1　石油コンビナート周辺における有害化学物質の調査手法とその事例

以下は昭和61年1月15日から同月17日までタイ王国，バンコク市において開催された，「Regional Workshop on Environmental Toxicity and Carcinogenesis」に招待され，講演した表題の要旨である。

大気研究部門　佐　藤　静　雄

MEASUREMENTS OF SOME POTENTIALLY HAZARDOUS ORGANIC CHEMICALS IN AND AROUND PETROCHEMICAL COMPLEX AREA

REGIONAL WORKSHOP on
ENVIRONMENTAL TOXICITY and CARCINOGENESIS

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BY

Shizuo Satoh

Kawasaki Municipal Research Institute for Environmental Protection, 20-2 Tajima-cho, Kawasaki-ku, Kawasaki City, 210 JAPAN : Department of Public Health, School of Medicine, Akita University, Hondo 1-1-1, Akita City, 010 JAPAN

ABSTRACT

Petrochemical complex is the main sources of organic air pollutants in the seaside industrial area of Kawasaki City, Japan. Air samples in this area were collected to examine hazardous organic chemicals by highly sensitive gas chromatographic-mass spectrometer. About 170 organics detected in this area included the following carcinogenic or co-carcinogenic compounds :

- chloroethylene
- vinylchloride
- 1, 1-dichloro-ethylene
- chloroprene
- acrylonitrile

It was thought that primary source of organic chemicals was mostly attributed to fugitive emissions from storage and shipping facilities rather than from the manufacturing plants which have closed processing systems.

INTRODUCTION

The purpose of the paper reported here is to explain not only the results of measurements but also usefulness of GC/MS for monitoring hazardous organic chemicals in the industrial city as Kawasaki。

Gas chromatography was being used almost exclusively for analyzing various organic chemicals in the past。 However, qualitative analysis can not be carried out completely by GC alone。

Recently computerized highly sensitive gas chromatographic-mass spectrometer has been widely used for both qualitative analysis and quantitative analysis of organic chemicals。 In particular, the development of the Selective Ion Monitoring method by GC/MS has made it possible to analyse on ppt level。

Petrochemical complex is the main sources of organic air pollutants in the seaside industrial area of a Kawasaki City, Japan. Of emissions from many factories such as power plants, iron works, chemical plants, petroleum refineries, petrochemical plants etc, SO_2, NO_x, CO, total suspended particulated matters, and nonmethane-hydrocarbons are severely regulated by national laws and local government regulations。

However, many toxic air pollutants are not legally controlled and are needed to be surveyed systematically。

Hazardous organic chemicals were investigated in and around the petrochemical complex of Kawasaki, from 1975 to 1985 according to the toxic air pollutants control program。

GENERAL BACKGROUND OF AIR MONITORING SYSTEM IN KAWASAKI CITY

Kawasaki, a large industrial city in Japan, is located between Tokyo and Yokohama as shown in Figure 1. City area is about 140 km^2 and its population is about 1 million.

There are nine automatic measuring stations in Kawasaki City and the following 11 parameters are continuosly measured at each station :

- SO_2
- NO
- NO_2
- Ox
- Dust
- CO
- NMHC
- Wind direction
- Wind speed
- Temperature
- Humidity

Data measured at each station are telemetered regularly to the center. Annual averages concentration of the pollutants in 1983 at Tajima station near industrial area are as follows[3]:

SPM	46 ug/m^3
SO_2	0.012 ppm
NO_2	0.032 ppm
NMHC	0.50 ppmC

Usually some organic chemicals are also measured for surveying the precursor of photochemical oxidants and their concentrations are shown in Table 1.

METHODS OF SAMPLING AND ANALYSIS

Figure 2 and Figure 3 show the sampling apparatuses used for volatile and non-volatile organic chemicals respectively. Table 2 shows parameters for sampling and analysis of ambient organic chemicals. As shown in Figure 2 and Figure 3, GC-sampling tube is useful for sampling volatile organics and TENAX-tube is suitable for non-volatile organics.

Figure 4 shows the apparatus for injection of the collected air sample from TENAX tube to GC.

Figure 5, is an example of the identification of organic chemicals by mass chromatogram obtained from collected air samples.

RESULTS AND DISCUSSION

Table 3 shows the number of organic chemicals detected in and around the petrochemical complex area in Kawasaki.

Of the total 179 organics detected, the numbers of halogenated hydrocarbons are twenty three and each of them are shown in Table 4.

Table 5 shows thirteen organic chemicals regarded as carcinogenic and/or mutagenic compounds[4]. Compound marked (*) in Table 4 were registered as substances which should be surveyed in the priority list by Environment Agency, Japan, in 1979[5] (Appendix).

In addition, acrylonitrile concentrations determined by GC/MS ranged from non detectable to 103 ppb. This is thought to be typical example of the results of measurement by the Gc/MS SIM method.

Organic chemicals detected in ambient air are mostly attributed to fugitive emissions from storage and shipping facilities rather than from emission sources as stack.

REFERENCES

1) H. Suzuki and S. Satoh, Gas chromatography-mass spectrometric identification of organic compounds and determination of acrylonitrile in the air of the Kawasaki industrial area. Proceeding of the 4th meeting of the Japanese society for medical mass spectrometry (1979)

2) T. Kato, et al., Pollution from chloroprene plant and counter-plan for its control, Bulletin of the Institute of Environmental Science and Technology, Yokohama National University, 8, No.1 (1982)

3) Air pollution in Kawasaki (in Japanese), No.23 (1985) published by Kawasaki City pollution control Dept

4) Fishbein, L., Potential Industrial Carcinogens and Mutagens, Elesevier (1979)

5) Priority list for the environmental survey, December (1979) published by Environment Agency, Japan

APPENDIX

Outline of Priority List 5)

Rationale for the selection of chemical substances

In making up this list, the selection was made from among the existing substances with special reference to the four types of substances given below. However, the presently available information on the toxicity, production and the form of use of such individual substances is often fragmental and the choice had to be made on the basis of the rather limited information available at the present time and therefore this list is considered to be of such nature that it should be reappraised as such information is further expanded in the future.

a) Substances which have been found or reported to possess a degree of toxicity higher than a definite level
b) Substances which are judged to have a property similar to a) above in view of their chemical structure
c) Substances which are considered to be stable or highly accumulated in the environment
d) Substances which are produced industrially in considerable amounts and have the possibility of being emitted into the environment

Table 1 Average concentration of hydrocarbons in 1982

(ppb)

Compound	Sampling points	
	Ohgimachi	Chidoricho
Ethane	7.6	20.8
Ethylene	13.0	173
Acetylene	5.3	4.2
Propane	33.0	10.0
Propylene	3.5	15.6
iso-Butane	32.0	10.8
n-Butane	61.4	29.2
iso-Pentane	53.3	10.9
n-Pentane	25.3	8.1
2-Methylpentane	8.9	4.2
3-Methylpentane	4.5	4.2
n-Hexane	8.4	12.4
Benzene	6.8	5.8
Toluene	13.7	12.7
Ethylbenzene	2.8	2.0
p-Xylene	1.9	1.2
m-Xylene	4.1	2.7
o-Xylene	2.2	3.2
Total	287.7	331.0

Table 2 Parameters for Sampling and Analysis of Ambient Organic Chemicals

	Volatile Compound	Non-Volatile Compound
GC Column	20%TCP on Uniport HPS (packed column)	* Silicone OV-101 0.25mm I.D., 30m * 5%Phenyl Methyl Silicone 0.21mm I.D., 25m (open tubular column)
Sampling tube	GC-SAMPLING TUBE	TENAX-TUBE
Collection Temperature	-183°C	20~30°C
Desorption Temperature	below 100°C	Approximately 250°C
Sample Air Volume	1~200 liter	10 liter~10 m³

Table 3 Atmospheric organic chemicals in Kawasaki city

Group name	Number of compounds found
Halogenated hydrocarbons	23
Oxygen compounds	48
Hydrocarbons	99
Other compounds	9
Total	179

Table 4 Halogenated Hydrocarbons

‡ Registered in the Priority List

Volatile Compounds Detected	
Ethylchloride	‡
Vinylchloride	‡
2-Chloro-1,3-butadiene (Chloroprene)	‡
Methylenechloride	‡
Difluorodichloromethane	‡
1,2-Dichloroethane	‡
1,1-Dichloroethane	‡
1,1-Dichloroethylene	‡
cis-1,2-Dichloroethylene	‡
1,2-Dichloropropane	‡
Trichloromethane	‡
Trichlorofluoromethane	‡
1,1,1-Trichloroethane	‡
Trichloroethylene	‡
1,1,2-Trichloro-1,2,2-trifluoroethane	‡
Carbon Tetrachloride	‡
Tetrachloroethylene	‡

Non-Volatile Compounds Detected	
1,2-Dichlorobenzene	‡
1,4-Dichlorobenzene	‡
1,3-Dichlorobenzene	‡
2-Chloro-1,3-butadiene,dimer	
1,6-Dichloro-1,5-cyclooctadiene	
1-Chloro-4-(1-chloroethenyl)-cyclohexene	

Table 5 Carcinogenic and/or Mutagenic substances

Chemical substances	Carcinogenicity*	Mutagenicity*
Vinylchloride	+	+
2-Chloro-1,3-Butadiene (Chloroprene)	+	+
Methylenechloride		+
1,2-Dichloroethane		+
1,2-Dichloroethylene		+
1,2-Dichloropropane		+
Trichloromethane	+	
1,1,1-Trichloroethane		+
Trichloroethylene		+
Carbon tetrachloride	+	
Tetrachloroethylene		+
1,4-Dichlorobenzene	+	
Acrylonitrile	+	+

* Fishbein,L.:Potential Industrial Carcinogens and Mutagens, Elesevier (1979)

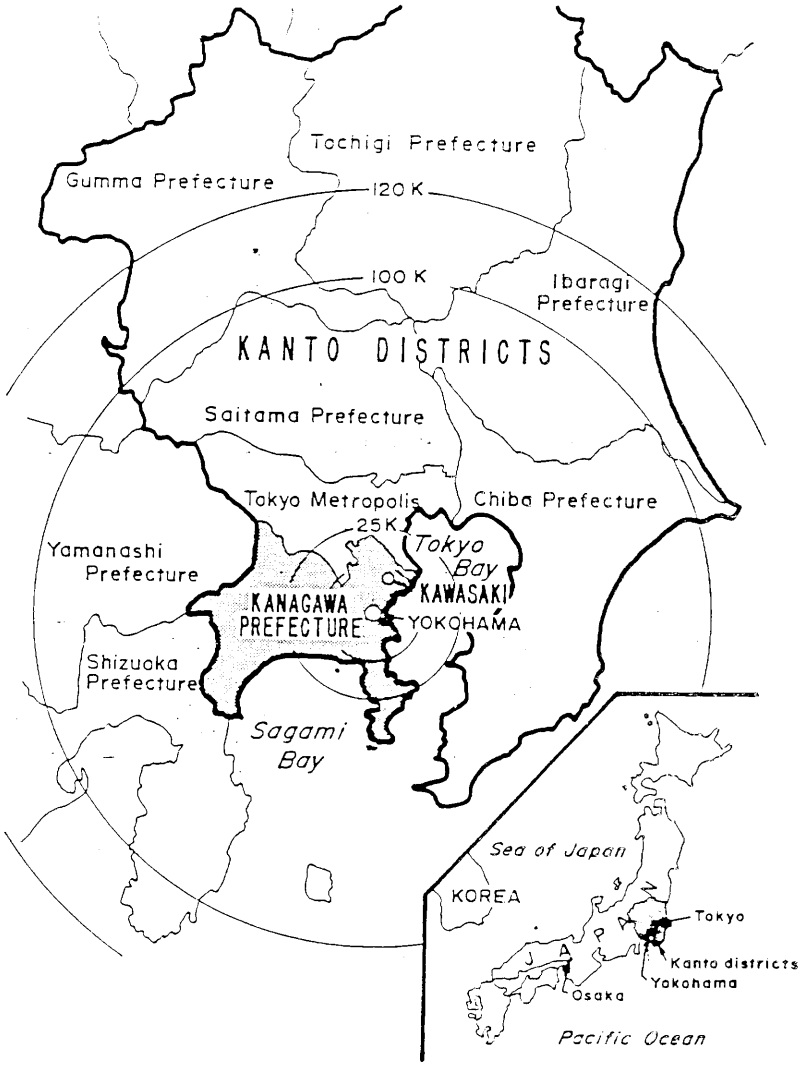


Figure 1 Map of Tokyo Bay area.

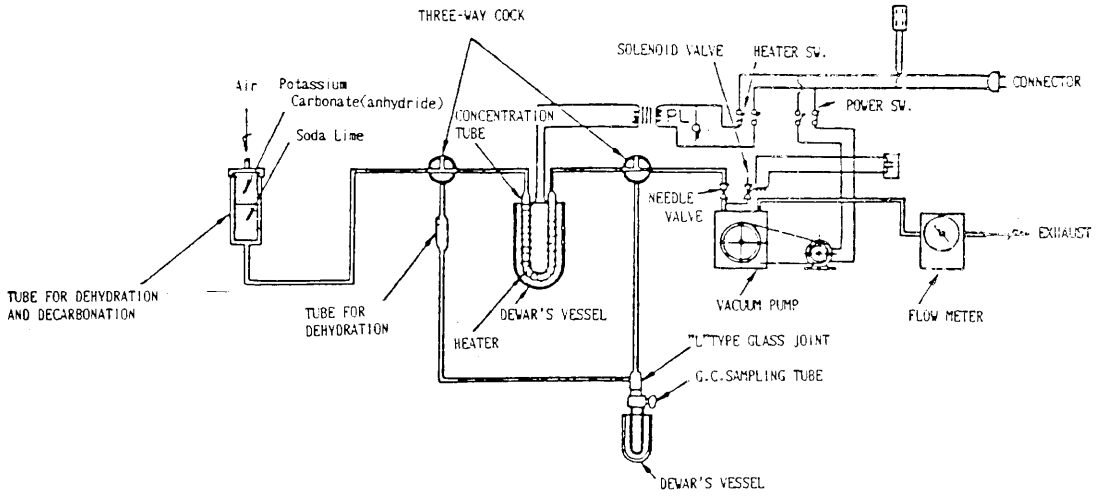
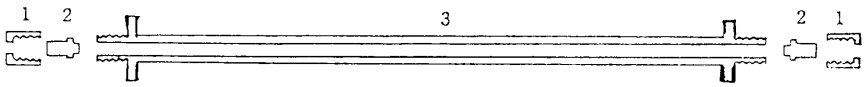


Fig. 2 Block Diagram of the Air Sampling System for Volatile Organics using G. C. SAMPLING TUBE



1:Stainless Steel Nut , 2:Stainless Steel Nipple ,
3:Stainless steel Sampling Tube (I. D. :4~6mm, L:100~180mm)

Fig. 3 Cross-section View of TENAX-TUBE for Sampling Non-Volatile Organics

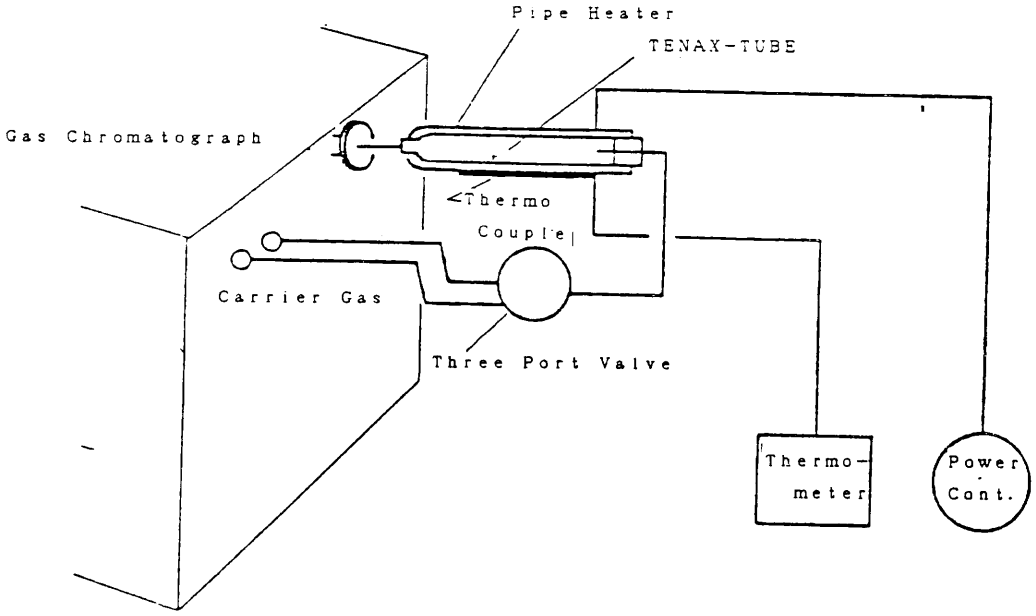
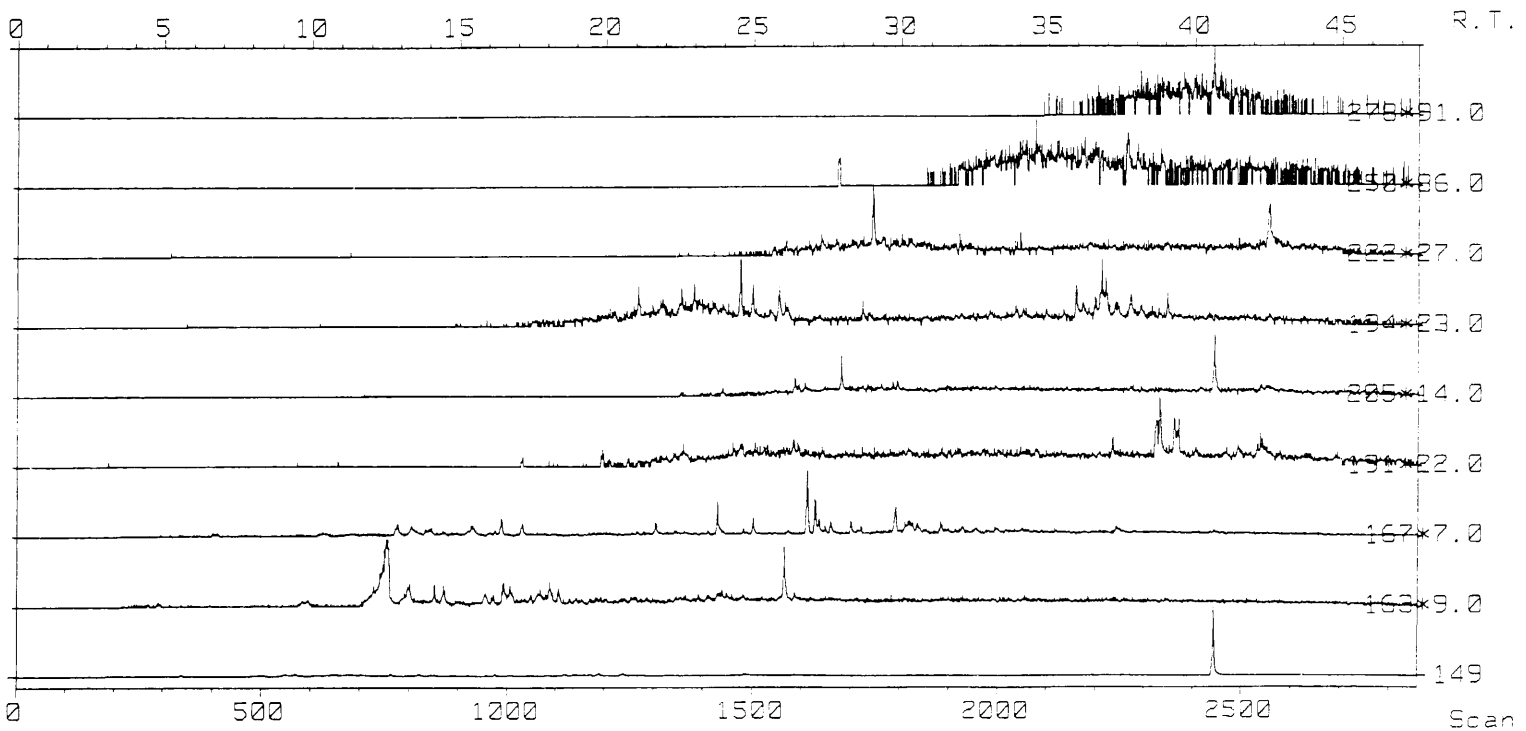


Fig. 4 Schematic Diagram of an Apparatus for GC Injection of TENAX-TUBE


MASS CHROMATOGRAM Data File: DM0:TNX33.DAT 24-JUL-85 19:18
Sample: TENAX ROOMT-240(5') CAR.G2ML HOLD40'
Scan# 1 to 2857(2857) RT 0'00" to 47'33"(47'33") EI(Pos.) Lv 0.00
Mass: 149.0,163.0,167.0,191.0,205.0,194.0,222.0,250.0,278.0
0
5
10
15
20
25
30
35
40
45
R.T.
278×91.0
250×86.0
222×27.0
194×23.0
205×14.0
191×22.0
167×7.0
163×9.0
149
0
500
1000
1500
2000
2500
Scan