

Chemical Determination of Odorants in Air from Sewage Treatment Works

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Background of odor study

- Public awareness and concern on odorous emissions from waste treatment facilities.
- Odorous emissions contain a large volatile chemicals with different toxicities each, which may cause harmful health effects.
- Olfactometry test has been a standard method for couple decades. Odor concentration were determine by nose sensory method (EN13725).
- According to GB14554-93, six levels are defined: 1. no feeling; 2. little feeling, but no stimulation; 3. feeling obviously, but no stimulation; 4. stimulation; 5. stimulation strongly; 6. can not endure.

Instrumental Analysis

- **For individual compound**

- Hydrogen sulphide is absorbed and determined colorimetrically by the methylene blue method.
- Formaldehyde and acetaldehyde absorbed and reacted with HCl/2,4-dinitrophenylhydrazine (DNPH); derivatives are determined by HPLC-UV.

- **For mixture**

- GC-MS is commonly used, but sensitivity is often not enough for all odor compounds with the direct injection method.

Sorbent Tube - Thermal Desorption Unit (TDU) coupled with GC-MS

DEMP11/05, DSD

Sorbent Tube for On-site Sampling

- TDU Sorbent tube with resins (Tenax, Graphitized carbon, Carboxen, XAD) was linked to a pump. Gas following rate was set at 30 ml/min for 40 min and 60 min, with the volumes of total gas through sorbent tube of 1.2 and 1.8 liter, respectively.



Nutech 2702 sampler



TDU tube, Restek

- Tube was connected to TDU-GC-MS system set up in Dioxin Laboratory, Hong Kong Baptist University.
- Liquid nitrogen was used to condense odorants from absorbed tube followed by thermal desorption. Concentrated odorants were directly injected into GC column.



Ambient air sampling

Sampling at Shatin WWTW influent window



Inlet or outlet sampling in Wastewater Treatment Work (WWTW)



Inlet or outlet sampling in Wastewater Treatment Work (WWTW)

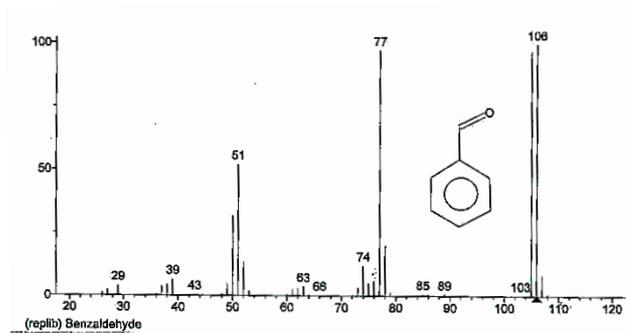
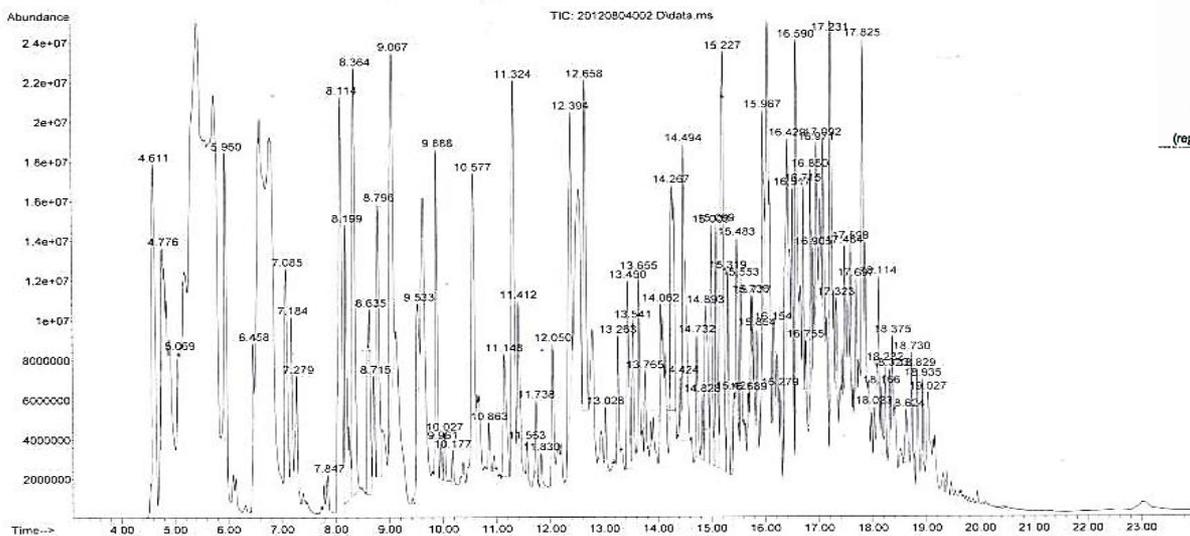
TDU-GC-MS (Nutch 2502 TDU, Agilent 7890A GC - 5975 MSD)



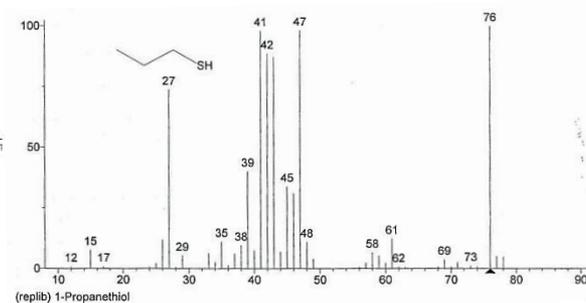
Odorous testing team, Dioxin Analysis Lab., HKBU

A typical GC-MS total ion chromatogram and mass spectra

File :D:\VOC\Data\20120804\20120804002.D
Operator :
Acquired : 4 Aug 2012 12:21 using AcqMethod ODOR.M
Instrument : 5975C
Sample Name: MI191922
Misc Info :
Vial Number: 2



Benzaldehyde



Propanethiol

Method development and validation

- Identification based on criteria of chromatographic retention time and characteristic ions (e.g., molecular ion and fragmentation ions).
- Standard EI-MS spectrum library searching used for confirmation.
- Library searching also provides the analysis of “unknown” (**valuable for emerging testing**).
- Authentic standards of 56 odorants and TO-14 Standard mixture available for confirmation.
- A total 74 compounds were monitored.
- The “odorous chemicals” classified in four groups: sulfur-compounds, nitrogen-compounds, volatile fatty acids and others (mainly aldehydes/ketones).

74 odor compounds and their specific ions

Chemicals	Ion mass	Chemicals	Ion mass
• n-Butylamine	30	• Crotonaldehyde Solution	39, 41
• sec-Butylamine	44	• n-Butyraldehyde	44, 43
• tert-Butylamine	58, 41	• Isovaleraldehyde	44, 43
• Isobutylamine	30, 73	• Valeraldehyde	44, 58
• Diethylamine	58, 30	• Hexaldehyde	44, 56
• Diisopropylamine	44, 86	• Benzaldehyde	106, 105
• Dipropylamine	72, 32	• o-Tolualdehyde	120, 119
• Dimethylamine (in water)	44, 45	• m-Tolualdehyde	120, 119
• Ethylamine (anhydrous)	30, 28	• p-Tolualdehyde	120, 119
• n-Propylamine	30	• 2,5-Dimethylbenzaldehyde	134, 133
• Trimethylamine	58, 59	• Acetone	43, 58
• Triethylamine	86, 58	• Acetic acid	43, 45
• Formaldehyde	30, 29,	• Propionic acid	74, 45
• Acetaldehyde	29, 44	• Butyric acid	69, 73
• Propionaldehyde	58, 29	• Isobutyric acid	60, 73

- 2-Methylbutyric acid 43, 73
- Valeric acid 60, 73
- Isovaleric acid 60, 43
- 2-Methylvaleric acid 74, 43
- 3-Methylvaleric acid 60, 41
- 4-Methylvaleric acid 57, 74
- Hexanoic acid 60, 73
- Heptanoic acid 60, 73
- 2-Ethylhexanoic acid 73, 88
- Octanoic acid 60, 73
- Nonanoic acid 60, 73
- Indole 117, 90
- Carbon disulfide 76, 44
- Dimethyl disulfide 94, 79
- Diethyl sulfide 75, 90
- Methyl sulfide (dimethyl sulfide) 62, 47
- Skatole 130, 131
- Ammonia 17, 16
- Methylamine 30, 31
- Isopropylamine 44, 42
- iso-Butyraldehyde 43, 42
- Ethyl mercaptan 62, 29
- Ethyl methyl sulfide 61, 76
- Carbonyl sulfide 60, 32
- 3-Methylindole 130, 131
- Thiophene 84, 58
- Tetrahydrothiophene 60, 88
- 3-Methyl thiophene 97, 98
- Methyl mercaptan 47, 48
- n-Propyl mercaptan 76, 43
- Isopropyl mercaptan 43, 76
- n-Butyl mercaptan 41, 56
- Isobutyl mercaptan 41, 43
- Hydrogen sulfide 34, 32
- Dimethyl disulfide 94, 79
- Diethyl Disulfide 122, 66
- Sulfur dioxide 64, 48
- 2-Ethylthiophene 97, 112
- 2,5 - Dimethylthiophene 111, 112
- Benzene 78, 77
- Toluene 91, 106
- o-xylene 91, 106
- m-xylene 91, 106
- p-xylene 91, 106
- Tetrachloroethylene 166, 164
- hyl-2-propanethiol (tert-Butyl mercaptan) 57, 41, 90

Calculation curves from TO-14 standards & 56 gas mixture standards

TO-14	A	B	C	D	E	F	G
50 ppbv	0.071	0.082	0.042	0.09	0.54	0.29	401.37
100 ppbv	0.11	0.15	0.098	0.12	1.10	0.56	618.55
150 ppbv	0.16	0.23	0.11	0.16	1.63	0.73	872.32
200 ppbv	0.22	0.29	0.15	0.51	2.16	0.93	1102.64

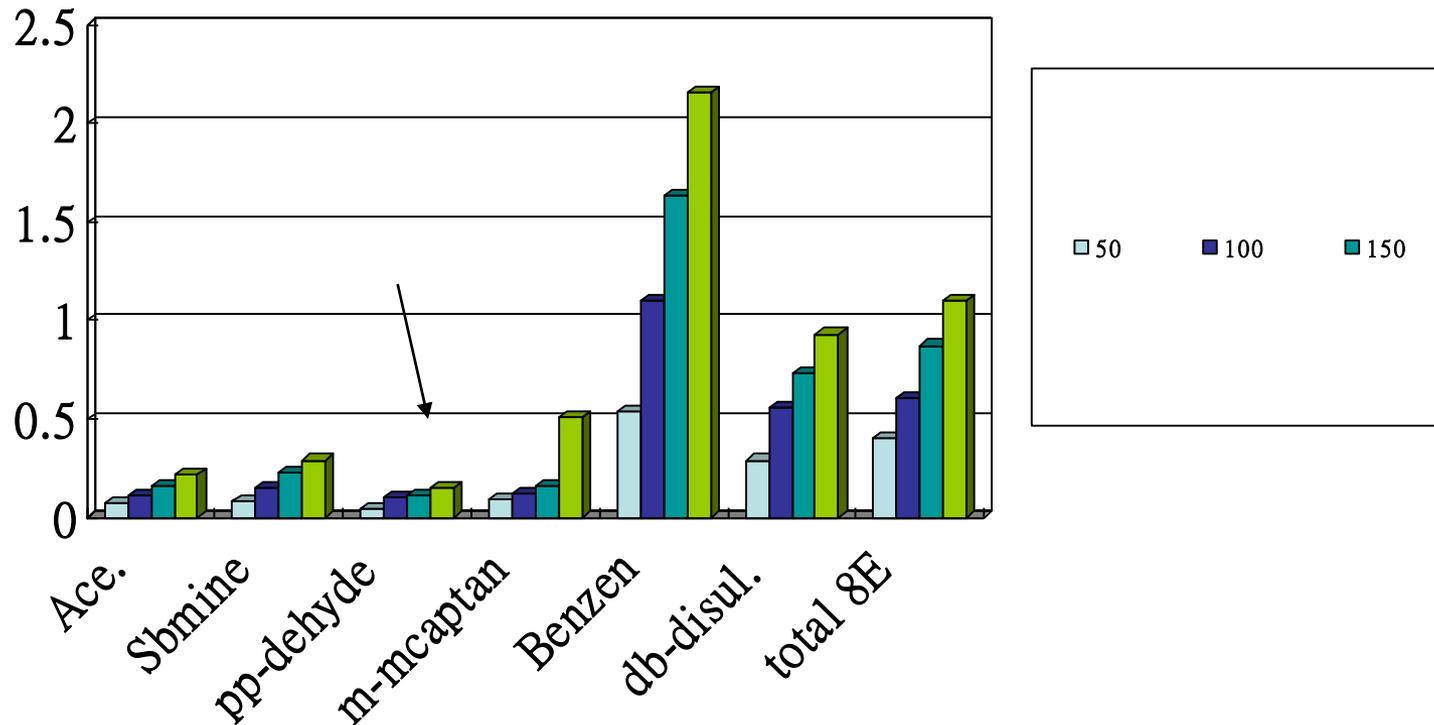
56 Species Mix

50 ppbv	0.066	0.085	0.039	0.014	0.54	0.12	345.10
150 ppbv	0.15	0.21	0.11	0.15	1.54	0.53	864.11
200 ppbv	0.28	0.34	0.18	0.63	2.54	1.02	1403.22

A: Acetone, B: Sec-butylamine, C: Propionaldehyde, D: Methyl mercaptan, E: Benzen F: Dibutyl disulfide, G: total intensity (all peaks integrated from chromatogram)

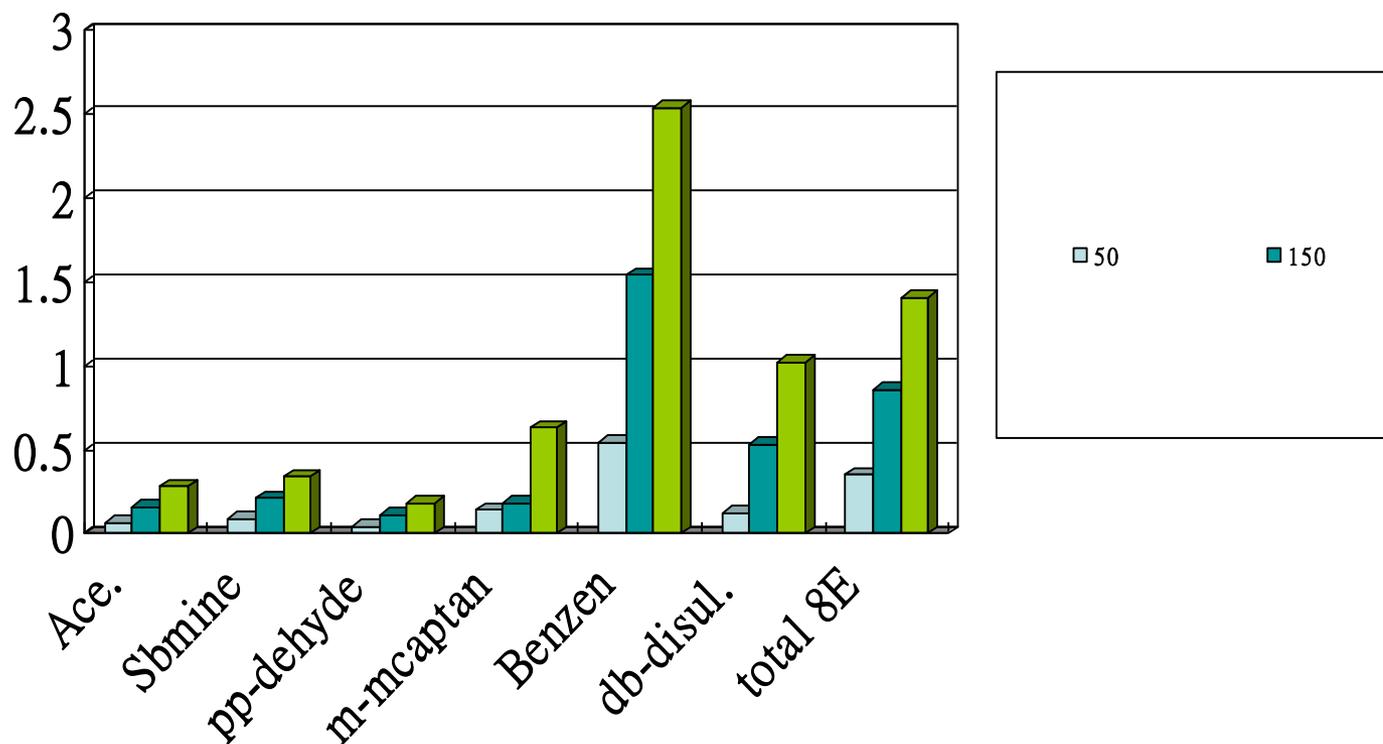
TO-14 standard for calculation curves

Standard calculation curve from TO-14 standard gas mixture at four different concentrations



56 gas standards for calculation curves

Standard calculation curve from 56 standard gas mixture at three different concentrations



Low background: percentage of TDU-GC-MS blank

TO-14 standard mixture

56 std mixture (ppbv)

Conc.	50	100	150	200	50	150	200
Peak Signal	401	618	872	1102	345	864	1402
Blank (%)	3.1	2.0	1.4	1.1	3.6	1.4	0.88

Instrument blank was between 0.88% - 3.58%

TDU-GC-MS analysis

- Field blank (from sorbent tube and instrument): 1.5 - 6.2%.
- Duplicate test showed repeatability were good (Table 6).

Table 6. Duplicate odor components from sludge transfer site of Stonecutters Waste Water Treatment Works											
(basic on comparison with 50 species of gas standards)					ppbv					01/22/2013	
Stonecutters	1	2	3	4	5	6	7	8	9	1010	Total
昂船洲	Acetone	SCO	PHCs	H2S	In Amines	Dehydes	Acids	Mercaptans	Disulfide	Sulfide	
Duplicate A	0.075	0.897	9.276	0.188	0.218	0.274	0.060	0.079	0.166	0.011	11.244
Duplicate B	0.068	1.031	8.757	0.219	0.191	0.302	0.068	0.073	0.181	0.009	10.899
Average	0.072	0.96	9.017	0.204	0.205	0.288	0.064	0.076	0.174	0.01	11.072
(A-B)/Ave.(%)	9.8	13.9	5.8	15.2	13.2	9.7	12.5	7.9	8.6	20.0	3.1

Summary on Tube TDU-GC-MS method

- Coverage of a wide range volatile and semi-volatile organic compounds (VOC).
- Suitable for odor determination from wastewater treatment facilities.
- LOD range were 0.2 - 0.5 ppbv for normal odor source points and deodorizing units.
- Relatively good selectivity, sensibility and precision according to Compendium Method TO-17 (USEPA) .
- Testing on more than 70 compounds from sludge transfer site, dewater workshop and waste water treatment facilities.

Method applications

Sample nature

of testing

Wastewater Treatment Work (WWTW)

Before June 2012	80
June2012-June 2013	340
July2013 –Sept.2013	108

Method/Study

H2S, SCO conversion test	51
VOC (acids, amine etc.)	51
Standard TO-14, VOC std	16
Laboratory air	18

Comparison with Oflactometry test (HKPC)

153

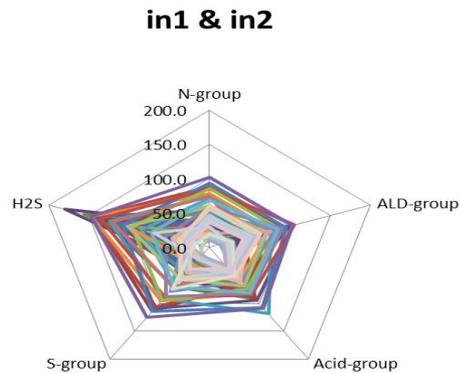
•Total sample No:

817

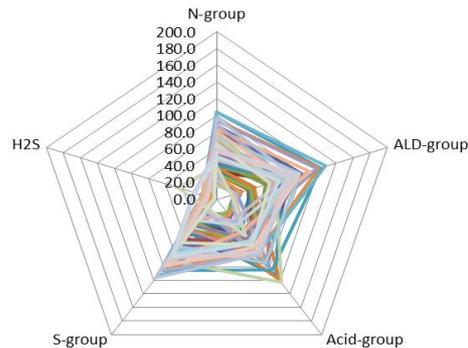
name list	LOD	Q-M/Z	DOU 1 #3		Gate #2 DWH Sil Ambient		Jan. 9, 2014	
			inlet	main outlet	air(WKTs)	Sil	air	
1 n-Butylamine	0.5	30	21.1	14.6	0.7	12.3	0.0	
2 sec-Butylamine	0.5	44	21.7	10.7	0.3	33.9	0.4	
3 tert-Butylamine	0.5	58, 41	4.6	0.5	0.8	5.3	0.3	
4 Diethylamine	0.5	58, 30	1.7	0.9	0.7	38.2	1.1	
5 Di isopropylamine	0.5	44, 86	11.0	1.5	1.1	40.9	0.4	
6 Dimethylamine	0.5	44, 45	52.9	11.2	0.9	15.7	0.0	
7 Dipropylamine	0.5	72, 30	6.8	3.3	1.4	6.6	0.5	
8 Ethylamine	0.5	44, 46	30.8	11.9	0.7	40.2	0.0	
9 Isobutylamine	0.5	30, 73	8.5	1.7	0.7	41.1	0.7	
10 Isopropylamine	0.5	44, 42	1.5	1.2	1.5	5.5	0.4	
11 Propylamine	0.5	30, 59	31.0	1.2	1.1	7.0	0.7	
12 Tri ethylamine	0.5	86, 58	31.9	20.7	1.1	6.8	0.0	
13 Trimethylamine	0.2	58, 59	5.1	1.2	2.2	5.3	0.3	
14 Ammonia	0.5	17	0.0	0.0	0.0	0.0	0.0	
15 Indole	0.5	117, 90	0.0	0.0	0.0	0.0	0.0	
16 Skatole	0.2	130,131	27.0	10.3	1.0	5.1	0.5	
17 Methylamine	0.5	30, 31	10.1	6.3	2.1	11.7	0.9	
18 Formaldehyde	0.5	30, 29	3.6	1.5	1.1	30.7	0.4	
19 Acetaldehyde	0.5	29, 44	11.9	5.9	2.4	8.9	0.3	
20 Propionaldehyde	0.5	58, 29	6.8	8.5	1.1	5.3	0.3	
21 Crotonaldehyde	0.5	39, 41	40.6	21.2	0.8	34.3	0.1	
22 n-Butyraldehyde	0.5	44, 43	22.7	10.3	0.5	41.2	0.7	
23 iso-Butyraldehyde	0.2	44, 45	62.7	31.9	0.8	31.0	1.2	
24 Benzaldehyde	0.5	106,105	10.7	8.7	0.4	48.2	1.5	
25 Isovaleraldehyde	0.2	44, 45	20.6	11.2	0.7	41.1	0.0	
26 Valeraldehyde	0.2	44, 58	26.6	19.2	0.2	2.2	1.2	
27 o-Tolualdehyde	0.5	120,119	19.2	14.7	0.0	41.2	0.9	
28 m,p-Tolualdehyde	0.5	120,119	14.7	11.2	2.2	5.1	0.5	
29 n-hexanaldehyde	0.2	120,119	1.2	0.9	1.1	7.0	0.9	
30 2,5-Dimethylbenzaldehyde	0.5	134,133	0.9	0.5	0.7	30.7	0.7	
31 Acetone	0.5	43, 58	0.5	0.9	0.0	8.9	1.2	
32 Benzene	0.5	78, 77	10.5	1.5	0.3	5.3	0.3	
33 Tetrachloroethylene	0.5	166,164	3.9	1.2	0.2	34.3	0.9	
34 Toluene	0.5	91, 92	2.9	0.3	0.1	41.2	0.0	
35 o-Xylene	0.5	91, 106	1.7	1.9	0.2	31.0	1.2	
36 m-Xylene	0.5	91, 107	1.4	1.7	0.7	48.2	0.0	
37 p-Xylene	0.5	91, 108	1.0	1.2	0.0	41.1	0.0	
38 Acetic ester	0.5	43, 45	29.0	14.6	1.1	2.2	0.2	
39 Butanoic ester (Butyric ester)	0.2	60, 73	33.1	14.7	0.7	41.2	0.9	
40 Heptanoic ester	0.5	60, 73	32.9	11.2	0.3	37.5	0.0	
41 n-Hexanoic ester	0.5	60, 73	24.7	20.9	0.5	29.0	0.4	
42 iso-Hexanoic ester	0.2	60, 73	24.9	14.6	1.1	30.0	0.3	
43 2-Methyl butanoic ester	0.5	74, 57	29.5	11.9	1.4	12.6	0.0	
44 Isovaleric ester	0.2	60, 43	20.8	14.1	0.3	10.4	4.8	
45 Isobutyric ester	0.5	43, 73	10.4	10.4	1.7	19.8	0.0	
46 2-Methylpentanoic ester	0.5	74, 43	6.5	6.0	0.2	35.4	0.7	
47 3-Methylpentanoic ester	0.5	60, 41	19.8	16.0	0.9	5.8	0.0	
48 4-Methylpentanoic ester	0.5	57, 74	15.5	11.5	1.0	14.5	0.4	
49 Octanoic ester	0.2	60, 73	30.0	19.0	0.3	22.5	0.0	
50 n-Valeric ester	0.5	60, 73	27.8	15.6	1.2	12.6	0.5	
51 Propionic ester	0.5	74, 45	19.3	17.7	0.8	14.1	0.1	
52 2-Ethyl hexanoic ester	0.5	73, 88	7.7	2.4	1.0	49.2	0.1	
53 Nonanoic ester	0.5	60, 73	23.2	17.8	0.7	13.8	0.0	
54 n-Butyl mercaptan	0.2	41, 56	24.1	19.8	1.2	40.0	0.3	
55 tert-Butyl mercaptan	0.2	41, 56	18.7	15.5	0.4	7.5	0.4	
56 Carbon disulfide	0.5	76, 44	5.8	12.3	0.1	28.3	0.0	
57 Carbonyl sulfide	0.5	61, 76	32.1	27.8	0.1	41.2	0.0	
58 Diethyl disulfide	0.5	122, 66	31.5	11.9	0.8	40.0	0.4	
59 Diethyl sulfide	0.2	75, 90	8.5	7.7	1.0	41.1	0.0	
60 Dimethyl disulfide	0.5	94, 79	38.0	23.2	0.3	41.2	0.0	
61 Dimethyl sulfide	0.5	62	19.1	14.1	1.2	42.2	0.5	
62 2,5-Dimethylthiophene	0.5	111,112	11.5	8.7	0.9	47.5	0.4	
63 Ethyl mercaptan	0.2	62, 29	9.2	5.8	0.4	63.7	0.0	
64 Ethyl methyl sulfide	0.5	61, 76	3.9	5.8	0.0	24.5	0.4	
65 2-Ethylthiophene	0.5	97,112	12.9	10.2	1.7	4.9	0.2	
66 *Hydrogen sulfide	0.2	34, 32	2751.4	111.2	6.5	111.4	8.1	
67 Isobutyl mercaptan	0.2	41, 43	15.3	11.2	1.8	34.9	1.0	
68 Isopropyl mercaptan	0.2	43, 76	35.8	23.9	1.1	24.4	0.3	
69 Methyl mercaptan	0.2	47, 48	13.2	7.0	0.5	6.3	0.3	
70 3-Methyl thiophene	0.5	97, 98	2.9	1.0	1.7	7.8	1.1	
71 n-Propyl mercaptan	0.2	76, 43	27.2	19.4	0.1	17.6	1.0	
72 Tetrahydrothiophene	0.5	60, 88	25.8	20.7	0.8	17.0	0.0	
73 Thiophene	0.5	84, 58	3.4	0.5	0.3	8.0	0.2	
74 Sulfur dioxide	0.5	64, 48	4.1	3.1	1.1	6.8	0.0	
Odalog H2S ppm			3.2	0.1	0.0	0.1	0.0	

A typical table report

Odorant profile of SCI & ST Stonecutters Island WWTW

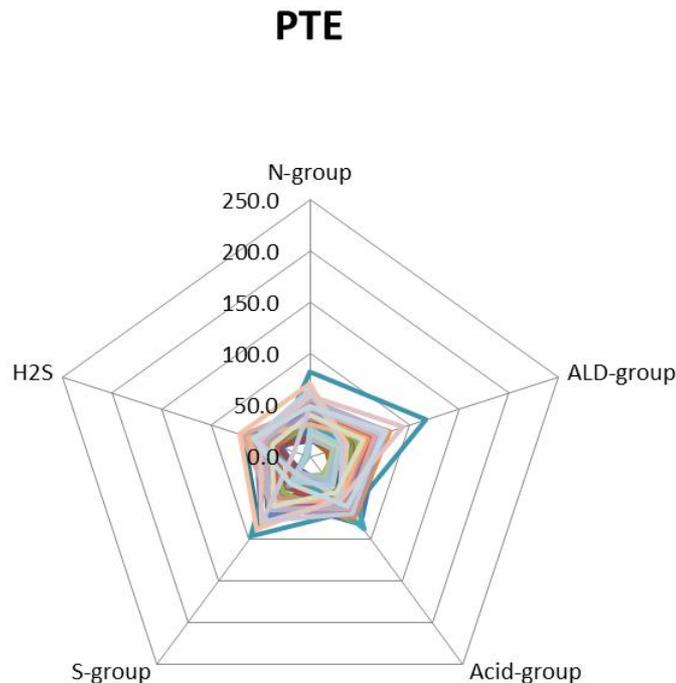


4). de1, de2, de3



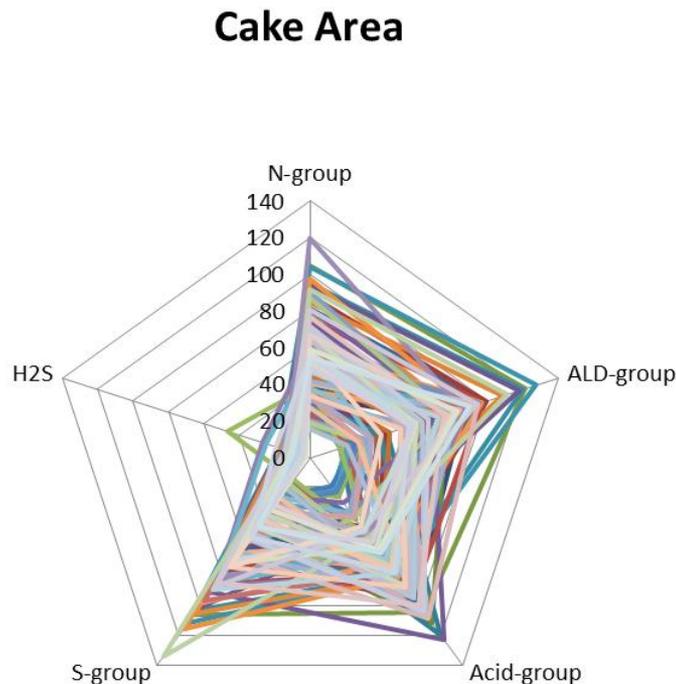
- Inlet samples were the influent zone with high conc. of H₂S and other S-, ALD-, acid- and S-groups compounds.
- Dewater House samples have abundant S-, N-, Acid-, and ALD-group compounds, but little H₂S.

Odorant profile of SCI & ST Shatin WWTW



- aa1, aa2 ambient air showed more S-, and ALD-group compounds.
- aa3, aa4 air showed the air was affected by influent water and sludge emission.
- Primary treatment influent and effluent was very difference, showing different air odor after the treatment.

Odorant profile of SCI & ST Dewater House (Cake Area)



- For “Cake” area in dewater House, the sludge have abundant S-, N-, Acid-, and ALD-group compounds and their levels changed in large scale, due to rain or wind.
- Extreme stimulating odor existed.
- **However, little H₂S was detected.**
- H₂S might have been degraded to other odorous compounds.
- Further investigation is needed.

General observation on point source and ambient air of SCI & ST WTTW

- Odorants levels from ambient air from SCI was higher than those from ST at most times of sampling.
- Higher odorants levels during Summer period and on sunshine day compared to Winter period and windy days.
- Dewater house, wastewater influent, anoxic zone, primary sedimentation points have higher odorants levels and strong stimulating odor in both SCI and ST.
- **Investigation on deodorizing units:** odor levels in inlet point were several times higher than in outlet unit. Deodorizing efficiency was significant.
- But during Nov. 21 and Dec. 2, 2014, the SCI deodorizing unit system (new) showed strange data, which was agreed with HKPC conclusion.
- If sludge is stored in a closed room (e.g., anoxic zone), the environment would be not suitable for people who work with sludge.

Interesting observation

- Dewater House (“Cake”) area always had a very strong stimulating odor, which means that a large volatile chemicals exists in the air environment. But the odorant levels varied in large scale due to wind and rain effect.
- H₂S reading was **very low** (0.0 - 0.1ppm) in the open areas.
- Low H₂S level might be due to its evaluation and/or oxidation to degradation products.

Future perspectives – supporting research



“Direct Source Sampler” for Cake study

- In order to avoid weather impact on odor concentrations and to understand the original sludge character in dewater house, “**Direct Source Sampler**” (box) with two holes on top cover was designed.
- The sludge was placed in the box, odorants emission was collected; one hole for TDU-GC-MS analysis and another hole for Odalog meter H₂S reading.
- The TDU-GC-MS method was applied for identification of the odorants and potential degradation products.

Preliminary results on sludge “cake”

Sample	H₂S (ppm from Odalog meter)
Open system	0.0 - 0.1
Box covered for 5-10 min	0.5 - 0.8
Box covered for 2-3 hrs	36.7 - 69.7

Box was then re-opened and stirred frequently, allowing VOCs be evaporated

Open system	0.0 - 0.1
Box re-covered for 30 min	9.9 - 19.5
Box re-covered overnight	4.9 - 7.6 (?)

Discussions

- When the sludge “cake” was placed into the plastic box in a closed system, H₂S level reached up to 69.7 ppm.
- When the box was opened, H₂S was gone, probably due to its evaluation and/or oxidation to degradation products.
- When the box was re-covered for 30 min, H₂S level increased from 0 to 9.9 -19.5 ppm, indicating that the sludge might have an abundant sulfate to generate H₂S.
- “Direct Source Sampler” might be served for pilot study on “cake” in dewater house under the special weather conditions.
- Further study is needed for (1) degradation products of H₂S under open and oxygen-rich conditions, and (2) the formation of H₂S in the covered “cake”.
- GC-MS method might be applicable to support the study.

Conclusions

- Resin Sorbent-Thermal Desorption Unit coupled with GC-MS is suitable for odorant analysis.
- The volatile and semi-volatile odor components can be determined.
- Major odorants from WWTW were amines, organic acids (detected as esters), aldehyde, mercaptan and petroleum hydrocarbons.
- Hydrogen sulfide is a major odorant with high toxicity. Degradation and formation of H₂S in the wastewater treatment environment and in the sludge, needs to be further studied.
- Study on “Direct Source Sampler” (the “Frankie Box”) should be continued.

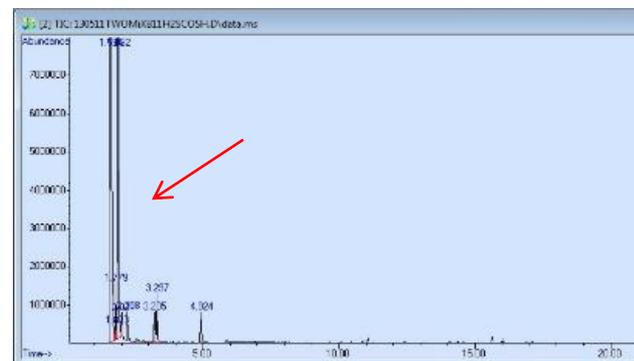
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- DSD of Hong Kong SAR (DEMP11/05)

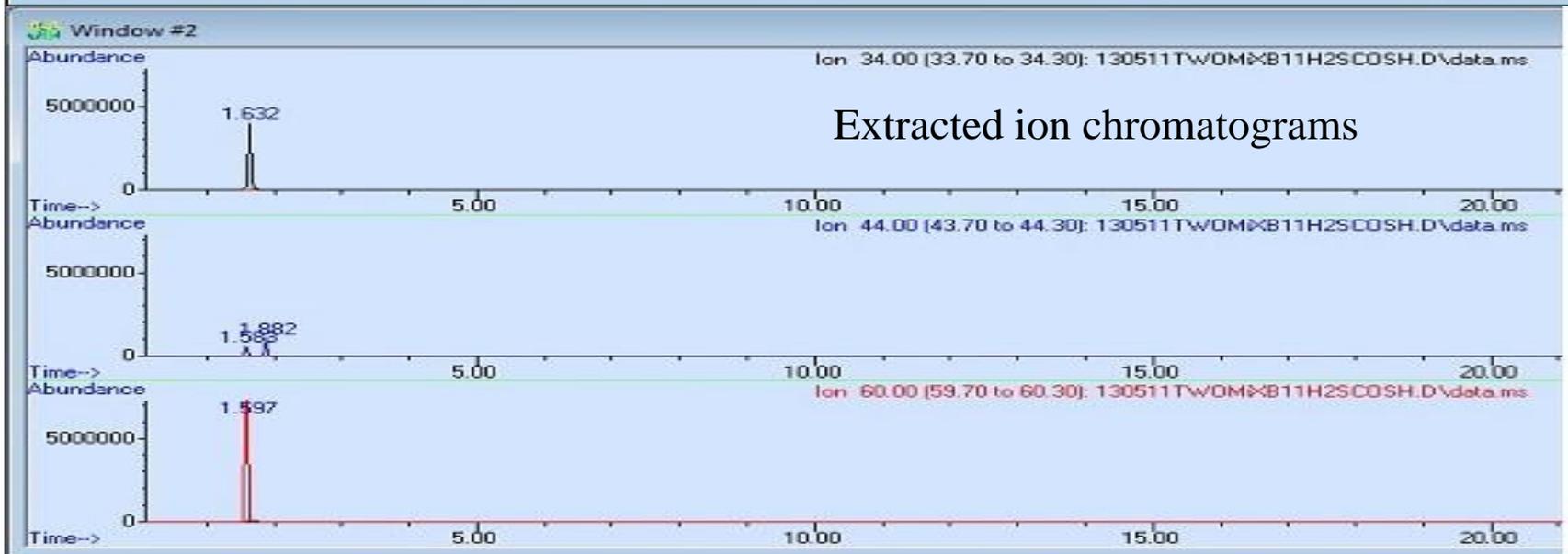
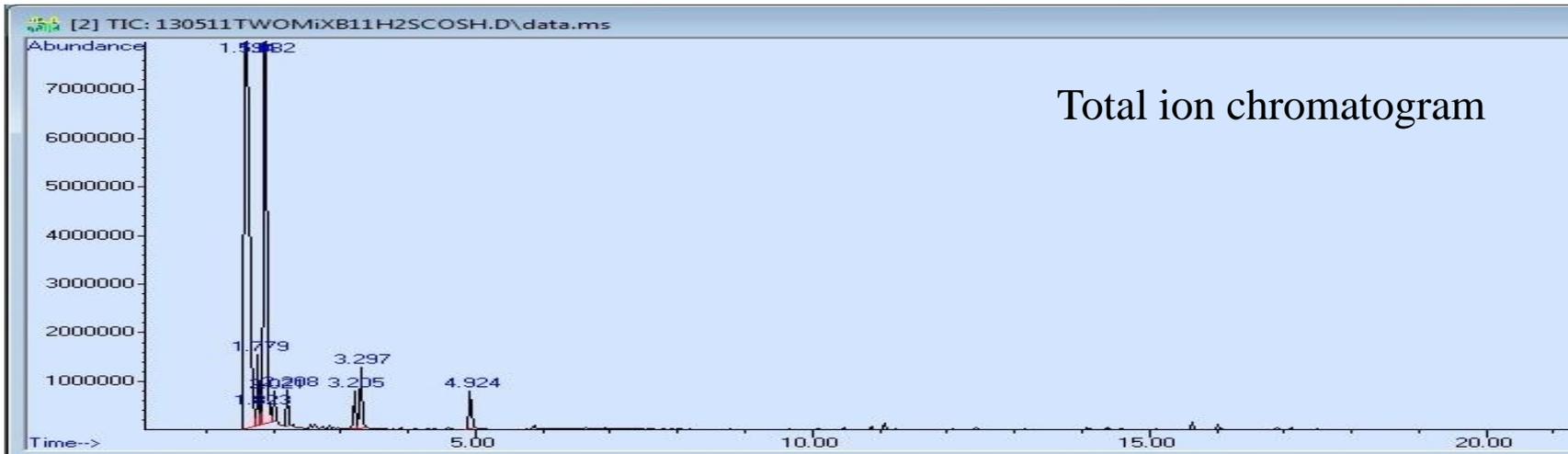
Thank you

Challenge: hydrogen sulfide study

- H₂S was considered as the main odorant with strong bad-egg smell and high toxicity to human. Its toxicity can be as high as HCN and CO.
- H₂S was found to be converted to carbonyl sulfide (SCO羰基硫) when reacting with O₂ and CO₂.
- In TDU-GC-MS, CO₂ peak overlapped the SCO peak and H₂S peak, at retention time of 1.583-1.632min.
- Characteristic ions: H₂S at m/z 34, CO₂ at m/z 44 and SCO m/z 60.



Identification of H₂S from CO₂ and SCO



H₂S study summary

- When H₂S was direct injected into TDU-GC-MS, no degradation & conversation occurred.
- When using tube absorbing ~98% of H₂S converted to SCO
- Measurement of H₂S was performed by considering the adjustment with convention rate.
- The determination was confirmed with the analysis of SCO.
- The results were comparable with those from Odalog meter reading.