MS user database and provide documents in Adobe portable document format (PDF). It must also provide printouts of the spectra and of the accompanying information on request, and verify that the information provided to the Group is a true copy of the information submitted.
- 6. Submission of GC data**
- 6.1 GC data submitted for possible inclusion in the OCAD must meet specific criteria before the Group can evaluate it. The data must be accompanied by the information specified in Appendix 1. The accompanying information must be in electronic form.
- 6.2 The GC conditions recommended for the production of the retention index (RI) data are as follows:  
Column: length 30 m, internal diameter 0.25 mm, film thickness 0.25 µm  
Stationary phase: 95% dimethyl, 5% phenylsiloxane  
Temperature programme: 40 °C (2 min)-10 °C/min-280 °C (10 min)
- 6.3 GC(RI) data will not be accepted without the corresponding MS or IR data.
- 6.4 Laboratories are strongly encouraged to provide a table linking the OPCW codes for the MS and/or IR and corresponding GC(RI) data.

**7. Submission of data on compounds that have multiple chromatographic peaks**

7.1 For compounds that have multiple chromatographic peaks, laboratories are requested to submit data for all of the peaks for which high quality data are available.

7.2 The compound shall be given one single OPCW Code number followed by a letter. The letters shall start at “a” for the first peak eluting, “b” for the second peak, and so on and shall be consistent between the two techniques (GC(RI) and MS).

7.3 There should be a consistent set of data from each laboratory. For example, if a laboratory submits three mass spectra, there shall be three retention indices as well, ordered such that the first peak to elute has an OPCW Code ending in “a” for both spectra corresponding to the GC(RI) “RI(a)” column, “b” the second to the GC(RI) “RI(b)” column, and “c” the third, and so on.

**8. Submission of predicated GC(RI) for the compounds for which only MS data is available in the OCAD**

8.1 The calculation shall be fully explained with a description of the predication methodology in the submission.

8.2 An estimated uncertainty of the predicted data shall be provided.

8.3 Calculations shall be carried out for a minimum of three similar chemicals for which the GC(RI) data already exists in the OCAD.

**9. Evaluation of mass spectra data and GC(RI) data outside the Group’s scheduled meetings**

9.1 The validation of data shall follow the normal validation rules of the Group.

9.2 Communication between the Laboratory, the Chairperson of the Group, the coordinators of the various analytical techniques, and Group members can be conducted via e-mail, telephone, or during in-person meetings.

9.3 The Laboratory shall prepare more detailed sets of information to aid Group members in the evaluation, and will include the following for MS data:

- (a) an explanation for each major and all important ions;
- (b) if available, spectra of comparable chemicals from the OCAD, with a brief discussion of the differences (e.g. the m/z shift due to propyl vs. methyl substitution); and
- (c) if appropriate, the relative isotope ratios of the spectra will be contrasted with the calculated values.

9.4 Additional information for GC(RI) data will include a comparison of the RI value obtained with the RI of other similar chemicals, including the measurements of the differences between the observed data and the comparable data, and the corresponding

differences (e.g. the shift that is observed when P=O is replaced by P=S) to other data in the OCAD.

- 9.5 A copy of the GC-MS data file, together with a discussion of the method of sample preparation, shall be given to both subgroups.
- 9.6 The data shall be submitted to the MS and GC(RI) subgroups. At least three evaluators from each group shall have to agree to the acceptance of the data, with no member of the Group raising objections to it. Data can only be accepted if both the MS and GC(RI) data are considered to be acceptable.

## **10. Submission of IR spectra**

- 10.1 IR data submitted for possible inclusion in the OCAD must meet specific criteria before the Group can evaluate it. The data must be accompanied by the information specified in Appendix 1. The accompanying information must be in electronic form.
- 10.2 The IR spectra shall be submitted in Joint Commission on Atomic and Molecular Physical Data (JCAMP-DX) format.

## **11. Submission of NMR spectra**

- 11.1 NMR data submitted for inclusion in the OCAD must meet specific criteria if they are to be evaluated by the Group. In addition, the spectra are requested to be provided to the Secretariat in specified formats.
- 11.2 The following requirements and recommendations govern the submission of data:
- (a) Spectra must be accompanied by the information specified in Appendix 1 and must satisfy the minimum requirements listed there. The accompanying information must be in electronic form.
  - (b) Additionally, the Secretariat requests the submitted data is accompanied with the original spectra in JCAMP-DX format as follows:
    - (i) in version 5.0 or higher;
    - (ii) preferably with both real and imaginary parts included to facilitate phasing; and
    - (iii) including peak picking, if available.
- 11.3 The Secretariat will provide the submitted data and the accompanying information to the Group in Adobe portable document format (PDF) showing the graphic display of the NMR and a text display of the appropriate numeric value for the NMR parameters. The Secretariat must also provide original spectra in submitted JCAMP-DX electronic format so that Group can verify, if needed, that the information provided to the Secretariat corresponds to the original data.

## 12. Submission of tandem mass spectrometry (MS/MS) spectra

12.1 MS/MS spectra submitted for inclusion in the OCAD must meet specific criteria if they are to be evaluated by the Group. In addition, the spectra must be provided to the Secretariat in specified formats.

12.2 The following requirements and recommendations govern the submission of data:

- (a) Spectra must be accompanied by the information specified in Appendix 1 and must satisfy the minimum requirements listed there. The accompanying information shall be in electronic form.
- (b) The Secretariat requires that electronic spectra be submitted in NIST MS database format. Contributing laboratories are requested to place the OPCW code, the schedule number and additional information, including the instrument, precursor ion, collision energy and ionisation information, in the synonym field. NIST software has special codes for the additional information in the synonyms field:

\$:07	Instrument:
\$:06	Instrument type:
\$:08	Special fragmentation:
\$:00	Spectrum type:
\$:03	Precursor type:
\$:04	Precursor m/z:
\$:05	Collision energy:
\$:09	Sample inlet:
\$:10	Ionization:
\$:11	Ion mode:

- (c) Product ion spectra shall be submitted together with reference spectra of tributyl phosphate for positive ion mode or dibutyl phosphate for negative ion mode recorded using the same experimental conditions as for the spectra of the submitted compounds.
  - (d) The spectra shall be recorded at three different collision conditions: low, medium and high energy. For ion trap instruments, the submission of multistage MS/MS ( $MS^n$ ) spectra to increase structural information for relevant compounds is recommended.
- 12.3 The Secretariat must provide the spectra and the accompanying information to the Group as a NIST MS user database and provide documents in Adobe portable document format (PDF). It must also provide printouts of the spectra and of the accompanying information on request, and verify that the information provided to the Group is a true copy of the information submitted.



## Appendix 1

### ANALYTICAL DATA AND ACCOMPANYING INFORMATION

#### MASS SPECTROMETRY

1. The following information must be supplied for each spectrum submitted:

**Data identification:**

OPCW Code

**Chemical identification information:**

Chemical name

Schedule number

CAS registry number (optional)

Chemical structure

Molecular formula

**Sample information:**

Sample purity (optional)

Source (optional)

2. The following information must be supplied but may be given for an entire set of measurements:

**Data identification:**

Contributor's name and address:

**Instrument information:**

Manufacturer

Model

Data system (optional)

Software version (optional)

**Experiment information:**

Inlet system

GC:

Column

Temperature programme

Carrier gas

Injection temperature

Direct probe

Other

Inlet temperature (optional)

Ion source temperature

Ion source pressure (optional)

Electron energy

Emission current (optional)

Scan range

Scan cycle time (optional)

Ion acceleration voltage (optional)

Date of experiment (optional)

**Minimum requirements:**

Lowest starting mass:  $m/z$  40 or lower

Ion list (recorded  $\geq 0.1\%$ )

Ion intensities specified to 1 part in 999 or better

Spectra recorded to  $\geq 50$  amu above the molecular weight of the compound

**Electronic Format:**

Type of electronic format: NIST MS

## EXAMPLE OF A SUBMISSION

### 1. Common information

Analytical conditions for 07-2-0347 to 07-2-0349

Instrument: Finnigan TSQ 7000

Ion source: 180 °C, 70 eV

Range: 33-500 amu, 0.50 s

Inlet system: GC

Column: DB-5, 30 m x 0.25 mm

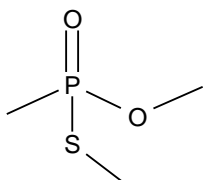
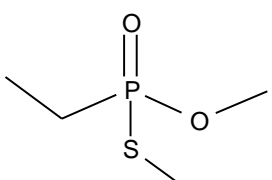
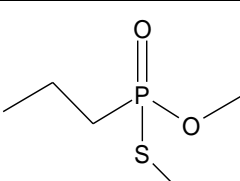
Temperature programme: 40 °C (1 min)-10 °C/min-280 °C (5 min)

Carrier gas: helium

Injection temperature: 250 °C

Laboratory name: Spiez Laboratory, Spiez, Switzerland

### 2. Spectrum-specific information

OPCW Code	Structure	Name	Formula	Schedule Number	CAS No.
07-2-0347		O,S-Dimethyl methylphosphonothiolate	C3H9O2PS	2.B.04	58259-60-2
07-2-0348		O,S-Dimethyl ethylphosphonothiolate	C4H11O2PS	2.B.04	84044-17-7
07-2-0349		O,S-Dimethyl propylphosphonothiolate	C5H13O2PS	2.B.04	90220-19-2

## **GC(RI) DATA**

1. The following information must be supplied for each retention index submitted:

### **Data identification:**

OPCW Code

### **Chemical information:**

Chemical name

Schedule number

CAS registry number (optional)

Chemical structure

Molecular formula (optional)

### **Sample information:**

Sample purity (optional)

Source (optional)

2. The following information must be supplied, but may be given for an entire set of measurements:

### **Data identification:**

Contributor's name and address:

### **Instrument information:**

Manufacturer

Model

Data system (optional)

Software version (optional)

### **Experiment information:**

Dimensions of the GC column

Stationary phase (as indicated by the manufacturer)

Film thickness

Temperature programme

Carrier gas

Injection system

Injection temperature

Detection system

Flow conditions: constant pressure, constant flow

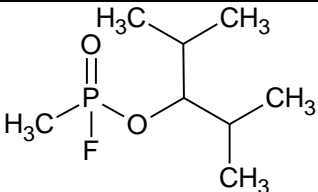
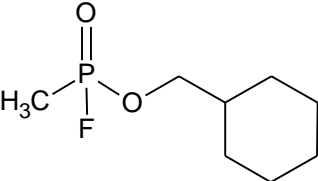
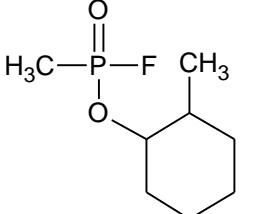
Retention-index standards (n-alkanes)

Date of experiment (optional)

### **Retention index information:**

Standard deviation ( $n \geq 3$  determinations) of the retention indices of the quality control chemicals used over the period of the experiments.

**EXAMPLE OF A SUBMISSION**

<b>OPCW Code</b>	<b>Structure</b>	<b>Name</b>	<b>Formula</b>	<b>CAS No.</b>	<b>Schedule No.</b>	<b>RI(a)</b>	<b>RI(b)</b>
07-4-0425		1-Isopropyl-2-methylpropyl methylphosphonofluoridate	C <sub>8</sub> H <sub>18</sub> FO <sub>2</sub> P	113548-85-9	1.A.1	1137	
07-4-0426		Cyclohexylmethyl methylphosphonofluoridate	C <sub>8</sub> H <sub>16</sub> FO <sub>2</sub> P		1.A.1	1311	
07-4-0427		2-Methylcyclohexyl methylphosphonofluoridate	C <sub>8</sub> H <sub>16</sub> FO <sub>2</sub> P	85473-32-1	1.A.1	1249	1251

(a): RI of the compound or of the first isomer

(b): RI of the second isomer

If there are more isomers, additional columns labelled (c), (d), and so on, are added.

## **NMR SPECTROMETRY**

The following information must be supplied for all NMR spectrometry data submitted:

### **Data identification:**

OPCW Code

Contributor's name and address

### **Chemical information:**

Chemical name

Schedule number

CAS registry number (optional)

Chemical structure with numbering of atoms

Molecular formula (optional)

### **Sample information:**

Sample purity (optional)

Sample concentration (optional)

Solvent

pH (if relevant)

Source (optional)

Reference chemical shift (internal/external)

### **Instrument information:**

Manufacturer

Model

Spectrometer frequency

Data system (optional)

Software version (optional)

### **Experiment information:**

Nucleus measured

Sample temperature

Spectral width (Hz)

Data points in a Fourier-transformed spectrum

Spectra peak picking (labelling)

Repetition time (optional)

Pulse angle ( $\mu$ s and degrees) (optional)

Line width of a certain line (e.g. TMS) (optional)

Window function (e.g. matched window, line broadening factor) (optional)

Date of experiment (optional)

Data points in FID (optional)

Number of scans (optional)

Baseline correction, if used

### **Spectrum information (if available):**

Chemical shifts assigned except for acidic protons, if applicable

Coupling constants

Impurities marked with asterisks

### **Electronic Format:**

Type of electronic format: JCAMP-DX

## IR SPECTROMETRY

The following information must be supplied for all IR spectrometry data submitted:

### Data identification:

OPCW Code

Contributor's name and address

### Chemical information:

Chemical name

Schedule number

CAS registry number (optional)

Chemical structure

Molecular formula (optional)

### Sample information:

Sample purity (optional)

Source (optional)

Sample phase

### Instrument information:

Type (Fourier/grating/prism)

Manufacturer

Model

ATR crystal type

Number of reflections

Angle of incidence

Data system (optional)

Software version (optional)

### Experiment information:

Sampling mode: liquid, solid, solution, gas, light-pipe, tracer, bulk, ATR, or micro

Measurement mode: transmission, absorbance, or reflectance

Baseline correction: (manual/automatic/none)

Matrix

Detector (optional)

Wave-number range

Indication of ordinate scale

Resolution

No ATR correction used, if submitting ATR data

Number of scans (optional)

Date of experiment (optional)

### Electronic Format:

Type of electronic format: JCAMP-DX

## TANDEM MASS SPECTROMETRY (MS/MS)

1. The following information must be supplied for spectra of each of the submitted compounds:

**Data identification:**

OPCW Code

**Chemical identification information:**

Chemical name

Schedule number

CAS registry number (optional)

Chemical structure

Molecular formula

**Sample information:**

Sample purity (optional)

Source (optional)

2. The following information must be supplied but may be given for an entire set of measurements:

**Data identification:**

Contributor's name and address

**Instrument information:**

Manufacturer

Model

Instrument type

Data system (optional)

Software version (optional)

**Experiment information:**

GC inlet:

Manufacturer/model

Column

Temperature programme

Carrier gas

Injection temperature

Interface temperature (optional)

Ionization type

Reagent gas

Ionization mode

Ion source temperature

Ion source pressure (optional)

Electron energy

Emission current (optional)

Ion acceleration voltage (optional)



LC inlet

Manufacturer/model  
Column brand/phase  
Column length, i.d., particle size  
Eluent A  
Eluent B  
Eluent programme  
Flow rate  
Column temperature  
Ionization type  
Ionization mode  
Ion source temperature  
Desolvation gas flow & temperature  
Sample cone/fragmentor voltage

Other inlet:

Type  
Solvent  
Flow rate  
Ionization type  
Ionization mode  
Ion source temperature  
Desolvation gas flow & temperature  
Sample cone/fragmentor voltage

MS/MS

Precursor ion isolation width  
Product ion mass resolution  
Collision gas  
Collision gas pressure  
Collision energy  
Scan range  
Scan cycle time (optional)

Date of experiment (optional)

**Minimum requirements:**

Lowest starting mass:  $m/z$  40 or lower (Ion trap instruments: 50% of the precursor ion mass or lower)

Ion intensities specified to 1 part in 999 or better

Spectra recorded to at least  $\geq 10$  amu above the precursor ion mass

**Electronic Format:**

Type of electronic format: NIST MS

## EXAMPLE OF A SUBMISSION

1. Common information:

Analytical conditions for 14-5-0001 to 14-5-0048

Instrument: Waters Micromass Quattro Micro

Inlet system: HPLC, Agilent Technologies 1200 series

Column: 100 mm x 2.1 mm x 2.7  $\mu$ m

Elution composition: A=10 mM ammonium formate in water

B=10 mM ammonium formate in methanol

Elution programme: 5% B, 5-98% B, 1-10 min; 98-5% B 12-13 min

Flow rate: 300  $\mu$ L/min

Column temperature: 40  $^{\circ}$ C

Ionization type: ESI

Ionization mode: pos

Ion source temperature: 150  $^{\circ}$ C

Desolvation gas flow/temperature: 400 L/h, 300  $^{\circ}$ C

Sample cone voltage: 17 V

Precursor ion mass resolution: 0.7 FWHM

Product ion mass resolution: 0.7 FWHM

Collision gas: Argon

Collision gas pressure: 2.0 mBar

Collision energy: 7/15/25 eV (see spectrum header, NIST user library)

Scan range: 20 to mass of precursor ion +20

Laboratory name: FOI Laboratory, Umea, Sweden

2. NIST user database spectrum information:

Spectrum Information

Name: Tributyl phosphate

Formula: C<sub>12</sub>H<sub>27</sub>O<sub>4</sub>P From structure

Other Names (Synonyms):  
14-5-0001  
\$.06QqQ  
\$.08CID, argon  
\$.00ms2  
\$.03[M+H]<sup>+</sup>

Comments:

Mol. Weight: 266 ID Number: 22  
CAS Number: 0 Peaks: 5

Library: msmsr  
Add to Library Replace Add to List

Peak information:

m/z	Abund.
99	784
152	1
155	599
211	474
267	999

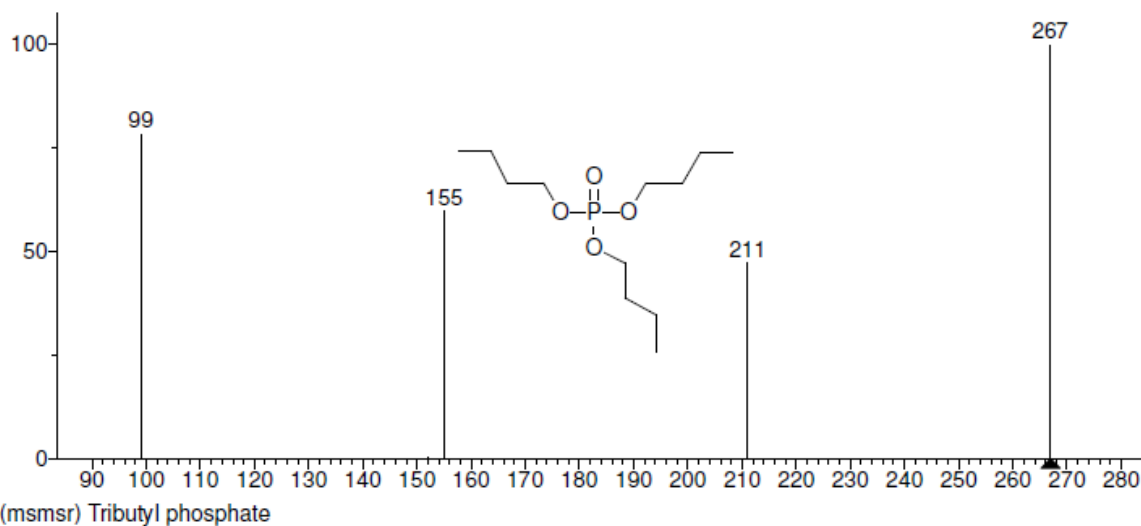
Accept

Attach Struct Clipboard Struct

Structure: TRIBUTYL PHOSPHATE/Library ID = 1

Exit Help

3. NIST user library print out:



Name: Tributyl phosphate

Formula: C<sub>12</sub>H<sub>27</sub>O<sub>4</sub>P

MW: 266 Exact Mass: 266.164696 ID#: 22 DB: msmsr

Instrument type: QqQ

Special fragmentation: CID, argon

Spectrum type: ms2

Precursor type: [M+H]<sup>+</sup>

Precursor m/z: 267

Collision energy: 7 eV

Sample inlet: HPLC

Ionization: ESI

Ion mode: Pos

5 m/z Values and Intensities:

99 784 | 152 1 | 155 599 | 211 474 | 267 999 |

Synonyms:

1.14-5-0001

2.Standard

3.OPCW-2310

## Appendix 2

### EVALUATION CRITERIA FOR ANALYTICAL DATA

#### MASS SPECTROMETRY (EI-MS)<sup>2</sup>

##### 1. Evaluation criteria

The following criteria apply:

- (a) Spectra that are submitted without the required accompanying information (see Appendix 1) or that are not in one of the allowed formats must be discarded.
- (b) Spectra that do not meet the minimum requirements specified in Appendix 1 must be discarded.
- (c) If there are two or more peaks in a mass spectrum with relative intensities at or close to 100%, this spectrum must be discarded, unless it is clear from the isotope pattern that no saturation has taken place.
- (d) If a mass spectrum contains masses that cannot be explained by fragmentation rules and that are not present in other spectra of the same or similar chemicals, that spectrum must be discarded.
- (e) If a mass spectrum contains peaks with isotope patterns that are not in reasonable agreement with the expected pattern, the spectrum must be discarded. As a guideline for further evaluation and with due consideration for other factors, the absolute intensity of the important isotope peak must be checked, and the corresponding theoretical intensity must be calculated according to the following criteria:
  - (i) when a mass peak in an isotope pattern due to high mass natural abundances is  $\geq 10.0\%$  of the base peak, in which case the measured relative intensity may deviate to a maximum of 10% of its theoretical value;
  - (ii) when a mass peak in an isotope pattern due to high mass natural abundances is  $< 10.0\%$  of the base peak, in which case the measured relative intensity may deviate to a maximum of one relative intensity unit (1.0%) from its theoretical value; and
  - (iii) where relative intensity is defined as the intensity expressed as a percentage of the base peak.

---

<sup>2</sup>

EI-MS = electron impact-mass spectrometry

## 2. Examples of isotope calculation

### 2.1 Example 1

Measured:

m/z 181 is 13.9%.

m/z 182 is 1.2%.

The ion at m/z 182 is < 10%. Therefore rule 1(e)(ii) above applies.

Calculated for the elemental composition C<sub>6</sub>H<sub>16</sub>NO<sub>3</sub>P:

m/z 181 is 13.9%.

m/z 182 is 1.0% (calculated relative to m/z 181 at 13.9% based on the theoretical isotope ratio).

The deviation is 0.2% (= 1.2% - 1.0%), which is within the allowed ± 1% of the measured value.

### 2.2 Example 2

Ion Composition C <sub>3</sub> H <sub>6</sub> ClS	Measured Relative Intensity	Theoretical Relative Intensity	APPLICATION OF THE ISOTOPE RULE
m/z 109	100 %	100 %	
m/z 110	6.1 %	4.2 %	Rule 1(e)(ii) applies: larger than the 1% permitted
m/z 111	32.2 %	36.5 %	Rule 1(e)(i) applies: larger than the 10% deviation permitted
m/z 112	1.1 %	1.5 %	Rule 1(e)(ii) applies: smaller than the 1% permitted
m/z 113	1.0 %	1.5 %	Rule 1(e)(ii) applies: smaller than the 1% permitted

## 3. Documentation of each individual evaluation

Each evaluation should be documented by an accompanying form containing the information indicated below.

**EVALUATION OF MASS SPECTRA**

OPCW Code	Chemical Name	CAS No.	Schedule No.	Previously Approved Spectra	Criterion *	Comments	Decision
					No saturation		
					No unexplained masses		
					Isotope pattern		
					Ion list		
					Low mass ( $\leq m/z$ 40)		
					High mass (MW + 50 amu)		
					Ion intensities		
					OPCW Code		
					Chemical name		
					Structure		
					Formula		
					MS manufacturer		
					Model		
					Inlet system		
					Ion source temperature		
					Electron energy		
					Scan range		
					Contributor's name		

Name of evaluator: \_\_\_\_\_

Date: \_\_\_\_\_

---

\* In the box next to each criterion, please write a "Y" if it has been met, or an "N" if it has not.

## NMR SPECTROMETRY

Only one-dimensional NMR spectra that are of the following types and that are measured on FT spectrometers with a proton frequency of 200 MHz or higher are to be evaluated:

- <sup>1</sup>H spectra
- <sup>13</sup>C spectra (<sup>1</sup>H-decoupled)
- <sup>31</sup>P spectra (coupled and <sup>1</sup>H-decoupled)
- <sup>19</sup>F spectra

### 1. Evaluation criteria

The following criteria apply:

- (a) The spectrum must be consistent with the assigned structure.
- (b) The name, CAS number (if assigned), and chemical structure with the numbering of atoms indicated on the spectrum must be provided.
- (c) All signals must be assigned whenever reasonably possible.
- (d) Coupling constants must be included when easily extractable.
- (e) Expansions must be displayed where relevant.
- (f) Any impurity must be marked with an asterisk.
- (g) Impurities must not overlap the lines of the chemical of interest.
- (h) The solvent and its pH (if relevant) must be specified.
- (i) The reference chemical must be indicated. Its chemical shift must be included if the reference is not TMS or TSPA for <sup>1</sup>H and <sup>13</sup>C, H<sub>3</sub>PO<sub>4</sub> (external) for <sup>31</sup>P, and CFCl<sub>3</sub> for <sup>19</sup>F.
- (j) The spectra must have been recorded with an adequate resolution to enable all the required information to be derived.
- (k) The spectra must be phased correctly.
- (l) The signal-to-noise ratio must be sufficient to detect all relevant signals.
- (m) The spectrometer type and frequency must be indicated.
- (n) The spectrum width must be indicated.
- (o) Peak picking (labelling) in spectra must be indicated.



**2. Documentation of evaluation**

The evaluation should be documented with a form containing the information indicated below.

**EVALUATION OF NMR SPECTRA**

OPCW Code	Chemical Name	CAS No.	Schedule	Criterion*	Comments	Decision
				Nucleus		
				Consistency with structure		
				Structure with numbering of atoms		
				Assigned signals		
				Coupling constants		
				Relevant expansions displayed		
				Impurities marked		
				Impurities not overlapping signals		
				Solvent and pH (if relevant)		
				Reference chemical included		
				Adequate resolution		
				Correctly phased		
				Adequate S/N ratio		
				Type and frequency		
				Spectrum width		
				Data points in spectrum		
				Sample temperature		
				Spectra peak picking (labelling)		

Name of evaluator: \_\_\_\_\_

Date: \_\_\_\_\_

\*

In the box next to each criterion, please write a "Y" if it has been met, or an "N" if it has not.

## IR SPECTROMETRY

### 1. Evaluation criteria

The following criteria apply:

- (a) The spectrum must be consistent with the molecular structure of the chemical.
- (b) The spectrum must show the absence of extraneous spectral features attributable to impurities or contaminants.
- (c) The method used to prepare the sample for measurement must be stated.
- (d) The minimum resolution must be  $4\text{ cm}^{-1}$  for condensed-phase and normal-gas phase spectra, and  $8\text{ cm}^{-1}$  for GC light-pipe spectra.
- (e) The minimum spectral range must at least be  $3700 - 700\text{ cm}^{-1}$  for condensed-phase spectra and  $3700 - 750\text{ cm}^{-1}$  for normal-gas phase spectra.
- (f) The signal-to-noise ratio must be sufficient to detect all relevant peaks.
- (g) The largest absorbing peak must not be saturated.
- (h) The spectra must be adequately compensated for atmospheric carbon dioxide and water (less than 5% of the highest absorption band).
- (i) The intensity of the bands arising from water contained in the sample should be less than 5% of the highest absorption band in the sample.
- (j) In order to be included in the OCAD, a spectrum must fulfil at least one of the following criteria:
  - (i) It is consistent with other IR data for the same chemical.
  - (ii) It is supported by accepted NMR or MS spectra obtained from the same sample with consistent results.
- (k) Raw data (without any ATR correction) should be submitted.

**2. Documentation of evaluation**

The evaluation should be documented with a form containing the information indicated below.

**EVALUATION OF INFRARED SPECTRA**

OPCW Code	Chemical Name	CAS No.	Schedule	Criterion *	Comments	Decision
				No unexplained peaks		
				Sample preparation method		
				Resolution		
				Spectral range		
				Adequate S/N ratio		
				No saturation		
				Compensation for CO <sub>2</sub> /H <sub>2</sub> O		
				Consistent with other IR data		
				Consistent with NMR/MS		

Name of evaluator: \_\_\_\_\_

Date: \_\_\_\_\_

---

\*

In the box next to each criterion, please write a “Y” if it has been met, or an “N” if it has not.

**GC(RI) DATA****1. Evaluation criteria**

The following criteria apply:

- (a) A GC(RI) must be supported by additional determinations such as:
  - (i) an independent measurement; or
  - (ii) extrapolation from a series of homologous chemicals.
- (b) The recording conditions must be fully documented.
- (c) The standard deviation of the quality control chemicals used is <10 RI units.
- (d) The difference between two independently measured retention indices for the same chemical must be within acceptable limits (e.g. 20 RI units) after any corrections for column type.
- (e) Retention index standards (n-alkanes) eluting both before and after the analysed chemical must be used.

**2. Documentation of evaluation**

The evaluation should be documented with a form containing the information indicated below.

**EVALUATION OF GC(RI) DATA**

OPCW Code	Chemical Name	CAS No.	Schedule	Criterion *	Comments	Decision
				Retention index		
				Consistent with other GC data		
				Consistent with other determinations		
				Recording conditions		
				Consistent with structure		
				Accuracy		
				Standards used		

Name of evaluator: \_\_\_\_\_

Date: \_\_\_\_\_

\*

In the box next to each criterion, please write a "Y" if it has been met, or an "N" if it has not.

## TANDEM MASS SPECTROMETRY (MS/MS) DATA

### 1. Evaluation criteria

The following criteria apply:

- (a) Spectra that are submitted without the required accompanying information (see Appendix 1) or that are not in NIST user library format must be discarded.
- (b) Spectra that do not meet the minimum requirements specified in Appendix 1 must be discarded.
- (c) For each set of data, reference spectra of tributyl phosphate and/or dibutyl phosphate must be provided at 3 different collision energies and with experimental conditions.
- (d) The collision energies used for each spectrum are not required to match those of the reference spectra. However, at least one of the collision energies selected must generate diagnostic product ions.
- (e) Mass spectra recorded under three different collision conditions—low, medium, and high energy—must be consistent with fragmentation rules and at least one spectrum must have the precursor ion present.
- (f) If a mass spectrum contains masses that cannot be explained by fragmentation rules and that are not present in other spectra of the same or similar chemicals, that spectrum must be discarded.
- (g) The ionisation type and mode must be indicated.
- (h) The collision gas and collision energy for each spectrum must be indicated.
- (i) The inlet system conditions must be fully documented.

## 2. Documentation of evaluation

The evaluation should be documented with a form containing the information indicated below.

### EVALUATION OF MS/MS DATA

OPCW Code	Chemical Name	CAS No.	Schedule	Criterion *	Comments	Decision
				Reference spectra		
				No unexplained masses		
				Precursor ion		
				Ion list		
				Low mass		
				High mass (precursor ion mass + 10 amu)		
				Ion intensities		
				OPCW Code		
				Chemical name		
				Structure		
				Formula		
				MS manufacturer		
				Model		
				Inlet system conditions		
				Ionization type		
				Ionization mode		
				Ion source temperature		
				Collision gas		
				Precursor ion isolation width		
				Product ion mass resolution		
				Collision energy		
				Scan range		
				Contributor's name		

Name of evaluator: \_\_\_\_\_

Date: \_\_\_\_\_

--- 0 ---

\*

In the box next to each criterion, please write a "Y" if it has been met, or an "N" if it has not.