B.Sc. Course(Second Semester)

University of Babylon-College of Engineering

Environmental Engineering Department

Hazardous Waste Auditing:

H.W audit :

   The tracking of hazardous wastes within an industry , a waste transfer station or after excavation from a contaminated site.

   The basic for H.W audit is a source material balance, which is the same as reactor balance.
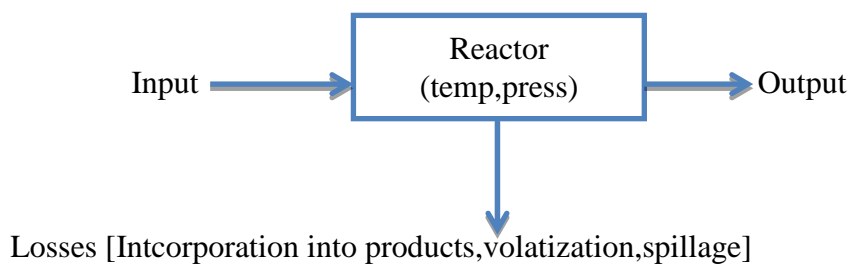
Example:

If 20-208L (55gal) drums are generated per month that contain 800 mg/L trichloroethylene (TCE), the mass of TCE in the drums is:

$20 \times 208L = 4160L$

$800\dfrac{mg}{L} \times 4160L = 330000mg$

$TCE = 3.33kg\ TCE$

   One of the goals of pollution preventation programs is the optimization of process condition (reactor temperature and pressure), to improve yields of the products while decreasing the volume of side streams that contain unreacted materials and waste products.

Input ⟶ | Reactor (temp,press) | ⟶ Output

Losses [Intcorporation into products,volatization,spillage]

Acquisitions

Wastes

Catalysts →

Driers →

Absorbents →

Lubricating oils →

Analytical chemicals →

Filters →

Packaging materials →

Cleaning solvents →

Water treatment chemicals →

Cooling tower additives →

Maintenance materials →

Shops, motor →
vehicle supplies

Industrial
Facility

Losses:
Incorporation
into products

Volatilization

Spillage

● Spent catalysts
● Spent absorbents
● Waste oils
● Laboratory chemical wastes
● Spent and dirty filters
● Solids
● Spent chemicals
● Blowdown sludge
● Scrap pipe
● Equipment
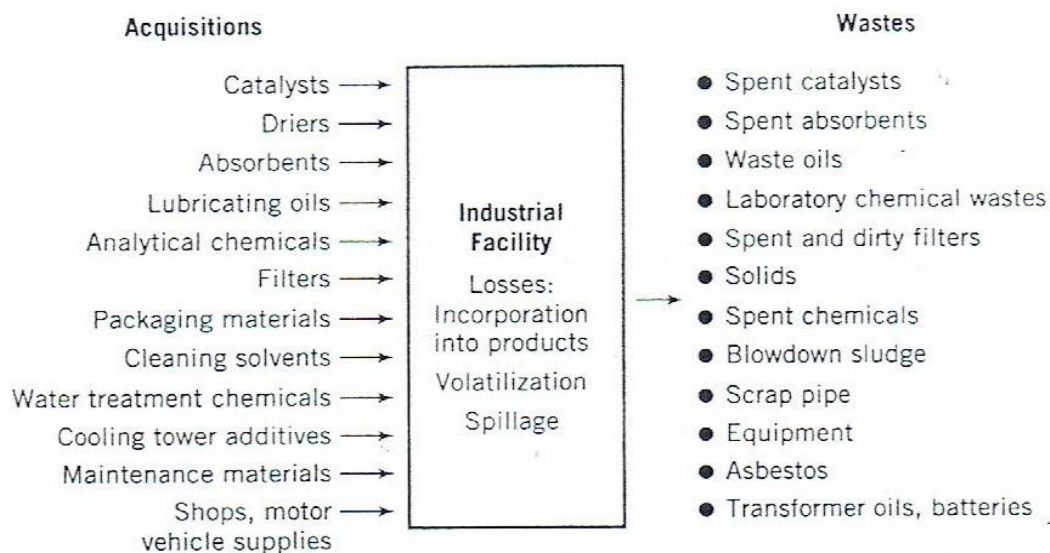● Asbestos
● Transformer oils, batteries

Figure8: Procedure for performing a materials balance to serve as a basis for waste audits.

For industrial synthesis processes (e.g., the production of pesticides, dyes, etc. from chlorobenzenes, chlorophenols, and anilines), most of the source material is converted to the products. One of the goals of pollution prevention programs is the optimization of process conditions (e.g., reactor temperature and pressure) to improve yields of the products while decreasing the volume of side streams that contain unreacted materials and waste products.

The primary routes by which unreactive wastes leave an industrial facility are :

1-industrial wastewater discharges,

2-RCRA-related waste management activities,

3-volatilization(e.g., fugitive emissions), and

4-spillage and other unaccounted losses.

Such unreactive wastes include solvents, paint removers, and other chemicals that are not consumed in chemical reactions. Chlorophenols, hexachlorocyclopentadiene, and other industrial intermediates are usually consumed in chemical reactions during industrial synthesis processes, and their output is usually minimal. In fact, the goal in the chemical processing of reactive materials is to incorporate these intermediates into products. They are the building blocks of the products of synthesis, and the presence of an unreacted intermediate results in extra cost. The use of a hazardous waste audit for tracking wastes in industrial facilities is demonstrated in below example.

Example : Hazardous Waste Audit of a Waste Transfer Facility

The state regulatory agency has accused your company, a waste transfer facility, of massive spillage due to improper housekeeping practices over the past year. The agency alleges that the upper 5 cm of the soils on your property (approximately 140000kg of soil) are contaminated with polychlorinated biphenyls (PCBs) above the regulatory action level of 50ppm. You can sample your property and analyze the soils for PCBs to refute the agency's claims, but the cost is estimated at $60000. As an alternative, perform a waste audit on the transformer oils that were exchanged at the waste transfer facility over the past year. Based on your company's records given here, can you show that PCBs were not spilled on the property at a level greater than 50 ppm? Because PCBs are characterized by low volatility and water solubility, you can assume that volatilization and leaching losses were negligible.

Industrial Records
Incoming shipments of transformer oils:

Invoice No.	Volume (L)	Volume (gal)	PCB Concentration (mg/L)
01137	208	55	42,000
01138	1740	460	1,300
01139	795	210	22,000
01140	3260	860	8,200
01141	1440	380	38,000

Industrial wastewater:

Flow: 1,890,000 L/day
Mean concentration: 0.002 mg/L

RCRA disposal manifests:

Manifest No.	Volume (L)	Volume (gal)	PCB Concentration (mg/L)
0124	500	1890	22,100
0125	500	1890	18,400
0126	500	1890	9,550
0127	500	1890	6,420

Solution:

1- Determine the incoming mass of PCBs to the waste transfer facility.

Invoice No.	Volume		PCB Concentration (mg/L)	Mass (kg)*
	(L)	(gal)		
01137	208	55	42,000	8.75
01138	1740	460	1,300	2.27
01139	795	210	22,000	17.5
01140	3260	860	8,200	26.7
01141	1440	380	38,000	54.6
Total				109.8 kg

*Total volume (L) × PCB concentration (mg/L) × kg/1,000,000 mg

2- Determine the mass leaving the facility.

Wastewater:

$$1890000 \, L/day \times 365 \, d \times 0.002 \, mg/L = 1.38 \, kg$$

RCRA Manifests:

Manifest No.	Volume		PCB Concentration (mg/L)	Mass (kg)
	(L)	(gal)		
0124	1890	500	22,100	41.8
0125	1890	500	18,400	34.8
0126	1890	500	9,550	18.0
0127	1890	500	6,420	12.1

Total: RCRA Manifests   106.7 kg
Total: Wastewater and RCRA Manifests   108.1 kg
Total mass unaccounted for: 109.8 kg − 108.1 kg = 1.7 kg
Total mass to trigger regulatory action: 50 mg/kg × 140,000 kg soil =
                                          7,000,000 mg = 7.0 kg

Because the total mass unaccounted for in waste disposal practices is less than the regulatory action level, a case could be presented to the state regulatory agency that the losses do not provide sufficient PCB concentrations in the soil to exceed the regulatory action level.

Hazardous Waste Site Assessments

Abandoned landfill, surface impoundments, and other hazardous waste sites must be assessed to determine the extent of contamination before cleanup is initiated. Unlike municipal wastewater or industrial waste streams, hazardous wastes disposed of improperly at waste sites are not usually evident to the naked eye because most of the contamination lies below the soil

surface. Therefore, a series of site assessment procedures must be conducted, ranging from record searches to detailed subsurface sampling.

Site assessments follow a common procedure that is divided into three phases, each of which is increasingly complex. Site assessments are initiated whenever the existence of a hazardous waste site is suspected, which may include a leaking underground storage tank (UST), the discovery of hazardous chemicals in a drinking water supply, a high incidence of localized illness, or a routine property transfer. The pattern is much the same for small sites as for large ones. In fact, the Preliminary Assessment and Remedial Investigation/Feasibility Study (RI/FS) programs of CERCLA follow the same format as the general site assessment phases described below.

The three site assessment phases are appropriately named Phase I, Phase II, and Phase III, and each builds upon the previous phase with more extensive information. A Phase I assessment, which may also be called a Level1 assessment, preliminary assessment, or initial assessment study, is begun in an attempt to confirm the suspicions of the presence of hazardous waste. The procedure focuses on "soft" or non.

The primary routs by which unreactive wastes leave an industrial facility are:

1-Industrial waste water discharge.

2-Volatilization.

3-Spillage and other uncounted losses.

Hazardous Waste Site Assessment:

There are three site assessment phases each builds upon the previous phase:

1-PhaseI [level 1, preliminary, initial assessment] start with:

a-A search of historical documents including newspaper, reports of spills, official records of any safety violation that may have taken place.

b-Also focus on information from the past few decades.

c-On site inspection and personal interviews.

d-Awalk-through of the site can provide class of improper waste disposal.

2-Phase II

a-Confirm the presence of hazardous waste at the site[depending on phase I].

b-Finalizing any record searches that were not completed in phase I assessment.

c-A detailed evolution of pathways and potential receptors is begun, include analysis of surface to assess ground water flow directions and travel times of drinking water wells or other receptor.

d-Involve an increased sampling effort based on where the contamination is expected, if phase II studies show that the site is contaminated.

3-Phase III

Study is initiated.

Investigation is to detail the extent of contamination in terms of area , volume, and the contamination concentrations. [soil, subsurface and / or groundwater may be sampled extensively lead to provide sufficient information to assess the site hazard and provide criteria for the design of remedial processes.

Example:

A1890-L (500gal) tanker containing a 40% formulation of 2,4-D in acetone has spilled contaminating an area of soil approximately $200m^2$ and 50cm deep-if the soil bulk density is 1800 kg/m^3 estimate 2,4-D concentration in the soil?

Sp.gr.(2,4-D) 1.416

Source Sampling:

Sampling of source materials, including contaminate soil, lagoons and drum contents is necessary to assess their degree of hazard and to comply with regulations.

Statistical Fundamental For Sampling:

Two fundamental statistical concepts that are important in developing sampling plans they are:

Accuracy: How close a measured values is to the true value.

Precision:

The measure of the variability between samples. Soils and sludge's are characteristically heterogeneous, and the concentration of hazardous chemical in each subsample is likely to be quite different as a result, hazardous waste samples are often characterized by low precision and high variability.

Statistical analysis are concerned with some aspects related to accuracy and precision:

1-The level of accuracy must be specified

α =error allowed

$1 - \alpha$ =is the corresponding confidence level.

Example:

A specified error of 5% correspond to a 95% confidence that the sample value is an accurate estimate of the true value.

2-Precision required (D) is the deviation from the true value , in H.W management, this value represented by a regulatory standard such as TCLP [Toxicity Characteristic Leaching Procedure] value.

3-Population: represents the true value of the global data set for the system under consideration, may be thought of as the universe of data within the system boundaries, may be described by such parameters as a mean $[\mu]$ with a variance $[\sigma^2]$ and standard deviation $[\sigma]$.

A sample is a data set regardless of size, collected from population. Sample variable include data point $[x_i]$ and the number of data points in the sample $[n]$.

The sample mean $[\bar{x}]$ is:

$$\bar{x} = \frac{\sum x_i}{n}$$

$$variance \approx S^2 = \frac{\sum(x_i - \bar{x})^2}{n - 1}$$

The sample standard deviation $S = \sqrt{S^2}$

Degree of freedom [df]: a parameter used in several statistical distributions, is an integer equal to the sample size [n]-no. of population parameter being evaluated through analysis of the sample.

In most cases, one parameter used df=n-1

Probability Sampling: is based on the t-distribution. A probability density function that is used to evaluate sample means when the population variance $[a^2]$ is not known but can be estimated by $[S^2]$.

The t-distribution is defined as:

$$t = \frac{\bar{x} - \mu}{S/\sqrt{n}} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots . (1)$$

$S/\sqrt{n}$ is also called the standard deviation of the mean $[S\bar{x}]$. Values of [t] listed in tables.

Rearranging the above equation gives:

$$n = \frac{t^2 S^2}{D^2} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots . \dots (2)$$

Where:

t = Students two sided t with n-1 degrees of freedom for a confidence level of $(1 - \alpha)\%$.

S^2 = the sample variance for the initial data.

D = a specified limit relative to the sample mean.

The value of D is derived from the term $[\bar{x} - \mu]$

Table1:Procedures for the Simple Randomized Sampling of RCRA Hazardous Waste Sources

1. Collect a few (3–6) random samples to obtain preliminary estimates of $\bar{X}$ and S^2.
2. Using Equation 4.6, estimate the minimum number of samples (n) using a specified confidence level, e.g., 95% or 99.9% (1 in 20 or 1 in 1,000).
3. Using a sampling grid and random number assignments, collect and analyze at least the minimum number of samples from the waste source.
4. Determine the values of $\bar{X}$ and S^2 for the detailed sampling plan.
5. If the sample mean, $\bar{X}$, is ≥ the regulatory threshold (RT), the compound is present in hazardous concentrations/However, if $\bar{X}$ < RT, determine the confidence interval using Equation 4.7. If the upper CI < RT, the compound is not present at a hazardous level and the sampling and analysis are finished.

A specific application of equation 1 is the strategy for sampling RCRA waste sources, that is, determining the number of samples that needs to be collected, a procedure that is outlined in table1. A more general application of a sampling design is demonstrated in below example.

Example: Source Sampling Design

A drying bed holding sludge from an electroplating process is to be sampled for cadmium content. The dimensions of the drying bed are 6m×8m, and the sample volume will require an area 40cm×40 cm. five preliminary samples were collected randomly with the following results: 25, 36, 49, 28, and 48 mg/kg Cd. Based on this information, develop a simple randomized sampling scheme. Determine:

1-The number of samples required for 95% confidence limits within 5 mg/kg of the sample mean and

2-The location of the samples in the sludge bed.

Solution:

For the five preliminary samples:

$$\bar{x} = \frac{25 + 36 + 49 + 28 + 48}{5} = 37\frac{mg}{kg}Cd$$

$$S^2 = \frac{\Sigma(X_i - \bar{X})^2}{n - 1}: (25 - 37)^2 = 144$$

$$(36 - 37)^2 = 1$$

$$(49 - 37)^2 = 144$$

$$(28 - 37)^2 = 81$$

$$(48 - 37)^2 = 121$$

$$\overline{\Sigma(X_i - \bar{X}) = 491}$$

$$S^2 = \frac{491}{4} = 123$$

$$S = \sqrt{123} = 11$$

From the students t table , $t_{95\%} = 2.776$ (*note*: *Use the* $\alpha = 0.025$ *column, because* $2 \times 0.025 = 0.05[5\%]$, which is the error level for the 95% confidence level). The number of subsequent samples (n) is

$$n = \frac{t_{95\%}^2 \, S^2}{D^2} = \frac{(2.776)^2 \, (123)}{S^2} = 37.9 \, samples; round \, up \, to \, 38 \, samples.$$

The number of sampling units in one direction is 8m/0.4m=20 units, the number in the other direction is 6m/0.4m=15 units. The 15×20=300 sampling units(Figure9) are numbered consecutively, and then 38 random numbers are selected from Appendix. Random number selection may be started at any point on the table: for this example, begin selection at line1, column5 and move down the columns. Three –digit numbers within the window 1 to 300 are taken from each group. During random number selection, only numbers within the range of 001 through 300 are selected (i.e., numbers outside of this range are disregarded). If a number comes up twice, it is ignored the second time, because it is assumed that the sampling unit does not contain sufficient medium to be sampled twice. Based on these procedures, the 38 locations of the random samples are

078	151	047	150
061	186	263	125
277	185	287	179
188	141	153	208
174	248	253	082
232	187	081	221
091	058	300	066
133	176	015	069
197	298	011	
279	136	234	

The locations of the sampling units are shaded in Figure9.

Stratified Random Sampling

The basis for stratified random sampling is dividing the site into layers, or strata, each of which is then sampled using randomized sampling techniques.

1	21	41	61	81	101	121	141	161	181	201	221	241	261	281
2	22	42	62	82	102	122	142	162	182	202	222	242	262	282
3	23	43	63	83	103	123	143	163	183	203	223	243	263	283
4	24	44	64	84	104	124	144	164	184	204	224	244	264	284
5	25	45	65	85	105	125	145	165	185	205	225	245	265	285
6	26	46	66	86	106	126	146	166	186	206	226	246	266	286
7	27	47	67	87	107	127	147	167	187	207	227	247	267	287
8	28	48	68	88	108	128	148	168	188	208	228	248	268	288
9	29	49	69	89	109	129	149	169	189	209	229	249	269	289
10	30	50	70	90	110	130	160	170	190	210	230	250	270	290
11	31	51	71	91	111	131	151	171	191	211	231	251	271	291
12	32	52	72	92	112	132	152	172	192	212	232	252	272	292
13	33	53	73	93	113	133	153	173	193	213	233	253	273	293
14	34	54	74	94	114	134	154	174	194	214	234	254	274	294
15	35	55	75	95	115	135	155	175	195	215	235	255	275	295
16	36	56	76	96	116	136	156	176	196	216	236	256	276	296
17	37	57	77	97	117	137	157	177	197	217	237	257	277	297
18	38	58	78	98	118	138	158	178	198	218	238	258	278	298
19	39	59	79	99	119	139	159	179	199	219	239	259	279	299
20	40	60	80	100	120	140	160	180	200	220	240	260	280	300

Figure9: Sampling grid developed for Example. The shaded sampling units have been selected using random numbers.

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Volatilization:

The transfer of chemicals from solids or liquids to the gaseous phase.

Volatilization is function of contaminates, vapor pressure and Henrys Law constant

- ❖ Vapor pressure of organic compounds ranges 10^{-10} mmHg to 760 mmHg at 20°C
- ❖ Vapor pressure increased with temperature
- ❖ Henrys Law States that the concentration of a compound in the aqueous phase is directly proportion to its partial pressure in the gaseous phase.

$$P = H.X$$

Where:

P=partial pressure (atm)

H= Henrys Law constant (atm. m^3/mole)

X=Concentration of the compound in water (mole/m^3)

Henrys Law constant is the best indicator of tendency of chemical to volatilize from water.

Volatilization Fluxes across liquid surfaces from an open container:

Hanna and Drivas provided a quantitative description of volatilization:

$$Q = \frac{\mu KA(V_P - P)}{RT}$$

Q= the evaporation rate (g/sec)

μ =Contaminant molecular weight (g/mole)

K=A mass transfer coefficient per area A (m/sec)

R=The ideal gas constant (8.21×10^{-5} m^3.atm/mole. k)

T=temperature (k)

V_P=the saturation vapor pressure of the liquid (atm)

For most cases, P=0 because the container is open

$$Q = \frac{\mu KAV_P}{RT}$$

The ratio of two mass transfer coefficient may then be related to their gas diffusion coefficients:

$$\frac{K_1}{K_2} = \left(\frac{D_1}{D_2}\right)^{2/3}$$

Where:

K_1 , K_2 =mass transfer coefficients for compound 1,2

D_1 , D_2 =corresponding gas diffusion coefficients.

A well-documented method for estimating gas diffusion coefficients uses the following equation:

$$\frac{D_1}{D_2} = \sqrt{\frac{\mu_2}{\mu_1}}$$

Where:

μ_1 , μ_2 = corresponding molecular weights

Combining the above two equations

$$K_1 = K_2 \left(\frac{\mu_2}{\mu_1}\right)^{1/3}$$

Water is used as a mass transfer coefficient reference K=0.83 cm/sec.

Example: An open vat(1.25m ×0.75m ×0.3m deep) is used to store spent *μIBK* prior to distilling it for reuse. The temperature is 20°C. estimate the rate of volatilization across the surface of the vat?

Volatilization Concentration in an Enclosed Area:

The calculation of the steady – state concentration resulting from volatilization is based on a mass balance on enclosed space below:
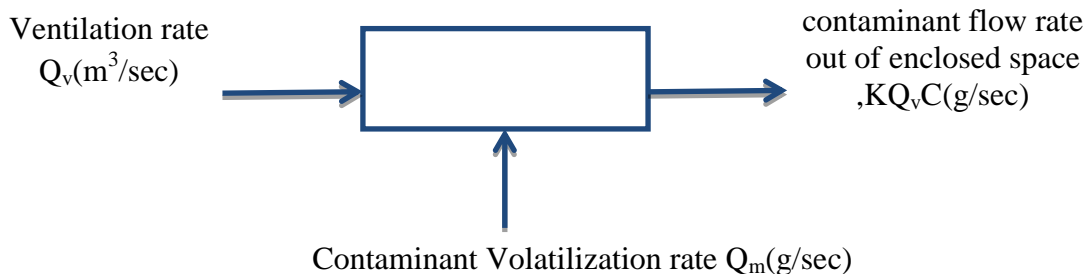
The rate of change of the hazardous compound in the system is:

$$\frac{V \, d_c}{dt} = Q_m - K \, Q_v \, C$$

Where:

C= the vapor , phase concentration of the compound (g/m^3)

V=volume of the enclosed area (m^3)

Q_m=volatilization rate of the compound (g/sec)

Q_v=ventilation rate for the enclosed area (m^3/sec)

K=a factor that accounts for incomplete mixing.

Assuming steady-state

$$\frac{V\ dc}{dt} = 0$$

Therefore, $C = \frac{Q_m}{K\ Q_v}$

Because C is more commonly expressed as ppm it may be converted using

$$C_{ppm} = C\left(\frac{RT}{R\mu}\right) \times 10^6$$

Combining the above equations

$$C_{ppm} = \frac{Q_m\ RT}{K\ Q_v\ P\mu} \times 10^6$$

Example:

A storage tank 1.5m in diameter containing waste toluene has been left open in a small RCRA 90-day drum storage area 220 m^3 in volume. The temperature is 20°C and the atmospheric pressure is 1 atm. ventilation in the structure provides 12 changes of air per hour. Determine the steady –state toluene concentration in the structure. Assume k=0.2