WASTE DETERMINATIONS CASE STUDY

Problem Statement: Multiple tar storage tanks at XYZ Corporation must be drained and cleaned prior to major refurbishment. This project is to be carried out over a 1-year period. Sediment on the bottom of the tanks cannot be recovered for process or product use. The hazardous waste stream is K142 - tar storage tank residues from the production of coke from coal or from recovery of coke by-products produced from coal. Must this waste be managed in a unit equipped with air emission controls as required under the Subpart CC rules?

Given:

1) Probable waste constituents include - ammonia, benzene, toluene, xylene, phenol, cresol based on knowledge of the coke by-product process.

2) Tank residue quantity - 20,000 gallons per tank from 6 tanks.

Required:

1) Analyses or knowledge to determine VO concentration to compare to the Subpart CC action level of 500 ppmw.

This case study will demonstrate procedures that can be used in waste determinations involving streams with multiple components with a variety of volatilities. The solution will involve sampling and analyses for batch wastes, checking for contributions of relatively nonvolatile components to VO concentration determinations, and final computation of average VO concentration to compare to the 500 ppmw action level.

Basis for Determination

1) The facility owner/operator does not have sufficient concentration data available to make a determination on the basis of knowledge. Therefore, ***direct measurement by sampling and analysis is required***.

2) Each tank's residue will be removed by truck. The loads can be considered batches of the overall process waste from the facility. Therefore a ***batch sampling plan is in order***.

3) Subpart CC requires that samples for direct measurement represent Vo concentrations over normal variations in operating conditions for a batch process performed repeatedly. Because this is residue being pumped from the tanks for cleaning and refurbishing, process operating conditions are not a factor influencing VO concentration.

4) One approach to sampling in this case is to extract samples from each tank prior to removal of the waste into trucks.

Site Sampling Plan

1) Written procedures are required for collection and handling of samples. ***These procedures are documented in a site sampling plan.***

2) The plan must address ***how "representative samples" will be collected.*** For example, if the waste in each tank is sampled, the plan must explain how representative samples would be obtained to account for variation in composition within the tank, and perhaps the form of the waste (i.e., sludge versus wastewaters), if multiple forms are present.

3) Since these tanks are out-of-service, there will be no variation in time as a result of changing process conditions. Because each of the 3 tanks served the same process train, by providing parallel storage, the owner/operator may be able to make the case that there should be no tank-to-tank variations. It may therefore be necessary to perform sampling on wastes in only one tank in each process train.

4) One or more waste determination test runs must be performed on the waste from the tank(s). ***The intent of the rule was that each waste determination test run be composed of a minimum of four samples taken within a one hour period.*** However, the time factor wouldn't be critical in this case for static wastes.

Analyses Choices for Direct Measurement

1) The amended rules include *EPA Method 25D* and a number of alternative EPA methods for direct measurement, including ***EPA Methods 624, 625, 1624, 1625, 8260, and 8270***.

2) The alternatives methods to Method 25D are used to measure specific organic components, as opposed to VO concentration. ***If methods that speciate are selected for the analysis, its the owner/operators responsibility to be sure that all volatile organic species in the waste are measured***. Where there are multiple constituents, such as in this case, it may be less costly or more convenient to use Method 25D and avoid the need to speciate.

3) In this case the owner/operator selected Method 25D.

Initial Analytical Results

1) This example has been simplified to demonstrate the process of converting analytical results into an average VO concentration. In real situations, analyses of waste from each of the 6 tanks might be required, depending on site specific considerations.

2) Given the static waste situation, one waste determination test run was made on one tank in each group of three tanks (for a total of 2 test runs) with the owner/operator providing adequate justification for this decision. And, in a further simplification, the minimum number of samples (4) constituted each waste determination test run. The initial Method 25D results are shown in the Table 1 below.

Table 1

Run 1	Method 25D ppm
Sample 1	480
Sample 2	410
Sample 3	720
Sample 4	800
Average[a]	603

Run 2	Method 25D ppm
Sample 1	290
Sample 2	355
Sample 3	550
Sample 4	450
Average[a]	411

Average of Two Runs[b]	507 ppm

Footnotes:

[a] The average concentration for a waste determination test run is the mass weighted average for each test within that run. The waste quantities are the same for each test (you're sampling the same waste each time) so the run average is just the average of the four tests without having to consider quantity or mass in the averaging calculation.

[b] Since the residues were reported to be 20,000 gallons each tank and it is assumed that there are no tank-to-tank variations in the waste, the mass weighted average concentration for all the waste (both groups of tanks) is the average of the two runs.

3) The initial analytical results show that the VO concentration as determined by Method 25D exceeds 500 ppmw.

Review of the Constituent Data

1) At this point the owner/operator sees the results are borderline, but ***above the action level of 500 ppmw*** and reviews the situation.

2) Based on his knowledge of the process that generates the waste, he knows there could be some organics present in the waste that might be relatively non-volatile. He decides to ***check the Henry's Law Constants*** to see which compounds might not have to be included in the waste determination VO concentration that is compared to the action level.

3) If the owner/operator has no compound specific property data available, they can be obtained from WATER8. ***WATER8 emission modeling software and chemical property data are available on the EPA OAQPS TTN bulletin board. Also a list of compounds has been published in the Federal Register with values of fraction measured by Method 25D (f_m) to assist with this process***. Data for compounds not on the list are also available from EPA OAQPS staff. Table 2 shows data extracted.

Table 2

Constituent	Henry's Law Constant atm/gm-mole/m^3	Fraction Measured by Method 25D (f_m)
Benzene	5.5×10^{-3}	1.00
O-Cresol	1.6×10^{-6}	0.06
Phenol	1.3×10^{-6}	0.04
Toluene	6.4×10^{-3}	1.00
Xylene	5.2×10^{-3}	1.00

Source: WATER8, 40 CFR Part 63, Subpart DD, EPA staff

4) From Table 2 he finds that phenol and cresol are not very volatile. In fact, ***phenol and cresol meet the criteria for exclusion from the VO determination (< 0.1 Y/X or <1.6 x 10^{-6} atm/gm-mole/m^3)***. The f_m values show that about 6 percent of cresol and 4 percent of phenol in a waste sample are actually measured by Method 25D. These percentages of the true concentrations of phenol and cresol in the waste can be subtracted from Method 25D results.

Removing Phenol and Cresol from Method 25D Results

1) On the basis of Table 2 information, the owner/operator requests that the samples (duplicates were taken) be analyzed specifically for phenol and cresol. The results are shown in Table 3 below.

Table 3

Run 1	Method 25D ppm	o-Cresol ppm	Phenol ppm
Sample 1	480	100	200
Sample 2	410	140	280
Sample 3	720	200	400
Sample 4	800	240	480
Average[a]	603	170	340

Run 2	Method 25D ppm	o-Cresol ppm	Phenol ppm
Sample 1	290	60	120
Sample 2	355	100	160
Sample 3	550	140	240
Sample 4	450	120	220
Average[a]	411	105	185

Average of Two Method 25D Runs[b]	507 ppm

Footnotes:

[a] The average concentration for a run is the mass weighted average for each test within that run. The waste quantities are the same for each test (you're sampling the same waste each time) so the run average is just the average of the four tests without having to consider quantity.

[b] Since the residues were reported to be 20,000 gallons each tank, the mass weighted average concentration for all the waste (both groups of tanks) is the average of the two runs.

2) To adjust the Method 25D results to remove the contribution of phenol and cresol, their concentrations are multiplied by their respective f_m values. The results of each multiplication are subtracted to yield a corrected Method 25D result.

Final Corrected Method 25D Results

1) The calculations to correct Method 25D results are shown below. Remember that weightings by quantity are ignored here because all tanks have the same volume of tank residue to be removed.

Cresol Correction:

Run 1 average measured concentration of cresol is 170 ppm. The correction to Method 25D for Run 1 is 170 x 0.06, or 10.2 ppm. Similarly the correction for Run 2 is 105 x 0.06, or 6.3 ppm.

Phenol Correction:

Run 1 average measured concentration of phenol is 340 ppm. The correction to Method 25D for Run 1 is 340 x 0.04, or 13.6 ppm. Similarly the correction for Run 2 is 185 x 0.04, or 7.4 ppm.

Run 1 Corrected Method 25D:

Uncorrected average:	603	ppm
Subtract phenol:	13.6	ppm
Subtract cresol:	10.2	ppm
Corrected average:	579	ppm

Run 2 Corrected Method 25D:

Uncorrected average:	411	ppm
Subtract phenol:	7.4	ppm
Subtract cresol:	6.3	ppm
Corrected average:	397	ppm

The overall average VO content for tank residues from both process trains is 488 ppm.

Based on these analyses and calculations, the VO concentration is below 500 ppm and the wastes would not have to be treated in units controlled for air emissions.