Experimental Investigations on the Combined Actions of Components Mixed in Odorous Gas

By

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Abstract

Odor problems are generally caused by many kinds of malodorous substances at low concentration. In practice, it is extremely difficult to carry out a complete analysis of odor causing components by means of any instrumental analytical methods. For this reason, there is a great demand for a more reliable odor evaluation method based on sensory measurement.

The present investigation was therefore carried out to solve the problems involved in conventional methods for sensory measurement and evaluation, and to establish a method which might be effectively utilized for odor problems. Using eight odorants, the co-operative action of the combined components in mixed odors are discussed and the results are as follows. (1) The interaction between the combined components of the duplex complex odor influences the intensity of mixed odors. It also varies with the composition of the constituents and the ratio of the dilution/threshold numbers for the constituents. (2) In some complex odors, the combined actions were found to change from a potentiality to a cancellation with a change of the dilution/threshold number.

1. Introduction

Since an offensive odor usually consists of various odor causing substances at low concentration, a complete analysis of the individual components by means of any instrumental method is extremely difficult. Even if the chemical analytical data may be obtained, it is still difficult tlo integrate the characteristics of the odor of each constituent to the complex odor. Also, the evaluation of the combined actions such as the potential or cancelling actions of each component is also difficult[1,2].

Thus, it has been requested to establish a regulation based on a sensory measurement system. In this connection, the present official federal regulation as to the odor measuring method is not beneficial to the practice of an odor control

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program. Then, some prefectural autonomies have started their own regulation systems based on the sensory method for the control of offensive odor problems[3). This trend has been followed by many other autonomies. There are many problems to be solved in the conventional method, such as how to correlate the concentration of odorants with the odor intensity, how to determine the threshold level and how to estimate the combined actions between odor causing components. Poor objectivity is also a reason for criticisms[4).

Hence, the present investigation was carried out with the intention of trying to solve those problems. Sensory measurements were made on 8 single odors and 3 duplex odors in this study. The results obtained were subjected to a discussion on the correlation between the concentration of odorants and odor intensity, on the threshold value and on the combined action of individual constituents in a complex odor.

2. Materials and Methods

2.1. Odorants

Five compounds with an offensive odor, namely Ammonia (NH_3), Hydrogen sulfide (H_2S), Methyl mercaptan (MM), Methylamine (MA), Dimethyl sulfide (DMS) and three substances with an aromatic flavor such as Ethyl alcohol (EA), iso-Amylacetate (IAA) and Benzaldehyde (BA) were used as experimental odorants. These eight substances were singly packed in plastic bags made of polyester film, and the mixtures of two from three compounds of MM, MA and DMS at five different concentrations were similarly packed as shown in Table 1.

Table 1. Conecntrations of component in the odor samples

(ppm)

Sample No.	Concentration; *Ci*	
	MM	MA
1	0.20	3100
2	0.83	2700
3	2.96	1132
4	5.35	200
5	6.41	27.0
	MM	DMS
6	0.65	106.2
7	2.56	95.39
8	5.46	52.12
9	11.50	10.20
10	11.28	1.11
	MA	DMS
11	24.7	27.74
12	182.5	22.01
13	1083	11.56
14	2300	3.07
15	2677	0.88

The odorant contained in a plastic bag was prepared on the day before the experiment in order to make the odorant concentration homogeneous. The concentrations of the individual components were measured after each test according to the method recommended by The Agency for Environmental Protection.

2.2. Instrument

The odorants placed in the bag were diluted with an odor concentration measuring apparatus, Psycro-Olfactometer Model AE705. The system of this instrument is shown in Fig. 1. The diluted odorous gas sample to be tested is supplied to a tester situated in a testing room, to which external fresh air filtered through an activated charcoal filter is supplied at the rate of 76 *l/min* for ventilation. The rate of the sample gas supply is 2.0 *l/min*.

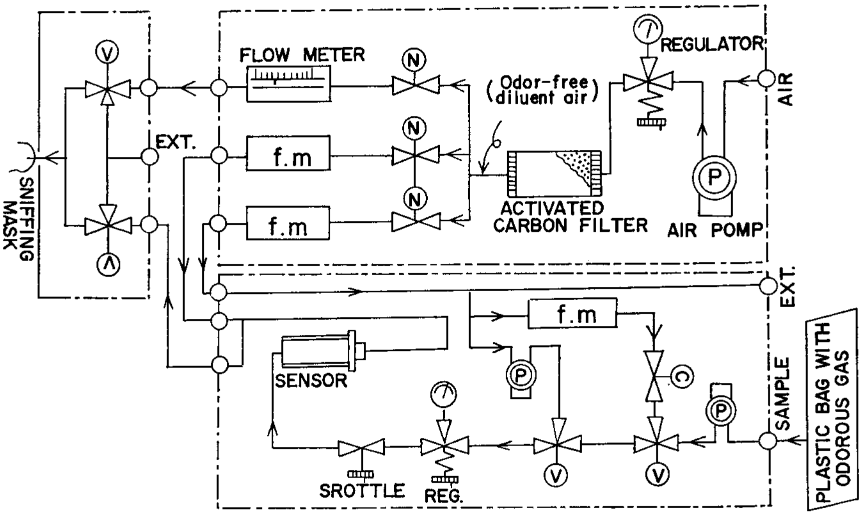

Fig. 1

2.3. Testers

Each group of testers consisted of from 8 to 11 civilians, the age ranging from 18 to 40 years old. As the victims of an offensive odor are ordinary civilians in general, and as they might consist of persons with various smelling abilities[5], no particular screening test nor smelling ability test was performed on the testers requested for this study.

2.4. Sensory test procedure

Two values, namely the odor vanishing point and the odor appearing point, which are thought to have a nature closely related to the detective threshold, were measured in this study. The odor vanishing point is the point where a gradually increased dilution attains the disappearance of the odor. On the other hand, the odor appearing point corresponds to the point where the increasing addition of the odorant gives rise to the existence of an odor. For each tester, the two values of each point were measured and geometrically averaged. Then, the cumulative frequency distribution for these mean values was constructed. A 90% range and a population perceptive threshold value, PPT50, were obtained for each odor sample from the distribution graph.

After the threshold measurement, each tester was next exposed to an odorous sample which contained an odorant with a concentration several times higher than the threshold value. The intensity of the odor was judged. Then, the odorous sample at 2, 4 and 8 times higher concentrations were similarly tested in this order. The odor intensity scale used in this study is shown in Fig. 2.

8 -- extremely strong
7 -- very strong
6 -- fairly strong
5 -- strong
4 -- relatively strong
3 -- slightly strong
2 -- easily detectable (smell)
1 -- barely detectable (faint smell)
0 -- no smell at all

Fig. 2

When the measurement was repeated by the same tester, the first test course was made in the morning only once, and the second was also once in the afternoon. In order to avoid a contamination with a remaining sample's odor in the diluting apparatus, it was throughly washed with warmed odor-free air after every measurement.

3. Theoretical Consideration of Combined Actions

Unpleasant smells which are actually encountered and cause public problems are the results of complicated interactions of various odor causing substances. It has been suggested that such interactions involve the additive, the potential or cancelling mutual actions of constituents[6]. According to the Weber-Fechner law, the relation between the odor intensity I and the odorant concentration C may be given by Equation (1)[7]:

$$I = k \log C + b \tag{1}$$

As the value of I becomes 0 when the value of C is equal to the threshold, Eq. (1) may be written as Eq. (2):

$$I = k \log (C/Th) = k \log Dt \qquad (2)$$

where k and b are the constants defined by the type and nature of the odor. The term C/Th is called the dilution/threshold number and denoted as Dt[8)]. The value of k varies with the type of odor[9)]. It was estimated by means of the least mean square method in this study from the relation observed between the odor intensity and the odorant concentration for the individual single odors, and duplex complex odor samples with various compositions. Little investigation, however, appears to have been carried out on the relation between the odor intensity and the combined actions. In this study, the interactions between two odorous components in a complex odor was considered as follows.

The sum of the dilution/threshold numbers of each odorous constituent, as single odorant Dt', was expressed by Eq. (3):

$$Dt' = \Sigma\,(Ci/Thi) \qquad (i=1,2) \qquad (3)$$

where Ci is the concentration of component i of a complex odor, and Thi is the threshold value of component i measured as a single odorant. In the case of the threshold, the concentration of each component is diluted by Dt with the equivalent. Therefore, the ratio Ci/Dt is newly denoted as Ci^*, and the ratio of Dt and Dt' is denoted as r, as shown by the next equation:

$$r = 1/\Sigma(Ci^*/Thi) = Dt/Dt' \qquad (4)$$

The comparison of the value of $r \cdot Dt'$ with the Dt obtained from the differential smelling test on complex odor samples provides the following three conditions:

$$\left.\begin{array}{l}\text{when } r>1, \text{ the combined action is potential,}\\ \text{when } r=1, \text{ it is addition, and}\\ \text{when } r>1, \text{ it is cancellation.}\end{array}\right\} \qquad \text{Def. (1)}$$

These criteria, however, simply indicate the change of the dilution/threshold number under the condition that the intensity I is 0, namely at the threshold level.

The slope of the linear relation between the odorant concentrations C and the odor intensities I in the absence of any interactions, which we denote as Kt, may be considered as the sum of the values which are obtained by multiplying the ratio of the dilution/threshold number for the each constituent of a complex odor to the slope Ki obtained from the measurement for single odor constituent. Thus, Kt may be expressed as Eq. (5). When the obtained slope, as the result of the presence of any combined action, is denoted as Ko and p is used as the ratio of Ko and Kt, Eq. (6) may be derived.

$$Kt = \Sigma(Ki \cdot Ci/Thi)/\Sigma(Ci/Thi) \qquad (5)$$

$$Ko = p \cdot Kt = p \cdot \Sigma(Ki \cdot Ci/Thi)/\Sigma(Ci/Thi) \tag{6}$$

Now supposing that the interaction between odorants only affects the slope, the type of combined action may be specified as follows.

$$\left.\begin{array}{l} \text{when } p > 1, \text{ the combined action is potential,} \\ \text{when } p = 1, \text{ it is addition, and} \\ \text{when } p < 1, \text{ it is cancellation.} \end{array}\right\} \qquad \text{Def. (2)}$$

The observed odor intensity *Io* may be expressed by combining Eqs (4) and (6). According to Eq. (7), it may be indicated as where the interaction affects

$$Io = p \cdot \{\Sigma(Ki \cdot Ci/Thi)/\Sigma(Ci/Thi)\} \cdot \log \{r \cdot \Sigma(Ci/Thi)\} \tag{7}$$

both the slope and the threshold value. Now, considering *It* is the theoretical additive intensity corresponding to the condition that both p and r equal 1, *It* is given as Eq. (8). Then, with the use of the parameters *Io* and *It*, the interaction may be divided as Def. (3).

$$It = \{\Sigma(Ki \cdot Ci/Thi)/\Sigma(Ci/Thi)\} \cdot \log \{\Sigma\ (Ci/Thi)\} \tag{8}$$

$$\left.\begin{array}{l} \text{when } Io > It, \text{ the combined action is potential,} \\ \text{when } Io = It, \text{ it is addition, and} \\ \text{when } Io < It, \text{ it is cancellation.} \end{array}\right\} \qquad \text{Def. (3)}$$

From the Eqs (7) and (8), Def. (3) may be finally rewritten as follows: the potential action may appear

when $p > 1$ and also $r < 1$ for $Dt' < r(p)$*,
when $p \geq 1$ and also $r < 1$, or
when $p < 1$ and also $r < 1$ for $Dt' < r(p)$.

the additive action may appear

when $p = r = 1$,
when $p < 1$ and also $r > 1$ or $p > 1$ and also $r < 1$ for $Dt' = r(p)$,

and the cancelling action may appear

when $p < 1$ and also $r < 1$ for $Dt' = r(p)$,
when $p \leq 1$ and also $r > 1$ or
when $p < 1$ and also $r > 1$ for $Dt' = r(p)$.

Thus, the type of combined action is not always fixed by the value of p or r, but can vary with the value of the dilution/threshold number.

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* $r(p) = r^{p(1-p)}$.

4. Results and Discussion

4.1. Odor Threshold

The values of the odors appearing and vanishing points and their geometrical mean value for individual substances are shown in Table 2. They are not very different. The odor appearing points, however, for the odorants other than MM and H_2S appear to be slightly greater than the odor vanishing points. In particular, for a strongly irritative odor such as that of NH_3 and MA, the value of an odor appearing point was estimated to be double that of an odor vanishing point. The ratio of the upper limit to the lower limit of the 90% range was 5 to 10 for NH_3 which, is the smallest, and was 20 to 100 for EA and DMS. The ratios for the other substances were in the range of 10 to 40, indicating relatively small individual differences.

Table 2. Values of the 90% range of threshold and population perceptive threshold (PPT50) of each substances

(ppm)

Substances		90% range	PPT50
Methylmercaptan	A.P.*	0.009–0.331	0.017
	V.P.**	0.010–0.447	0.021
	G.M.***	0.010–0.430	0.019
Methylamine	A.P.	1.26–29.5	6.17
	V.P.	0.91–10.0	3.20
	G.M.	1.20–18.2	4.68
Dimethyl sulfide	A.P.	0.007–0.794	0.076
	V.P.	0.010–0.398	0.063
	G.M.	0.010–0.437	0.063
Hydrogen sulfide	A.P.	0.007–0.224	0.038
	V.P.	0.019–0.209	0.063
	G.M.	0.018–0.159	0.053
Ammonia	A.P.	7.0–64.6	21.9
	V.P.	6.0–26.6	12.6
	G.M.	7.5–40.0	16.6
Ethyl alcohol	A.P.	14.5–1660	159
	V.P.	10.0– 174	132
	G.M.	16.0–1580	159
iso-Amyl acetate	A.P.	37.2–1510	240
	V.P.	45.7– 550	156
	G.M.	50.1– 891	209
Benzaldehyde	A.P.	178–3550	794
	V.P.	195–2400	676
	G.M.	178–3980	794

* Odor Appearing Point, ** Odor Vanishing Point,
*** Geometrical Mean of A.P. and V.P. values

4.2. Relation of Odorant Concentration and Odor Intensity

The 90% range and the central values of K obtained by all testers are shown in Table. 3. Each K value was calculated from the values of C and I, obtained by one tester for each odor sample. The concentrations at the value of odor intensity equal to zero, which may be estimated from the central *K* value by use of Eq. (2), are given in Table 4. The relations between these two values are shown in Fig. 3. The *K* values distributed in the range from 1.7 for BA-pleasant to 5.0 for NH_3, in general, an unpleasant smell showing a greater value than an aromatic flavor. Namely, strong irritating odors such as those of NH_3 and MA show large values such as 3.5 to 5.0, whereas rotten smells such as those of H_2S, MM and DMS show values such as 2.5 to 3.3. Aromatic flavors like those of iAA, EA and BA gave relatively small values such as 1.7 to 2.6. Thus, it was found that the value of *K* largely varies with the characteristics of the odor. For MM, H_2S and iAA, the threshold values calculated as the concentration when $I=0$, were about half as small as the geometrical means. Namely, the intensity around the threshold level was overestimated by about 0.8 for H_2S, MM and iAA. This indicates the necessity to take the following fact into consideration. That is, the intensity calculated by using the dilution/threshold number may vary by about one degree on the odor intensity scale at the level of the threshold.

Table 3. Values of the coefficient *K* ofr each substances

Substances	90% Range	Median
Methyl mercaptan	2.4– 5.1	3.3
Methylamine	2.0– 5.5	3.5
Dimethyl sulfide	1.6–11.7	2.5
Hydrogen sulfide	1.1– 4.2	2.5
Ammonia	4.0– 7.3	5.0
Ethyl alcohol	1.1– 4.7	2.6
iso-Amyl acetate	0.8– 2.6	2.1
Benzaldehyde (pleasant)	1.0– 3.2	1.7
Benzaldehyde (unpleasant)	1.6– 4.6	2.6

Table 4. Concentrations for each substances that give the 0 degree of odor intensity on regression lines

(ppm)

Substances	90% Range	PPT50
Methyl mercaptan	4.7 – 229.0	10.7×10^{-1}
Methylamine	0.87– 9.55	3.73
Dimethyl sufide	4.2 – 759.0	64.0×10^{-3}
Hydrogen sulfide	6.0 – 251.0	25.0×10^{-3}
Ammonia	14.6 –106.0	16.6
Ethyl alcohol	0.10–2240	160
iso-Amyl acetate	9.5 –2690	90
Benzaldehyde	—	—

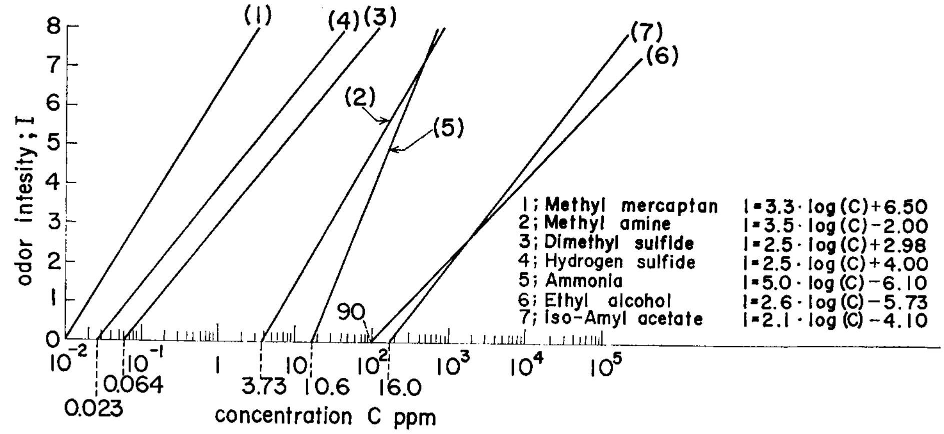

Fig. 3

4.3. Combined Actions in Complex Odor

For a complex odor, it is not easy to define the threshold concentration[10)], so in this study the dilution/threshold number *Dt* was tentitatively used as the indicator of the threshold value. The *Dt* values ranged from 1500 to 10000, and are shown in Table 5. The values of *r* were obtained from Eq. (4), and they were found to be larger than 1 for all complex odor samples tested. This indicats the existence of potential action for the threshold of a complex odor. The extent of such combined action varies with each sample, the maximum value being 16.8 for sample No. 12 and the minimum being 2.64 for sample No. 3.

Table 5. Values for investigating the effects of combined action in complex odor samples

Sample No.	Dt	r $1/\sum(Ci^*/Thi)$†	p Ko/Kt	$r^{p/(1-p)}$
1	3235	3.81	1.11	
2	—	—	—	
3	1533	2.65	1.41	
4	3343	6.04	1.00	
5	5947	9.78	1.20	
6	7511	4.37	0.83	1.3×10^3
7	8625	4.99	1.26	
8	4964	3.75	1.32	
9	9903	8.03	0.78	1.6×10^3
10	7025	6.55	0.91	1.8×10^8
11	3117	7.08	1.27	
12	6590	16.8	0.95	1.9×10^{23}
13	1850	3.93	1.15	
14	1907	2.87	1.14	
15	2610	3.57	0.95	3.1×10^{10}

† the term of *Thi* is threshold concentration of each sabstances as single odor and used following values: MM 0.0107 ppm, MA 3.73 ppm and DMS 0.064 ppm

The ratios of the dilution/threshold numbers of components of complex odors, when the mixed odor samples are diluted to the threshold levels, are shown in Fig. 4. The broken line shows the curve when the sum of the Ci^*/Thi equal to

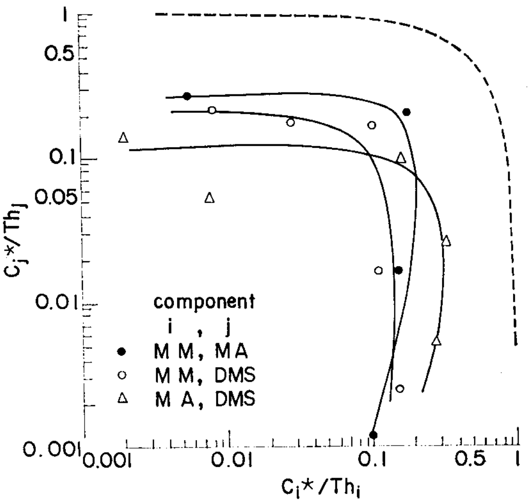

Fig. 4

1. According to the results given in Fig. 4, the odor intensity of a complex odor is more dependent upon the combination of odorants than the concentration differences between the components. If this property is termed as the dominancy of the component contributing to the odor intensity of a mixed odor, it may be said that, for example, DMS has a stronger dominancy than MM in the mixture of DMS and MM, while in the mixture with MA ,MA has the stronger dominancy. Similarly, MA has the stronger domiannacy in the mixture of MA and MM. Thus, the order of dominancy of the three odorants used in this study becomes MA> DMS>MM.

The relation between the dilution/threshold numbers Dt and the odor intensities I of individual complex odor samples are shown in Fig. 5-(a) (b) (c). The broken lines show cases where the components are in the form of a single odor. Although the value of K varies from 2.1 of sample No. 6 to 4.8 of sample No. 3, it is relatively small for the mixture of MM and DMS. Here, the mean value is 2.92, and tends to become larger for the mixture of MM and MA, where the mean value is 4.03. The variations of K, including those of single odor samples, are summarized as follows. The K value for a strong irritative odor is the largest, ranging from 3.3 to 5.0, that for a spoiled smell is 2.5 to 3.7, that for not a strongly irritative smell is 2.1 to 3.7, and an aromatic flavor shows small values ranging

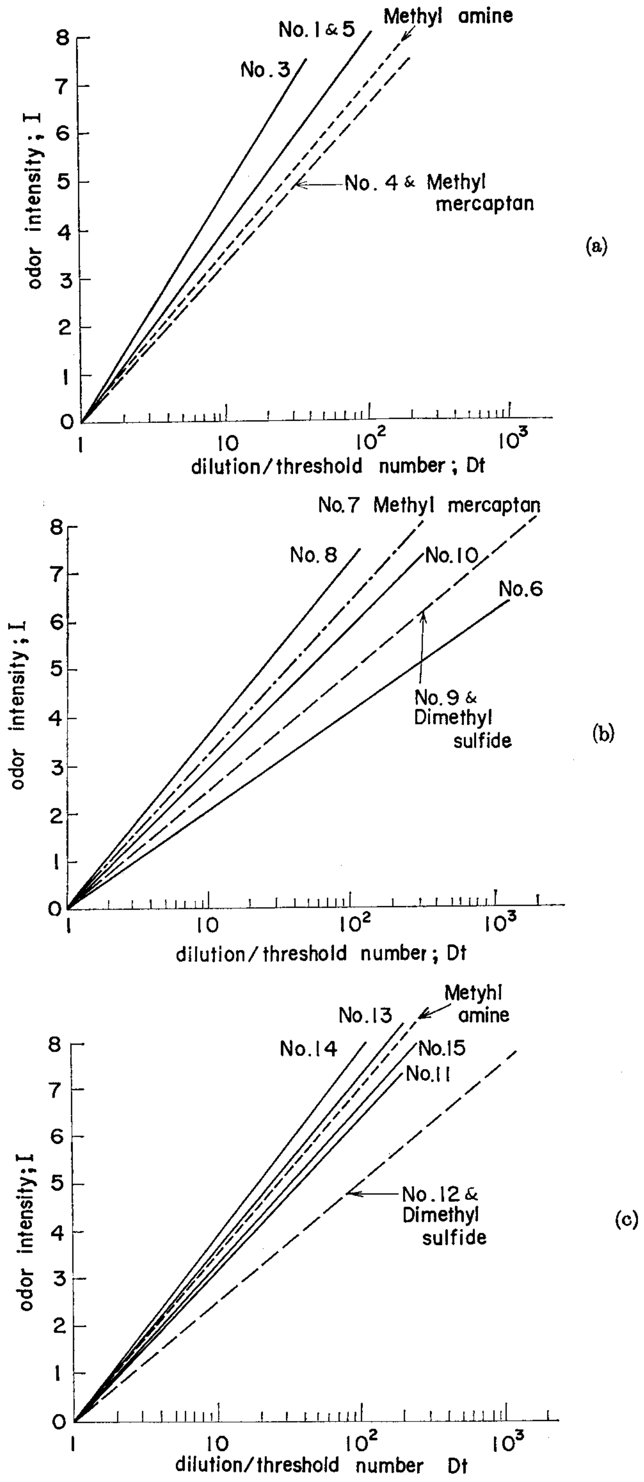
odor intensity ; I
8
7
6
5
4
3
2
1
0
1
10
10²
10³
dilution/threshold number ; Dt
No. 1 & 5
Methyl amine
No. 3
No. 4 & Methyl mercaptan
(a)
No. 7 Methyl mercaptan
No. 8
No. 10
No. 6
No. 9 & Dimethyl sulfide
(b)
Metyhl amine
No. 13
No. 14
No. 15
No. 11
No. 12 & Dimethyl sulfide
dilution/threshold number Dt
(c)

Fig. 5 (a), (b), (c)

from 1.5 to 2.5.

The ratio of the theoretical value Kt and the observed value Ko, namely p, was then calculated by using Eqs (5) and (6). On the basis of Def. (2), the effect of the combined action of odor components on the K value was thus examined. The result indicated that there exist a cancelling action in samples No. 6, 9, 10, 12 and 15, an additive action in sample No. 4 and a potential action in the other samples. (See Table 5)

Thus, odors practically experienced will have various characteristics. Therefore, it is questionable to regulate the actual odor by applying indiscriminately the dilution number method used in several autonomies[11].

This is because the odor intensity of a combined odor varies with either the concentration of its component or the dilution/threshold number of the component. It is improper to determine the combined action by simply comparing the intensity of the mixed odor Iij with the intensities Ii and Ij of the component i and j, which are both measured in the state of a single odor. Therefore, the combined actions were elucidated as the change of the relation of the threshold and concentration to the intensity.

The values of r for all complex odors examined were invariably larger than 1. However, the values of p were found to be smaller than 1 for samples No. 6, 9, 10, 12 and 15. Therefore, when $Dt'<r(p)$ the potential may appear, when $Dt'=r(p)$ the combined action is additive, and when $Dt'>r(p)$ it means a cancellation. The theoretical additive point of these complex odors varies from 1330 for sample No. 6 to 1.9×10^{23} for sample No. 12. For samples No. 9, 10, 12 and 15, the theoretical additive points become larger than the Dt' values corresponding to the strongest odor intensity degree of 8. It appears that only the potential action is taking place in these four samples. The other samples, except those mentioned above, gave the condition $p>1$. Hence, only the potential action is taking place regardless of the value of Dt'. Therefore, it might be considered that the change of interaction only occurs in sample No. 6, illustrated in Fig. 6. It was not possible to demonstrate the obvious cancelling actions such as invariable cancelling or the change from cancellation to potential in the present investigation, because only unpleasant odors were used. However, it becomes evident that the combined action may be altered by a change of the dilution/threshold number.

Further investigation, using a masking agent such as aromatic odorants, might be expected to show the tendency in a clearer manner. As the definition of the scoring scale is essential for sensory measurement, too, investigations are in progress on the appropriate number of grades in a scale, and also on the proper terminology[12]. It is necessary, in this connection, to develop a scale capable of ex-

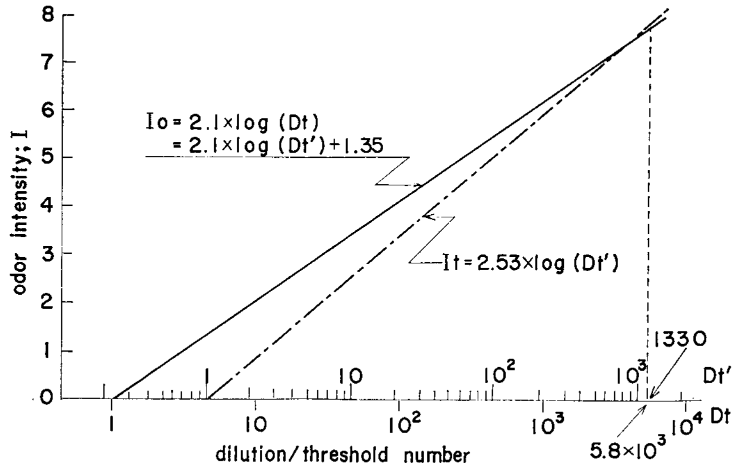

Fig. 6

pressing not only the intensity but also integrated differences of sensorily perceived odors.

5. Summary

Sensory tests on 8 single odors and 15 two-component combined odors were carried out to give the following conclusions; i) The coefficient *K* is small for an aromatic flavor and large for an unpleasant smell. In an offensive odor, an irritating odor shows a larger value of *K* than a spoiled odor. ii) The combined action between the mixed two-component of a complex odor influences the intensity of the combined odor, and varies with the composition of the constituents or the ratio of the dilution/threshold numbers for the constituents. iii) In some complex odors, the combined action was found to change from a potential to a cancellation with a change of the dilution/threshold number. It was thus indicated that the alteration of the combined action in a complex odor occurs as the combined result of a change of the threshold and the coefficient *K*.

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