Gas Chromatography Analysis of Odorous Compounds in Waste Handling Operations Using Air Sampling Canister Method

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Introduction

- Waste handling operations (WHOs) are increasing due to economic growth, population rise, and urbanization, leading to more odorous emissions.
- These odorous compounds negatively impact the environment, causing unpleasant smells and reducing air quality.
- Standardized methods are essential for evaluating the intensity and composition of these compounds for regulatory compliance and health risk mitigation, but each method requires different sampling techniques and is suited for specific compound groups.
- This study analyzes four categories of 43 odorous compounds commonly found in landfills using the GCMS-TQ8030 and air sampling canisters.

ASTM D5504	EPA TO-15	EPA TO-17	NIOSH
▪ Sulfurs (e.g: Benzene thiol, hydrogen sulfide) ▪ Collect samples in canisters and sampling bags ▪ Analyzes by GC, chemiluminescence	▪ VOCs (e.g: Propene, Hexane) ▪ Collect samples in canisters. ▪ Analyzes by GC-MS	▪ VOCs (e.g: Toluene, Octane) ▪ Collect samples in the sorbent tubes. ▪ Analyzes by GC-MS	▪ Air contaminants (e.g: Ketones, Acetic acid) ▪ Collect samples in sorbent tubes. ▪ Analyzes by GC-FID, GC-MS

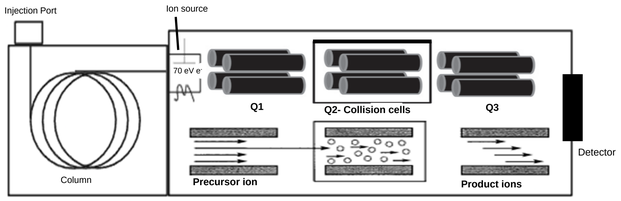
Table 1: Standardized Methods

Methodology

- The canisters were first cleaned after 11 cycles of the evacuation and pressurization process. The temperature will be maintained at 55˚C
- Background analysis must be done performed before sending canisters to the landfill for sampling
- Air samples were pulled into canisters using a passive air grab sampling kit. Depending on the loop size, the samples were pulled for 5-10 minutes.
- The air sample was introduced into GC-MS-TQ8030 using a gas-tight syringe for direct injection.
- Multiple reaction monitoring (MRM) was used to detect and quantify the odorous compounds in air sample.

Figure 1: Silcocanister, gas-tight syringe, and GCMS-TQ8030

Results



GC Oven — Triple quadrupole mass analyzer

Instrument	Shimadzu GCMS-TQ8030
Column	RTX-1: 60.0 m, 0.53 mmID, 7.00 µm
Oven Temp	35°C (hold for 5 min.) to 240°C (hold for 5 min.) at 25°C/min.
Linear Velocity	60.0 cm/sec
Inj Mode	Splitless
Inj Temp	200°C
Inj Volume	1.0 mL
Gas Carrier	Helium
Mode	MRM
Total Program Time	19 minutes

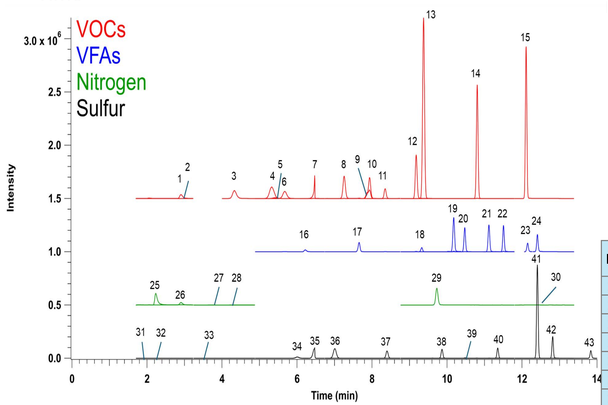


Figure 2: Separated chromatograms of 4 odorous classes of compounds extracted from TIC.

ID#	Name	m/z	Ret. Time (min)	Odor Thresholds (ppbV)	LOD (ppb)	LOD (ppbv)
1	Formaldehyde	30	2.045	27	2	1.5E-06
2	Acetaldehyde	44.00>29.00	2.8	1.5	8	4.0E-06
3	Ethanol	31.00>29.00	4.452	90	8	3.8E-06
4	Acetone	58.00>43.00	5.31	400	2	7.6E-07
5	Propanal	58.00>29.00	5.49	1	8	3.0E-06
6	Isopropyl Alcohol	45.00>43.00	5.73	1000	80	2.9E-05
7	tert-Butanol	59.00>31.00	6.51	3300	128	3.8E-05
8	1-Propanol	31.00>29.00	7.27	31	16	5.9E-06
9	Butanal	72.00>57.00	7.85	0.3	4	1.2E-06
10	2-Butanone	72.00>43.00	7.93	70	2	6.1E-07
11	Ethyl acetate	61.00>43.00	8.343	76.6	4	1.0E-06
12	1-Butanol	56.00>41.00	9.18	3.3	5.3	1.5E-06
13	Benzene	78.00>52.00	9.359	470	3.75	1.1E-06
14	Toluene	91.00>65.00	10.79	26	10.7	2.6E-06
15	Styrene	104.00>78.00	12.093	2.8	10.6	2.2E-06

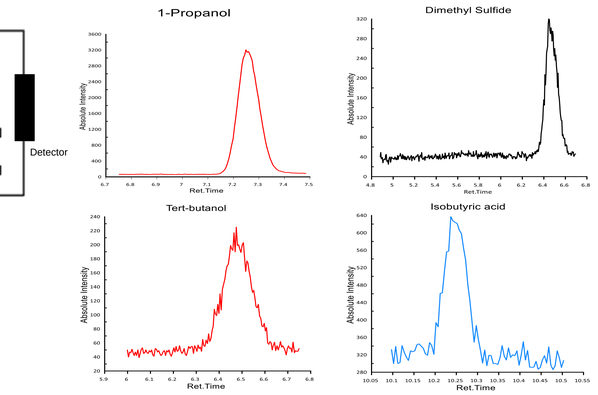


Figure 3: Chromatogram of detected odorous compounds from landfill

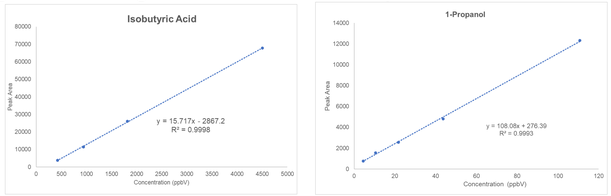


Figure 4: Calibration curve for Isobutyric Acid and 1-Propanol

Compound	Ret. Time (min)	Odor Threshold (ppbv)	Determined Concentration (ppbV)
Tert-Butanol	6.475	3300	1
Dimethyl Sulfide	6.451	0.12	1
1-Propanol	7.264	31	3
Isobutyric Acid	10.247	30	213

Table 1: Quantitation table of the sample from landfill

ID#	Name	m/z	Ret. Time (min)	Odor Thresholds (ppbV)	LOD (ppb)	LOD (ppbv)
16	Formic acid	46.00>29.00	6.258	520	750	0.0003593
17	Acetic acid	60.00>45.00	7.7	0.4	75	2.8E-05
18	Propanoic acid	74.00>56.10	9.345	1	150	4.5E-05
19	Iso-Butyric Acid	43.00>41.10	10.188	30	75	1.9E-05
20	Butanoic acid	60.00>42.00	10.477	20	75	1.9E-05
21	Iso-Valeric Acid	60.00>42.00	11.11	0.3	75	1.6E-05
22	Pentanoic acid	60.00>42.10	11.503	43	150	2.8E-05
23	Valeric Acid	73.00>55.10	12.14	2	75	1.6E-05
24	Hexanoic acid	60.00>42.00	12.403	8	150	2.8E-05
25	Ammonia	17.00>15.20	1.835	43	TBD	TBD
26	Methylamine	30.00>28.10	2.52	0.75	TBD	TBD
27	Dimethylamine	44.00>18.10	3.688	0.76	TBD	TBD
28	Trimethylamine	58.00>42.10	4.07	0.02	TBD	TBD
29	Triethylamine	101.00>86.20	9.72	5.3	TBD	TBD
30	Cavaderine	56.00>30.10	12.735	500	TBD	TBD
31	Hydrogen sulfide	34.00>32.00	1.99	0.04	TBD	TBD
32	Sulfur dioxide	64.00>48.00	2.22	330	TBD	TBD
33	Methanethiol	47.00>45.00	3.56	5.10E-10	40	0.0183
34	Ethanethiol	62.00>47.00	5.955	8.70E-03	28	9.94E-03
35	Dimethyl sulfide	62.00>47.00	6.425	0.12	50	0.0177
36	Carbon disulfide	76.00>32.00	6.98	16	50	0.0145
37	1-Propanethiol	76.00>42.10	8.345	50	50	0.0122
38	Diethyl sulfide	75.00>47.00	9.852	0.3	50	0.0117
39	Disulfide, dimethyl	94.00>79.00	10.47	0.03	50	8.74E-03
40	Dimethyl sulfate	96.00>32.00	11.34	520	50	9.00E-03
41	Diethyl disulfide	122.00>94.00	12.393	0.02	7	1.40E-03
42	Benzenethiol	110.00>66.10	12.8	40	28	4.97E-03
43	Benzenemethanethiol	124.00>91.10	13.81	0.013	7	2.03E-03

Conclusion

- The method was developed to determine all four categories of 43 compounds in one run using one instrument and one sampling technique.
- The odorous compounds from the real landfill sample were detected

Future works

- Complete limits of detection table for the remaining compounds
- Performing quality control to determine the accuracy and precision of the method.

Finish generating calibration curve for the remaining compounds out of the canister.

Future works

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