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# CCP-TP-176

Revision 0

# CCP
# Determination of Method Detection Limits for Gas Analysis

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RECORD OF REVISION

| Revision Number | Date Approved | Description of Revision |
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| 0 | 05/02/2007 | Initial Issue. |

# 1. PURPOSE

This Central Characterization Project (CCP) Procedure provides instruction for determining Method Detection Limits (MDLs) for gas analyses performed at the Environmental Chemistry Laboratory (ECL).

Personnel performing this procedure will be trained and qualified in accordance with CCP-QP-002, *CCP Training and Qualification Plan,* prior to performing this procedure.

# 2. SCOPE

This procedure provides instructions for determining MDLs for headspace gas analyses methods used in support of the CCP. The MDL determination procedures provided in this procedure meet the requirements of CCP-PO-001, *CCP Transuranic Waste Characterization Quality Assurance Project Plan*. If applicable, the procedure may also be used to support analyses for other programs or projects.

# 3. DEFINITIONS

*Method Detection Limit (MDL)*. The minimum concentration of a substance that can be measured and reported for a given method with 99% confidence that the analyte concentration is greater than zero.

# 4. PROCEDURE

## 4.1 Frequency of MDL Determination

4.1.1 Determine MDLs as part of initial method performance demonstration performed prior to analysis of samples by an analytical method.

4.1.2 Determine MDLs independently for each instrument used for an analytical method.

4.1.3 Determine MDLs for all target analytes of interest for a method.

4.1.4 After initial determination, redetermine MDLs at least semiannually.

4.1.5 Redetermine MDLs when major changes in instrument configuration or operating conditions are made in a method, and before sample analysis resumes.

## 4.2 Determination of MDLs

4.2.1 Determine MDLs by performing replicate analyses of a low-level standard containing all target analytes of interest that is matrix-matched to the samples to be analyzed.

4.2.1.1 Use a standard having analyte concentrations approximately 3 to 10 times the anticipated MDL.

**NOTE:** *When the anticipated MDL is far below the detection level required by the customer, it is allowable to use a standard concentration that is more than 10 times the anticipated MDL as long as the resulting MDL, although less than optimum, still satisfies customer requirements. This latter approach is recommended when establishing optimum MDLs would require extra effort and expense that would not normally be required for routine analysis of customer samples.*

4.2.2 Perform a minimum of seven replicate analyses of the standard in accordance with CCP-TP-173, *CCP Analysis of Gas Samples for VOCs by GC/FID*, CCP-TP-174, *CCP Analysis of Gas Samples for Hydrogen and Methane By Micro GC/TCD*, and CCP-TP-175, *CCP Analysis of Gas Samples for VOCs by GC/MS*.

4.2.3 Perform analyses of the MDL standard using the same instrument operating parameters as are used for sample analysis.

4.2.4 During analyses of the MDL standard, observe all daily instrument quality control requirements of the analytical method.

## 4.3 Calculation of MDLs

4.3.1 Calculate the sample standard deviation, *s*, using the following equation:

$$s = \sqrt{\sum_{i=1}^{n} \frac{\left(y_i - \bar{y}\right)^2}{n-1}}$$

where $y_i$ is the measured value of the $i^{th}$ replicate standard measurement, $\bar{y}$ is the mean measured value of the replicates, and *n* equals the number of replicates (usually 7).

4.3.2 Calculate MDLs for each target analyte using the results of the replicate analyses according to the equation:

$$MDL = t_{(n-1,\,1-\alpha=0.99)} \times s$$

where $t_{(n-1,\ 1-\alpha=0.99)}$ is the one-tailed *t* distribution value appropriate to a 99% confidence level and a standard deviation estimate with *n* - 1 degrees of freedom, and *s* is the standard deviation of replicate measurements.

For seven replicates, the above expression reduces to the following equation:

$$MDL = 3.143 \times s$$

where *s* is the standard deviation of the seven measurements.

4.3.3 Perform the MDL calculations using a computer spreadsheet (e.g., Excel).

4.3.3.1 Ensure that the spreadsheet has received independent 100% manual verification of the calculations.

4.3.4 Calculate MDLs in units of nanograms for GC/MS volatile organic compounds, ppmv and ng for GC/FID volatile organic compounds, and volume percent for hydrogen and methane.

## 4.4 Acceptance Criteria for MDLs

4.4.1 Compare the calculated MDLs to the CCP program requirements for acceptability.

4.4.2 IF MDLs are less than or equal to the program-required MDLs listed in Table 1 for volatile organic compounds,
OR less than or equal to 0.05 volume percent for hydrogen and methane,
THEN GO TO Step 4.5.

4.4.3 IF the calculated MDLs for all target analytes are not less than or equal to the program requirements,
THEN take appropriate corrective action.

4.4.4 After corrective action is complete, redetermine the MDL for all analytes that did not meet the acceptance criteria.

4.4.5 Do not continue with sample analysis until acceptable MDL performance has been demonstrated for all method target analytes.

## 4.5 Documentation and Reporting

4.5.1 Ensure that the computer file name of the verified calculation spreadsheet is referenced in the MDL file, or that 100% of the calculations are manually verified by an independent person.

4.5.2 Submit the MDL file, consisting of all raw and processed data generated during the MDL determination (including all instrument printouts, quantitation reports, and spreadsheet printouts) to the Independent Technical Reviewer for review and approval.

4.5.3 IF QC data such as CCALs, CCVs, and lab blank results are not filed with the MDL data,
THEN reference them in the MDL file such that they are easily retrievable.

## 5. RECORDS

Records generated during the performance of this procedure are maintained as QA records in accordance with CCP-QP-008, *CCP Records Management*. The records are the following:

QA/Nonpermanent

MDL Files

## 6. REFERENCES

6.1 CCP-PO-001, *CCP Transuranic Waste Characterization Quality Assurance Project Plan*

*6.2* CCP-QP-002, *CCP Training and Qualification Plan*

6.3 CCP-QP-008, *CCP Records Management*

Table 1. Headspace VOC Target Compounds and Required MDLs

| Compound | Method | MDL* (ng) | MDL*(ppmv) |
|---|---|---|---|
| Acetone | GCMS | 150 | NA |
| Benzene | GCMS | 10 | NA |
| Bromoform | GCMS | 10 | NA |
| Butanol | GCMS | 150 | NA |
| Carbon disulfide** | GCMS | 10 | NA |
| Carbon tetrachloride | GCMS | 10 | NA |
| Chlorobenzene | GCMS | 10 | NA |
| Chloroform | GCMS | 10 | NA |
| Chloromethane** | GCMS | 10 | NA |
| Cyclohexane | GCMS | 10 | NA |
| 1,1-Dichloroethane | GCMS | 10 | NA |
| 1,2-Dichloroethane | GCMS | 10 | NA |
| 1,1-Dichloroethylene | GCMS | 10 | NA |
| 1,2-Dichloroethylene (cis) | GCMS | 10 | NA |
| 1,2-Dichloroethylene (trans) | GCMS | 10 | NA |
| 1,2-Dichloropropane** | GCMS | 10 | NA |
| Ethyl benzene | GCMS | 10 | NA |
| Ethyl ether | GCMS | 10 | NA |
| Methanol | GC or GCMS | 150 | 11.5 |
| Methyl ethyl ketone | GCMS | 150 | NA |
| Methyl isobutyl ketone | GCMS | 150 | NA |
| Methylene chloride | GCMS | 10 | NA |
| 1,1,2,2-Tetrachloroethane | GCMS | 10 | NA |
| Tetrachloroethylene | GCMS | 10 | NA |
| Toluene | GCMS | 10 | NA |
| 1,1,1-Trichlorethane | GCMS | 10 | NA |
| Trichloroethylene | GCMS | 10 | NA |
| Trichlorofluoromethane** | GCMS | 10 | NA |
| 1,1,2-Trichloro-1,2,2-trifluoroethane | GCMS | 10 | NA |
| 1,2,4-Trimethylbenzene | GCMS | 10 | NA |
| 1,3,5-Trimethylbenzene | GCMS | 10 | NA |
| p/m-Xylene | GCMS | 10 | NA |
| o-Xylene | GCMS | 10 | NA |

* MDL = Method Detection Limit (values based on delivering 10 mL to the analytical system)

** Site-specific analytes; analysis may not be required for samples from all TRU Waste Generator/Storage Sites.