

## **THE METHOD DETECTION LIMIT AND PRACTICAL QUANTITATION LEVEL: THEIR DERIVATIONS AND REGULATORY IMPLICATIONS**

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### **ABSTRACT**

This paper focuses on the method detection limit (MDL) and practical quantitation level (PQL) used in the sampling and analysis plans for the waste characterization and remediation programs at many federal facilities. The paper discusses the derivation and use of the MDL and PQL by the Environmental Protection Agency (EPA) and others, concerns raised regarding how EPA derives and uses the MDL and PQL and the regulatory implications, and derivation and use of the MDL and PQL at Waste Isolation Pilot Plant (WIPP) and the associated technical difficulties.

EPA's derivations of the MDL and PQL and the statutory requirements in the Clean Water Act impacting these derivations are briefly presented. The present-day use of the MDL and PQL in the Resource Conservation and Recovery Act (RCRA) program and the "codification" of these analytical measurements in the SW-846 for RCRA and Part 136 of the Clean Water Act are also discussed. The derivation of the MDL and PQL by others and their guidelines for using them in regulatory programs are compared and contrasted with those of EPA. Also discussed are the concerns raised by statisticians regarding how EPA derives and uses the MDL and PQL and the associated regulatory implications.

Finally, how WIPP uses the MDL and PQL in its waste characterization program, the technical difficulties encountered, and their implications for waste characterization and remediation programs are discussed

Several terms in this paper are used analogously and they are listed here to aid the reader: practical quantitation level (PQL), estimated quantitation limit (EQL), program required quantitation limits (PRQLs) and the limit of quantitation (LOQ).

### **INTRODUCTION**

The Waste Analysis Plan (WAP) in the WIPP RCRA Part B Permit Application to New Mexico was developed to fulfill the requirements of 40 *CFR* § 264.13. It details the waste characterization process the generator sites across the country will implement to determine if their wastes are hazardous and to provide WIPP the information needed to safely store and dispose of the waste received. Integral to waste determination and characterization in the WAP is the use of program required quantitation limits (PRQLs), the program equivalent of EPA's practical quantitation levels (PQLs). PRQLs are used to determine (1) if the wastes are hazardous or not or (2) if the performance standards for the miscellaneous unit are being met.

The New Mexico Environment Department (NMED) approved the use of PRQLs when that element of the WAP was retained in the WAP as incorporated by the NMED into the WIPP draft permit. Because of the pivotal role of PRQLs in the waste determination process, it is essential to understand their derivation and use in the WAP and how this parallels the derivation and use of equivalent levels by other regulated entities and regulatory agencies. This paper briefly summarizes of the derivation of detection limits by EPA and others, discusses the concerns surrounding EPA's detection limits, and briefly compares the derivation of detection limits in WIPP's WAP with the derivations of the same limits by EPA and others.

A major difficulty in deriving analytical determination or detection limits is the public policy pressure to detect contaminants at increasingly lower levels. These limits, often set by regulation at very low levels— i.e., for carcinogens, near or at zero— create a technical challenge. In order to determine if these low regulatory limits have been met or exceeded, increasingly reliable analytical measurements of environmental samples are required. A crucial component in developing these analytical measurements is the ability to determine if the measurement truly indicates whether or not a contaminant or hazardous constituent has been detected and, if detected, whether or not the measurement can be reliably used to indicate quantity. These concerns are central to the derivation of the MDL and the PQL.

## **THE METHOD DETECTION LIMIT AND PRACTICAL QUANTITATION LEVEL: THEIR DEFINITIONS AND USE BY EPA**

### **Safe Drinking Water Act (42 USC 300f, et. seq.)**

The PQL and MDL were discussed extensively in EPA's proposed rulemaking for the Safe Drinking Water Act's (SWDA's) National Primary Drinking Water Regulations for volatile organic compounds (VOCs) (1). In this rulemaking, EPA defined the MDL and PQL as follows:

**Method detection limit:** “. . . the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the true value is greater than zero.” (1)

**Practical quantitation level:** “[t]he lowest level that can be reliably achieved within the specified limits of precision and accuracy during routine laboratory operating conditions. . . .” (1)

The MDL is a measurement used by a laboratory to determine its specific minimum detection capabilities for a particular method. In contrast, the PQL is a concentration measurement that is achievable on a routine basis. Basically, the PQL provides a measurement concentration that can be used to set standards because it is “time and laboratory independent for regulatory purposes,” whereas the MDL does “. . .not provide a uniform measurement concentration that could be used to set standards.” (2) Additionally,

In the range between the MDL and the PQL, quantitation of contaminants can still be achieved, but not necessarily with the same precision and accuracy possible at the PQL. As measurements approach the MDL, there is much less confidence in quantitation. Thus, PQLs set a target performance level for laboratories using a specified set of precision and accuracy limitations. In this

manner, PQLs provide consistency in implementing a regulatory program, in a practical way, where both quality control and quality assurance is critical. (2)

Thus, the regulatory significance of the PQL is the ability to use it as a measurement to determine if regulatory standards have been met or exceeded. However, the regulatory significance of the MDL is its use by EPA in calculating PQLs.

The PQL is determined through interlaboratory studies, such as the PE [performance evaluation] studies. Differences between MDLs and PQLs are expected since the MDL represents the lowest achievable level under ideal laboratory conditions whereas the PQL represents the lowest achievable level under practical and routine laboratory conditions.

If data are unavailable from interlaboratory studies, PQLs are estimated based upon the MDL and an estimate of a higher level which would represent a practical and routinely achievable level with relatively good certainty that the reported value is reliable. Traditionally, this level has been estimated at 5 to 10 times the MDL. (1)

In addition to its use as a measurement to set analytical limits, the PQL also influences the regulatory standards. This regulatory use began historically with the establishment of the recommended maximum contaminant levels (RMCLs) (health goals) and maximum contaminant levels (MCLs) for contaminants under the SDWA.

*RMCLs are non-enforceable health goals.* RMCLs are to be set at a level which, in the Administrator's judgment, "no known or anticipated adverse effects on the health of persons occur and which allows an adequate margin of safety." Section 1412(b)(1)(B).

*MCLs are the enforceable standards.* MCLs must be set as close to RMCLs as is feasible. Feasible means "with the use of the best technology, treatment techniques and other means, which the Administrator finds are generally available [taking costs into consideration]." Section 1412(b)(3). (1)

Additionally, EPA further indicated that

The SDWA specifies in section 1401 that an MCL is to be set for contaminants in drinking water if "it is economically and technologically feasible to ascertain the level of such contaminant in water in public water systems." If it is not, a treatment technique regulation is to be set. . . .

Obviously, monitoring data are only valid above the verifiable level of quantitation, and only those systems with VOC contamination at or above the verifiable level would have to install the technique. Therefore, setting the MCL at the limit of quantitation provides essentially the same level of protection as a treatment technique. . . .

The reliability of analytical methods used for compliance monitoring is critical at the maximum contaminant level. (1)

The PQL becomes critical because of this requirement that the MCL be set at a limit of quantitation. The PQL is the only verifiable quantitation level, the MDL is not. As Koerse indicated,

In those instances where it has set the MCLG [maximum contaminant level goal previously referred to as RMCL] at zero (e.g., for carcinogens), EPA has implicitly recognized that the detection limits for the substances it is regulating must be considered in determining what MCL is feasible. Toward that end, EPA has developed an approach that makes allowances for the elevated variability exhibited by laboratories measuring levels close to the detection limit. For contaminants whose MCLG is zero, EPA has set MCLs at the so-called PQL, . . . (3)

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### **Resource Conservation and Recovery Act (42 U.S.C. 6901, et. seq.)**

Generally, the RCRA toxicity characteristic (TC) regulatory levels are based on the constituent's toxicity and its expected fate when released into the environment. "The latter element is expressed as a dilution/attenuation factor (DAF), which, when multiplied by the toxicity value, results in the regulatory level." (4) In the final rule expanding the toxicity characteristic, EPA retained the DAF of 100 because ". . . EPA believes that a DAF data used for indicating dilution by two orders of magnitude (i.e. 100) is appropriate." (4) As an example, the MCL for carbon tetrachloride is 0.005 mg/l which, when multiplied by 100, gives the TC maximum contaminant concentration of 0.5 mg/l.

However, for three compounds, their calculated regulatory levels are below their MDLs using the currently available analytical methods. Consequently, the PQLs for these constituents have become their regulatory limits under the toxicity characteristic. For this situation, EPA proposed ". . . to use a value of five times the analytical detection limit as the quantitation limit and to set the regulatory level at the quantitation limit for those compounds for which the calculated regulatory level is below the quantitation limit, and interlaboratory studies were not available." (4)

Also under RCRA, EPA is presently allowing facility-specific PQLs to be proposed, particularly where the background level of a constituent is below the analytical detection limit. Any facility-specific approved PQL "must be the lowest concentration level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions." (5) Additionally,

. . . SW-846 contains MDLs together with PQL conversion factors. Unlike the SDWA program, which prescribes a factor between 5 and 10 . . . SW-846 prescribes several multipliers (sometime ranging from 10 to 1250) whose use depends on the matrix (e.g., groundwater, sludge), and the expected concentration range of the contaminant (e.g., high level, low level) being analyzed. (3)(Reprinted with permission from *Environmental Law Reporter*, 19: p.10211-10222.)

## **EPA Guidelines for Test Procedures**

The major guidelines presently available are:

*Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods (SW-846)*  
*40 CFR Part 136: Guidelines Establishing Test Procedures for the Analysis of*  
*Pollutants Under the Clean Water Act, Appendix B to Part 136—Definition and*  
*Procedure for the Determination of the Method Detection Limit (Appendix B)*

SW-846 is the guidance for analytical methods recommended and/or required under RCRA, and Part 136 is the guidance for the test procedures under the Clean Water Act. The definition of the MDL in Appendix B and the SW-846 is basically the operational definition of Glaser et al. (which they consider to be operational in that an analyte must be present for the method to be in a detection mode). (6)

In Appendix B and SW-846, the MDL is defined as:

The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte. (7, 8)

Additionally, both guidelines detail a procedure to be followed for the derivation of the MDL, and it is basically the same in both. This definition of the MDL has been incorporated into EPA's *National Environmental Laboratory Accreditation Conference: Constitution, Bylaws, and Standards*, EPA 600R-97/139 (9).

In SW-846, the estimated quantitation limit (EQL) is defined as:

The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected as the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs in SW-846 are provided for guidance and may not always be achievable. (7)

There is no equivalent definition in Appendix B.

The inclusion of these definitions, and the procedure for determining the MDL, in SW-846 and Part B basically codifies EPA's approach to the MDL and PQL/EQL. This approach differs from that of several other statisticians. Statistical approaches to detection limits and some criticisms of some of EPA's approach are discussed in the next section.

## NON-EPA DETERMINATION LIMITS

### Measurement Guidelines from the American Chemical Society

The guidelines included four definitions related to limits of detection and quantitation and they were:

**Limit of detection (LOD):** “. . . the lowest concentration level that can be determined to be statistically different from a blank.”

**Method detection limit (MDL):** “. . . the lowest concentration of analyte that a method can detect reliably in either a sample or blank.”

**Instrument detection limit (IDL):** “. . . the smallest signal above background noise that an instrument can detect reliably. Sometimes, the IDL and LOD are operationally the same.”

**Limit of quantitation (LOQ):** “. . . the level above which quantitative results may be obtained with a specified degree of confidence.” (10)(Reprinted with permission from *Analytical Chemistry*, December 1983, 55, pp. 2217)

In discussing detection levels, the guidelines indicate, as do others, that

The question of detection of a given analyte is often one of the most important decisions in low-level analysis. The question that must be answered is whether a measured value is significantly different from that found for the sample blank. (10) (Reprinted with permission from *Analytical Chemistry*, December 1983, 55, pp. 2217)

The guidelines then offer the following for determining the LOD:

Let  $S_t$  represent the total value measured for the sample,  $S_b$  the value for the blank, and  $s$  the standard deviation for these measurements. The analyte signal is then the difference  $S_t - S_b$ . It can be shown that for normal distributions  $S_t - S_b > 0$  at the 99% confidence level when that difference  $(S_t - S_b) > 3s$ . The recommended value of LOD is  $3s$ . LOD is numerically equivalent to the MDL as  $S_b$  approaches zero. (10) (Reprinted with permission from *Analytical Chemistry*, December 1983, 55, pp. 2217)

However, the guidelines indicate that the LOQ, not the LOD or the MDL, is the most appropriate measurement for determining the lower limit for the range of any measurement method because the confidence in the apparent concentration of the analyte increases as the analyte signal increases above the LOD. [ EPA considers its PQL analogous to the LOQ. (2)] The guidelines suggest the following for determining the LOQ:

The value for  $LOQ = 10s$  is recommended, corresponding to an uncertainty of  $\pm 30\%$  in the measured value ( $10 \pm 3s$ ) at the 99% confidence level.(10)(Reprinted with permission from *Analytical Chemistry*, December 1983, 55, pp. 2217)

Below is the table for reporting guidelines.

**Table I. Guidelines for Reporting Data\***

Analyte Concentration in Units of ( $S_t - S_b$ )	Region of Reliability
< 3	Region of Questionable Detection (and therefore unacceptable)
3	Limit of detection (LOD)
3 to 10	Region of Less-certain Quantitation
10	Limit of Quantitation (LOQ)
> 10	Region of Quantitation

\*In using the table, it should be remembered that the concentration levels indicated refer to interpretation of single measurements. Reprinted with permission from *Analytical Chemistry*, December 1983, 55, pp. 2217.

The guidelines emphasize the role of uncertainty in determining detection and quantitation limits and contend the most important characteristic of an analytical measurement is its range of uncertainty. Because of this uncertainty, the guidelines suggest several caveats to be considered in using any of these levels of detection.

Because the uncertainty can approach or equal an analytical result at the LOD and MDL, only data at or above the LOQ should be used for any decision making, regulatory calls, etc.

Cases involving litigation or enforcement actions should have the uncertainty interval clearly defined before any regulatory or permit level is considered as having been exceeded.

LOD and LOQ levels are not intrinsic constants, but are a function of the method, matrix, analyst, etc. and, consequently,

- Published LOD values are guidance only.
- Laboratories should determine and evaluate their own precision and detection levels.

The second bullet regarding the uncertainty interval is of import for WIPP's PRQL which is discussed below in the section on the MDLs and PRQLs as derived for the waste analysis plan.

### **Determination Limits Derived by L.A. Currie**

The limits developed by Currie, based on work by H. Kaiser, are considered the classic definitions and are built upon by others in discussing and developing determination limits.

Currie defined three levels for "a complete discussion of the (lower limits) for a measurement process" as follows:

$L_C$  - “decision limit/critical level” at which one may decide whether or not the result of an analysis indicates detection (the net signal level . . . above which an *observed* signal may be reliably recognized as “detected”)

$L_D$  - “detection limit” at which a given analytical procedure may be relied upon to lead to detection (the “true” net signal level which may be *a priori* expected to lead to detection)

$L_Q$  - “determination limit” at which a given procedure will be sufficiently precise to yield a satisfactory quantitative estimate (the level at which the measurement precision will be satisfactory for quantitative determination). (11)

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The mathematical definitions of these limits are given in the table below.

**Table II. Mathematical Definitions of Currie’s Determination Limits**

Equation	Definitions
$L_C = k \sigma_0$	$\sigma_0$ = the standard deviation of the net signal of a population of blank samples
	$k$ = the abscissa of the standardized normal distribution corresponding to probability level, $1 - \alpha$
$L_D = L_C + k \sigma_D$	$\sigma_D$ = population standard deviation of the net response signal after subtracting the background signal
	$k$ = the abscissa of the standardized normal distribution corresponding to probability level, $1 - \alpha$
$L_Q = k_Q \sigma_Q$	$L_Q$ is the true value of the net signal, $\mu_Q$ , having a standard deviation, $\sigma_Q$ , and $1/k_Q$ is the requisite relative standard deviation

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These “definitions” of the various  $\sigma$ ’s and  $k$ ’s are taken from Currie (11) and Gibbons (12).

As with the guidelines developed by the American Chemical Society, Currie developed “working expressions” for these definitions and they are given below.

**Table III. “Working Expressions for  $L_C$ ,  $L_D$ ,  $L_Q$ ”**

	$L_C$	$L_D$	$L_Q$
Paired observations	2.33 $\sigma_B$	4.65 $\sigma_B$	14.1 $\sigma_B$
“Well-known” blank	1.64 $\sigma_B$	3.29 $\sigma_B$	10.0 $\sigma_B$

\*Assumptions:  $\alpha = 0.05$ ;  $k_Q = 10$ ;  $\sigma_0 = \text{const}$ . Reprinted with permission from *Analytical Chemistry*, March 1968, 40, pp. 586-588.



According to Currie, “. . .the levels  $L_C$ ,  $L_D$ , and  $L_Q$  are determined entirely by the error-structure of the measurement process, the risks, and , and the maximum acceptable relative standard deviation for quantitative analysis.  $L_C$  is used to test an experimental result, whereas  $L_D$  and  $L_Q$  refer to the capabilities of measurement process itself. . . .” (11) (Reprinted with permission from *Analytical Chemistry*, March 1968, 40, pp. 586-588.)

### **Concerns Regarding the EPA MDL**

Gibbons (12) has been among the first to discuss at length the statistical underpinnings for the MDL and to express concerns regarding the EPA MDL. As indicated above, the EPA MDL is based on that derived by Glaser et al. (6) Gibbons’ main concern regarding the EPA/Glaser MDL is that, based on Glaser’s derivation formulae for the MDL, it is equivalent to Currie’s decision level, not the detection level. The Currie decision level is the “standard deviation of the net signal found in the population of blank samples.” (12) As an equivalent of the Currie decision level, the EPA MDL is in the unreliable analytical region; it is not in the qualitative or quantitative region. Consequently, its use in quantitative decisions is questionable. (12)

There are additional concerns. A single concentration is used to estimate the standard deviation, not multiple samples with several concentrations at each. Another concern is the statistical inconsistency as to whether or not Glaser et al. were using the standard deviation at a set concentration or the standard error at zero concentration. (12)

Another of Gibbons’ concerns is that in practice the EPA MDL is driven by the spiking concentrations used by the laboratories. Laboratories, because the MDL is not known, spike at concentrations near a risk-based level or the maximum contaminant level. These levels are usually far below the true analytical capabilities of the method. This can lead to grossly underestimating the true MDL, which in turn is used to determine the PQL. (12)

### **MDL AND PRQL AS DERIVED FOR THE WASTE ANALYSIS PLAN**

The details of the derivation of the MDL and PRQL contained in this section are derived from a written private report from Karen Knutson (13) developed at the request of CAO Area Counsel.

### **PRQLs for Solidified Waste Analysis**

The objective of the analysis of solidified waste forms destined for WIPP was to determine if the waste exhibits a toxic characteristic as defined by RCRA. PRQLs for metals that are toxic characteristic wastes were set at the regulatory threshold levels, which are “. . . TC levels expressed as total values.” (13) However, for VOCs and SVOCs that are TC wastes, benzene and nitrobenzene were chosen as the baseline VOC and SVOC, respectively, and their regulatory threshold levels (benzene, 10.00 mg/kg; nitrobenzene, 40.0 mg/kg) were established as the PRQLs for TC and non-TC VOCs and SVOCs. The factors used in choosing these baseline analytes were their toxicity characteristics, reported prevalence and concentrations in waste. For the very few VOCs and SVOCs that had regulatory threshold levels below those for benzene and nitrobenzene, their PRQLs remained their regulatory threshold levels (vinyl chloride, 4.0 mg/kg;

hexachlorobenzene, 2.6 mg/kg). Also, the PQRLs for the TC VOCs that were nonhalogenated were based on levels equivalent to those for the headspace gas alcohols and ketones (acetone, 100.0 mg/kg).

### **PQRLs for Headspace Gas Analysis**

**Originally, the function of the headspace gas analysis was to determine that no contaminant exceeded the health-based, no-migration standard of the land disposal restrictions (LDR). Only later was such analysis used to confirm acceptable knowledge used in waste characterization.** Because the initial concern was the LDR standard, the regulatory drivers for the headspace gas analysis were the following requirements in the conditional No-Migration Determination (NMD) issued by EPA on November 14, 1990 (14):

Concentration of hazardous constituents in the WIPP underground exhaust shaft

Allowable maximum and mean concentrations of hazardous constituents in container headspace gas

500 ppmv limit for total flammable VOCs in container headspace.

[Basis for 500 ppmv limit is as follows:

EPA, consequently, is requiring DOE to ensure that individual waste containers have met the prohibition of flammable gases. . . . below flammable levels (i.e., 50 percent of the mixture LEL (lower explosive limit)). . . . Significant levels of flammable VOCs are indicated by measured concentrations (excluding methane) . . . of 500 parts per million or greater, by volume, as determined by gas chromatography and mass spectrometry (GC/MS). (14)]

### **Derived PRQL of 100 ppmv for Selected Alcohols and Ketones**

These alcohols and ketones were included in the NMD based on their flammability or toxicity, and a PRQL of 100 ppmv was considered adequate to ensure that:

Flammable analytes would not violate the 500 ppmv total flammable VOC limit because these analytes are not prevalent in the wastes coming to WIPP.

Toxic alcohols and ketones would not migrate above the health-based, no-migration standard.

### **Derived PRQL of 1 ppmv and Then 10 ppmv for the Other VOCs**

These levels of PRQL were developed to comply with the most stringent of the NMD conditions, the allowable concentrations of hazardous constituents in the WIPP underground exhaust shaft. The factors in the development of these PRQLs were:

Calculations were based on the diffusion rates of VOCs through the carbon composite filters on each drum.

Carbon tetrachloride was the baseline VOC because of

- Its toxicity.
- Its prevalence, based on acceptable knowledge, in the containers.

Derived PRQL levels based on:

- Health-based limit for carbon tetrachloride of  $0.03 \text{ g/m}^3$ .
- To demonstrate that carbon tetrachloride would not migrate above the limit of  $0.03 \text{ g/m}^3$  required a PRQL of 1 ppmv for an individual container concentration during the test phase, or a PRQL of 10 ppmv for a waste panel during the disposal phase.
- “. . . data quantitated at 10 ppmv . . . needed to support ongoing CAO studies to evaluated [sic] headspace gas representativeness and potential flammable gas limits.” (13)

The result of these considerations was a PRQL developed to ensure that waste received at WIPP would not contain a contaminant at a level that could result in the contaminant migrating from the unit at a concentration that would exceed a health-based standard, as opposed to a PRQL based on an analytical confidence level.

### **MDLs for Solidified Waste and Headspace Gas Analyses**

After determining the PRQLs, the MDLs were set 8-10 times lower than the corresponding PRQLs. This calculation was based on the EPA statement in SW-846 that the PRQL is usually 5-10 times the MDL. (13)

### **COMPARISON WITH THE DERIVATION OF THE MDLs AND PQLs BY OTHERS**

The WIPP approach is interesting because it is the reverse of the other approaches, where the MDL is determined first and then a PQL is calculated from that MDL. There has been no assessment of the MDL and its relative standard deviation in order to calculate the PRQL in the WIPP case. As a result, the WIPP PRQLs have not had an assessment of the uncertainty interval associated with them. This in turn makes it very difficult to determine whether or not a permit or regulatory level has been exceeded.

Another concern is the use of the RTLs of two to three baseline contaminants to set a PRQL for many other contaminants. One of the reasons for using baseline contaminants was to avoid a wide range of calibration standards. If each RTL had been used for the toxicity characteristic VOCs, the PRQLs would have ranged from 4 mg/kg to 4000 mg/kg, resulting in a wide range of calibration standards. However, this very range indicates how the approach can be a double-edged sword. The approach of using the lowest RTL to determine a PRQL for many contaminants is conservative for ensuring that the regulatory limits are met, but it may be too restrictive analytically. More than one to two PRQLs may be needed.

## CONCLUSIONS

The derivation of the PRQLs is crucial because of their role in waste characterization for waste destined for WIPP. If a constituent is detected at a level above the PRQL, the waste is considered to be TRU mixed waste. The determination as to whether the waste is or is not a TRU mixed waste is a concern for WIPP because presently it can accept only TRU nonmixed waste. [Upon receipt of the hazardous waste permit from the New Mexico Environment Department, WIPP can receive both TRU nonmixed waste and TRU mixed waste.] Consequently, because the PRQLs play such a pivotal role in determining for the present whether or not a waste can be shipped to WIPP, their derivation must be fully understood to ensure that they are properly used in waste characterization.

In discussing the impact of the PRQLs on waste characterization, it must be remembered that they were developed at different stages and had different regulatory drivers. The first established PRQLs were for headspace gas analysis and, as indicated above, the original main objective in deriving these PRQLs was to establish a level for a contaminant such that WIPP could ensure that no contaminant exceeded the health-based, no-migration standard of the LDRs. The baseline contaminant was carbon tetrachloride with a health-based limit of  $0.03 \mu\text{g}/\text{m}^3$ . Based on this health-based limit, a PRQL of 1 ppmv was established for the test-phase and 10 ppmv for the disposal phase. The toxicity characteristic concentration for carbon tetrachloride is 0.5 mg/l. The present PRQL of 10 ppmv could be far too low given that it is based on limit of  $0.03 \mu\text{g}/\text{m}^3$ , not 0.5 mg/l.

The PRQLs for solidified waste were derived later and they are based on the threshold toxicity characteristic concentrations expressed as totals. Consequently, any contaminant exceeding its PRQL is probably exceeding the regulatory concentration and should be considered a hazardous waste. The PRQLs derived in this manner can be used appropriately for waste characterization.

As indicated above, one of the concerns regarding the derivation of the WIPP PRQLs is that the uncertainty interval is not known. For the solidified waste PRQLs, the interval is important for waste that is borderline. Because the uncertainty interval is not known, more samples—two to three— may be required before a waste classification call can be made. Because the PRQLs for headspace gas are not based on the toxicity characteristic levels, it is difficult to assess the impact of not knowing the uncertainty level. However, again, for waste that is borderline, more sampling should be considered.

As indicated above, the use of the RTLs of two to three baseline contaminants to set a WIPP PRQL for many other contaminants may be too restrictive, particularly when the range of the RTLs is as large as it is in WIPP's case. As indicated by the American Chemical Society, the PQL is not an intrinsic constant, but is highly dependent upon the matrix, method, etc. More PRQLs may be needed due to this variability and the range of RTLs involved.

On a broader overview, there is consensus between EPA and the regulated community that allowances are required for the increased variability at levels close to the detection limits.

Beyond that, further agreement will take considerable work. The regulating entities are driven by statutes and public policy pressure to ensure that toxic constituents are detected at lower levels. This demands increasingly sensitive and lower MDLs and PQLs. More important is the issue raised by Gibbons (12) regarding the statistical underpinning of the EPA MDL (6). If the EPA MDL, based on Glaser's derivation, places it in the unreliable detection area, that certainly is a concern for the regulated community.

Lastly, there may be a basis for the establishment of MDLs and PRQLs by WIPP for use by the complex in characterizing the waste to be managed, stored, and disposed of by WIPP. It is analogous to the EPA situation regarding compliance levels.

As indicated previously, one aspect of the EPA process for developing a regulatory level is to propose:

. . . . to use a value of five times the analytical detection limit as the quantitation limit and to set the regulatory level at the quantitation limit for those compounds for which the calculated regulatory level is below the quantitation limit, and interlaboratory studies were not available . . . . (4)

EPA's main objective is to ensure that the analytical results can be used to determine if regulatory levels have been met or exceeded.

WIPP is in a similar situation in that it must ensure the waste received meets its applicable regulatory levels. Consequently, it is setting programmatic MDLs and PRQLs. At the time these MDLs and PRQLs were developed, the RCRA regulatory levels of concern to WIPP were the TC levels for waste characterization and the health-based, no-migration standard of the land disposal restrictions, and, as discussed above, these levels have been used in deriving the PRQLs. The PRQLs for the totals analysis of solidified waste were the TC levels expressed as total values. For the headspace gas analysis, the most stringent criterion from the NMD was the concentration of hazardous constituents in the WIPP underground exhaust shaft. WIPP's use of PRQLs to ensure that regulatory levels are met or not exceeded is analogous to EPA use of MDLs and PQLs to ensure that regulatory levels, such as MCLs, are met or not exceeded.

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