OPCW

Technical Secretariat

S/2189/2023
12 July 2023
ENGLISH only

NOTE BY THE TECHNICAL SECRETARIAT

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

At its Fifty-Fifth Meeting, held on 4 and 5 April 2023, the Validation Group reviewed the document entitled "Procedures for the Evaluation of Data to Be Included in the OPCW Central Analytical Database" (S/1686/2018, dated 13 November 2018). This current Note by the Technical Secretariat (hereinafter "the Secretariat") supersedes S/1686/2018.

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

CS-2023-4375(E) distributed 18/07/2023

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[1] indicated; data does not have to be presented to the Group again, and there is no change to the OPCW Code;

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

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.

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 remeasured 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 ELECTRON IMPACT (EI) MASS SPECTRA

5.1 Mass spectra (MS) 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[2] 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.

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[2] GS-MS = gas chromatography-mass spectrometry.

(d) The Secretariat requires that electronic spectra be submitted in NIST[3] 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 (retention index) 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(RI) DATA

6.1 GC(RI) 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 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).

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3 NIST: National Institute of Standards and Technology.

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) DATA 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 MS 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 NUCLEAR MAGNETIC RESONANCE (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.

13. SUBMISSION OF GAS CHROMATOGRAPHY HIGH RESOLUTION MASS SPECTROMETRY (GC-HRMS) DATA

13.1 GC-HRMS 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 specific formats.

13.2 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) Elemental composition and mass error must be shown for major fragments (at least two) in a separate table.

(c) The mass accuracy ≤ 2.5 parts per million (ppm) must be fulfilled for the main fragments.

(d) Four decimal places for m/z values must be provided for all ions.

(e) Resolution must be higher than 10 000 at 200 FWHM.

13.3 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
  - Split/splitless conditions
- 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 ≥0.1%)
Ion intensities specified to 1 part in 999 or better
Spectra recorded to ≥50 amu above the molecular weight of the compound

Electronic Format:
Type of electronic format: NIST MS

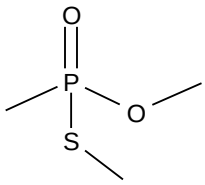
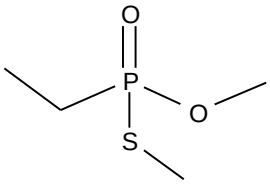
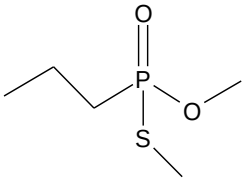
EXAMPLE OF A SUBMISSION

1. Common information

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

Instrument: Finnigan TSQ 7000
Ion source: 180 ºC, 70 eV
Range: 33-500 amu, 0.50 s
Inlet system: GC
Column: DB-5, 30 m x 0.25 mm
Temperature programme: 40 ºC (1 min)-10 ºC/min-280 ºC (5 min)
Carrier gas: helium
Injection temperature: 250 ºC
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:

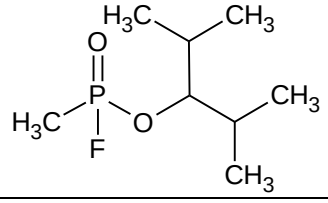
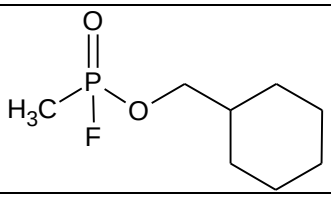
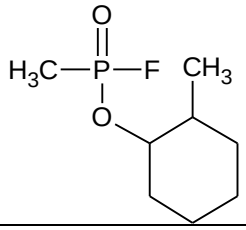
Data identification:
Contributor's name and address:

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

OPCW Code	Structure	Name	Formula	CAS No.	Schedule No.	RI(a)	RI(b)
07-4-0425		1-Isopropyl-2-methylpropyl methylphosphono-fluoridate	$C_8H_{18}FO_2P$	113548-85-9	1.A.1	1137	
07-4-0426		Cyclohexylmethyl methylphosphono-fluoridate	$C_8H_{16}FO_2P$		1.A.1	1311	
07-4-0427		2-Methylcyclohexyl methylphosphono-fluoridate	$C_8H_{16}FO_2P$	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 SPECTROSCOPY

The following information must be supplied for all NMR spectroscopy 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 (μs 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 SPECTROSCOPY

The following information must be supplied for all IR spectroscopy 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 ≥10 amu above the precursor ion mass

Electronic Format:
Type of electronic format: NIST MS

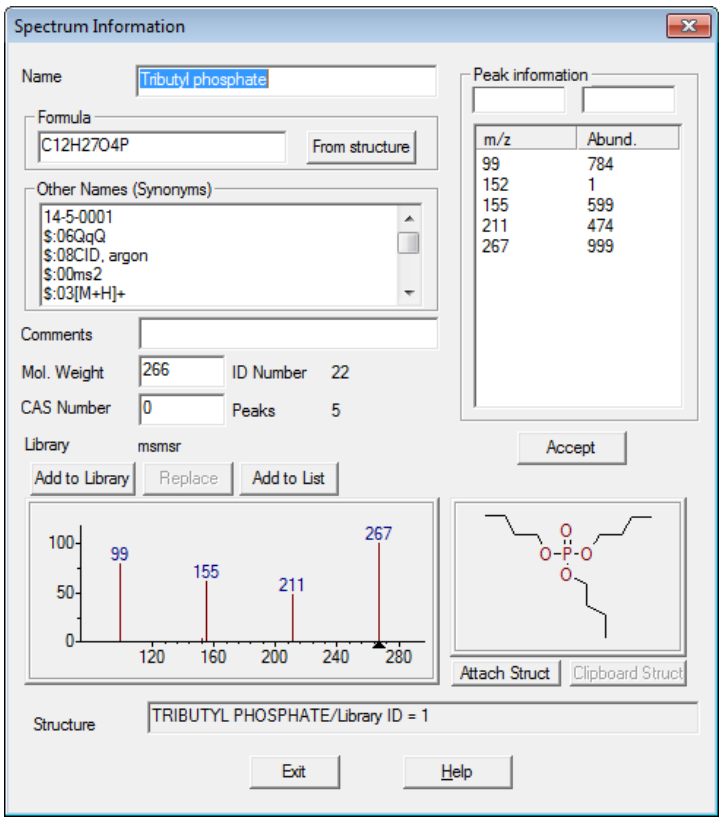
EXAMPLE OF A SUBMISSION

1. Common information:

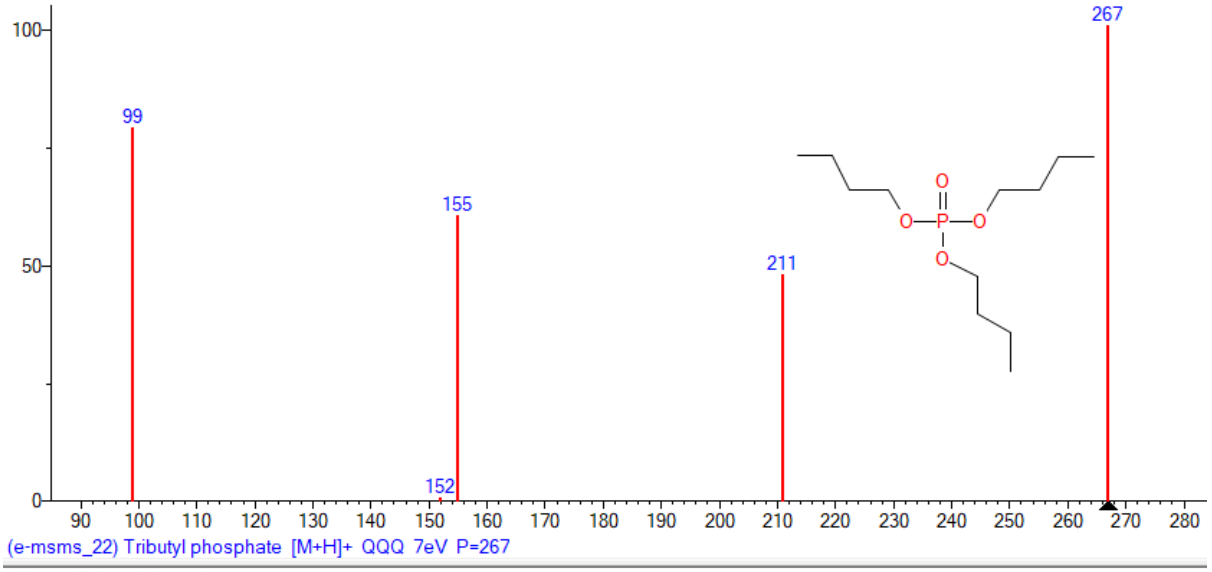
Analytical conditions for 14-5-0001 to 14-5-0048

Instrument: Waters Micromass Quattro Micro
Inlet system: HPLC, Agilent Technologies 1200 series
Column: 100 mm x 2.1 mm x 2.7 µm
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 µL/min
Column temperature: 40 º C
Ionization type: ESI
Ionization mode: pos
Ion source temperature: 150 º C
Desolvation gas flow/temperature: 400 L/h, 300 º 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:



3. NIST user library view:



Name: Tributyl phosphate
Precursor type: [M+H]+
Instrument type: QqQ
Collision energy: 7 eV
Precursor m/z: 267
Formula: $C_{12}H_{27}O_4P$
MW: 266 Exact Mass: 266.164696 CAS#: 126-73-8 ID#: 130 DB: e-msms_22
Other DBs: None
Comment: Standard, DISTRIBUTED
Special fragmentation: CID, argon
Spectrum type: ms2
Sample inlet: HPLC
Ionization: ESI
Ion mode: Pos
InChIKey: STCOOQWBFONSKY-UHFFFAOYSA-N Non-stereo
5 m/z Values and Intensities:
99 784 | 152 1 | 155 599 | 211 474 | 267 999 |
Synonyms:
1.14-5-0001
2.S.Standard
3.OPCW-2310

GAS CHROMATOGRAPHY HIGH RESOLUTION MASS SPECTROMETRY (GR-HRMS)

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

Analysis information:
Source: EI
Instrument type:
Spectrum type: accurate m/z

Evaluation information (preferable in a separate table)
Elemental composition and mass error must be shown for at least two main fragments

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)

Mass resolution (the setting in the used MS method)
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 ≥0.1%)
Ion intensities specified to 1 part in 999 or better
Spectra recorded to ≥50 amu above the molecular weight of the compound
Display four decimal places for HRMS data
Display elemental composition for HRMS data for major fragments in separate table
Resolution needs to be higher than 10 000 at 200 FWHM

Electronic Format:
Type of electronic format: NIST MS

EXAMPLE OF A SUBMISSION

1. Common information:

Contributor's name and address:
Bundeswehr Research Institute for Protective Technologies and CBRN Protection (WIS)
Humboldtstrasse 100, 29633 Munster, Germany

Data identification:
OPCW Code: 02-7-XXXX to 02-7-XXXX

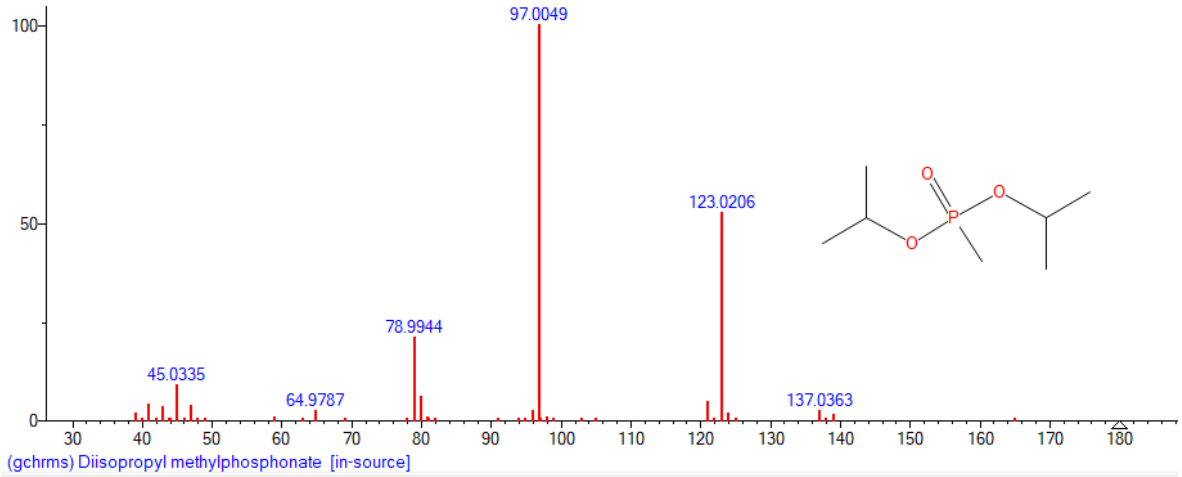
Instrument information:

Manufacturer:	Thermo Fisher Scientific
Model:	Q Exactive GC
Instrument type:	Q-Orbitrap
Software version:	Exactive Series 2.9 Build 2926

Experiment information:

GC inlet:	Thermo Trace 1310 GC
Column brand/phase	Agilent HP-5MS/5 % phenyl, 95 % dimethylpolysiloxane
Column dimensions:	30 m x 0.25 mm x 0.25 µm
GC temp. prog.:	non-derivatised compounds: 50 ° C (2 min), 10 ° C/min, 290 ° C (6 min); TMS-derivatives: 70 ° C (4 min), 10 ° C/min, 290 ° C (6 min)
GC carrier gas:	Helium
Flow control/rate:	Constant flow, 1.2 mL/min
GC injector temp.:	250 ° C
Ion source temp.:	250 ° C
Electron energy:	70 eV
Mass resolution:	60000 at m/z 272 (FWHM)
Scan range:	33-700 m/z

2. NIST user library view:



(gchrms) Diisopropyl methylphosphonate [in-source]

Name: Diisopropyl methylphosphonate
Formula: $C_7H_{17}O_3P$
MW: 180 Exact Mass: 180.091531 CAS#: 1445-75-6 ID#: 2 DB: gchrms
Other DBs: None
Comment: MS:02-7-0002, 2.B.04, RI=1071, Data sent to VG in OPCW format
Spectrum type: accurate m/z
Instrument: Thermo Q Exactive
InChIKey: WOAFDHWYKSOANX-UHFFFAOYSA-N Non-stereo
55 m/z Values and Intensities:

39.0228	19.32	40.0306	1.24	41.0384	42.18	42.0418	1.15	42.0463	4.74
43.0178	23.85	43.0542	34.30	43.9894	1.63	44.0257	1.20	45.0335	89.67
46.0369	1.13	46.9682	36.98	47.976	2.07	48.9839	4.47	59.0492	8.60
62.9995	2.16	64.9787	25.57	69.0699	4.21	77.9866	3.66	78.9896	1.18
78.9944	210.88	78.9992	1.20	79.9977	1.92	80.0022	59.64	80.9737	9.31
81.01	2.94	81.9814	1.69	90.9944	3.96	94.0179	1.68	94.9893	2.07
95.9971	24.87	96.9872	1.03	96.9981	5.98	97.0049	999.00	97.0114	7.18
97.022	1.15	98.0082	9.24	98.9842	1.61	99.0092	5.64	103.0307	2.62
105.01	3.33	121.005	2.53	121.0414	45.77	122.0128	1.88	122.0447	2.28
123.0112	2.47	123.0206	525.64	123.0303	2.26	124.024	17.45	125.0249	3.15
125.0364	1.10	137.0363	22.82	138.0441	4.98	139.052	14.03	165.0676	5.79

Synonyms:
1.02-7-0002
2.S.2.B.04
3.OPCW-1356

Appendix 2

EVALUATION CRITERIA FOR ANALYTICAL DATA

MASS SPECTROMETRY (EI-MS)[4]

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 ≥ 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.

[4] 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 $C_6H_{16}NO_3P$:

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_3H_6ClS	**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 (≤ 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 SPECTROSCOPY

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:

^{1}H spectra
^{13}C spectra (^{1}H-decoupled)
^{31}P spectra (coupled and ^{1}H-decoupled)
^{19}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 ^{1}H and ^{13}C, H_3PO_4 (external) for ^{31}P, and $CFCl_3$ for ^{19}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 SPECTROSCOPY

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 cm^{-1} for condensed-phase and normal-gas phase spectra, and 8 cm^{-1} for GC light-pipe spectra.

(e) The minimum spectral range must at least be 3700 – 700 cm^{-1} for condensed-phase spectra and 3700 – 750 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_2/H_2O			
				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: _____

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

GAS CHROMATOGRAPHY HIGH RESOLUTION MASS SPECTROMETRY (GC-HRMS)

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) Elemental composition for at least two main fragments must be provided. The mass accuracy of $\leq$ 2.5 parts per million (ppm) must be fulfilled for the main fragments.

(f) The same fragmentation pattern as seen in EI-MS must be seen in EI-HRMS but the intensities may vary.

(g) If a mass spectrum contains peaks with isotope patterns that are not in reasonable agreement with the expected pattern, the spectrum should be discarded. Control isotope pattern for main peaks, preferably those close to the molecular ion.

2. Documentation of each individual evaluation

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

EVALUATION OF GC-HRMS DATA

OPCW Code	Chemical Name	CAS No.	Schedule No.	Previously Approved Spectra	Criterion*		Comments	Decision
					No saturation			
					No unexplained masses			
					Isotope pattern			
					Ion list			
					Four decimal places for m/z values			
					Elemental composition for major fragments in separate table			
					Resolution higher than 10 000 at 200 FWHM			
					Low mass (≤ 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: _____

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