II - 546 Detection of Sulfur containing odorous compounds from aqueous solution in lower than Odor Threshold Concentration level

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Introduction

Background and purpose

As water available for domestic use is scarce, often treated waste water (TWW) can be seen as an alternative source. TWW can be used for many purposes but wide spread reuse is often hindered by the poor quality of TWW. Although TWW is now obtained by employing advanced (or tertiary) waste water treatment processes which are mainly physico-chemical processes, water quality can not meet the odor removal target unlike other water quality. This is because human nose is very sensitive. As such, odor removal at very low concentration is an interest of modern research.

Apart from dealing with reuse purpose, a good analytical method is essential for odor nuisance reduction process of treatment plants and other related fields. As Table 1 shows the OTC values are extremely low, we need some laboratory method to examine compounds with very low concentration, in the range of μg/l or ng/l level. As the existing method of this kind is not up to the mark, this study concentrated to improve the analytical method.

TABLE 1: Target compounds

NAME	FORMULA	OTC (μg/l)
Hydrogen Sulfide (HS)	H_2S	0.4
Di Methyl Sulfide (MS)	$(CH_3)_2S$	9.0
Di Ethyl Sulfide (ES)	$(C_2H_5)_2S$	0.25
Di Methyl Di Sulfide (DD)	$(CH_3)S\text{-}S(CH_3)$	1.0
Carbon Di Sulfide (CS)	CS_2	2.6
Methyl Mercaptan (MM)	$CH_3\text{-}SH$	1.1
Ethyl Mercaptan (EM)	$CH_3\text{-}CH_2\text{-}SH$	0.19
Propyl Mercaptan (PM)	$CH_3\text{-}CH_2\text{-}CH_2\text{-}SH$	0.5
OTC : Odor Threshold Concentration (ref. 2, 3, 4, 5)		

Statement of the problem and objective

In waste water, most of the odor causing compounds are nitrogen and sulfur containing. In this study, eight S-containing compounds are chosen as they are the most frequently occurring compounds which are shown in Table 1. Usually, they results from anaerobic decomposition of organic materials like human excreta etc.

Experimental setup

Hwang (ref. 1) proposed a purge & trap method, which can not detect lower than OTC level. To improve the detection limit and make the operation simple, a new purge & trap was set up (fig. 1). Some significant elements of the setup is shown in Table 2.

Procedure

Standard solutions were prepared with acetone and diluted in water. The acidity of the solution has been adjusted before purging. Pure water (Milli-Q) was used for this purpose and high precautions were taken against contamination, as contamination can interfere frequently.

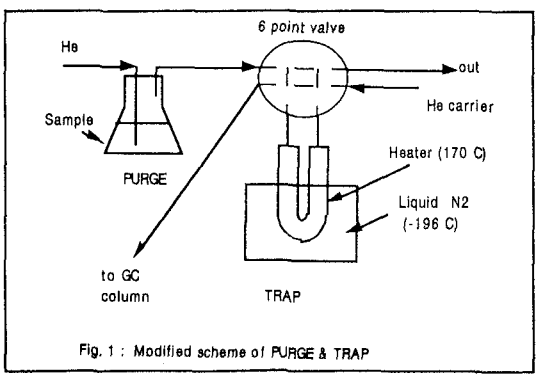

Fig. 1 : Modified scheme of PURGE & TRAP

Result

Recoveries and lowest detection limits are shown in Table 3. The recoveries seem to be acceptable for practical purpose. Because, it appeared that, this

low recovery does not depend on adsorption losses, but on purging efficiency. Due to the high water solubility of the compounds, more increasing of this efficiency is not readily accomplishable. As the average recovery is quite stable and as the lowest detections are less than OTC, this method can be accepted for routine tests.

TABLE 2 Analytical conditions

Parameter	Description
GC column	100% methyl polysiloxane fused silica megabore 30 m X 0.53 mm
Carrier gas	He, 10 ml/min.
Detector	FPD
Column temp.	35°C for 5 min., 10°C/min. upto 100°C,
Trap Cooling agent	Liquid N_2
Sample acidity	0.2 N by Sulfuric acid
Sample temperature	room temperature
Purge flow	50 ml/min.
Trap Heating	from -196°C to 170°C in 1 min.
Tube	Deactivated fused silica lined stainless steel tube
Sample Volume	5 ml
Purge time	5 min.

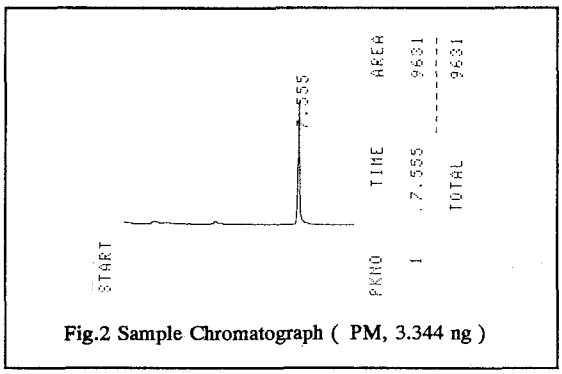

Fig.2 Sample Chromatograph (PM, 3.344 ng)

TABLE 3 : Recovery and lowest detection

Compound	Recovery (%)	Detection (ng)	Detection (μg/l)	OTC (μg/l)
EM	66	0.34	0.068	0.19
ES	91	0.35	0.070	0.25
CS	87	0.46	0.092	2.60
PM	88	0.33	0.066	0.50
MS	74	0.33	0.066	9.00
HS	43	0.20	0.040	0.40
DD	75	0.43	0.086	1.00
MM	69	0.40	0.080	1.10

Discussion

a. Trap temperature : As desorbtion temperature is 170°C, it seems that water vapor is going to the column but this particular column has no interference with water vapor.

b. Purge time : Purging time has a direct influence on purging efficiency. Longer purge time may seem better, but it cause shut off of GC flame. Optimum purge time was found to be 5 min. from practical consideration.

c. Residual effect : It means the GC response coming from the residuals of previous test. The potential source of this residual were found to be 1) trap, 2) valve, 3) connection lines, and 4) purge cylinder. To reduce residual effect, (1) whole trap was kept at 170°C in-between test time, (2) The 6-port valve was heated with a valve heater upto 120°C, (3) all lines from purge to trap and trap to GC was heated with wire heater upto 120°C and (4) purge volume was kept small.

d. Contamination : It was difficult to keep low water and sulfuric acid blank, hence very high precaution was necessary against contamination.

e. pH : Sample pH has influence on purging efficiency. After several tests optimum sample acidity was found 0.2 N with H_2SO_4.

f. Advantage : 1) low detection level *(less than OTC)*, 2) high and stable recovery, 3) single instrument, 4) single set up, 5) short test time, 6) short purge time, 7) less number of operational steps, 8) easy operation.

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