9.11 Offensive odor measurement methods

9.11.1 Overview of offensive odor measuring methods

Offensive odor measurement methods can be classified into two, instrumental analysis methods, which use analytical equipment to measure offensive odor substances, and namely sensory tests that determine the strength of an odor from the human olfaction. Offensive odor can be seen from the point of view as sensory pollution, and sensory tests can be considered as a means of easily obtaining the sense of damage inflicted by the odor in question directly. But there are problems when it comes to the issue of results objectivity. On the other hand, instrumental analysis methods evaluate as their results the relationship between the concentration of each substance and the strength of odor (the Weber-Fechner's rule) [1], and are deemed a method of measuring offensive odors, but it is not easy to accurately determine the odor components from each source and evaluate the condition of that source. In this way, both instrumental analysis methods and sensory tests have their pros and cons, so by employing them both, a more accurate evaluation of the offensive odor can be made.

The Offensive Odor Control Law initially designated 22 offensive substances to be regulated, determining their concentration by instrumental analysis method, and basing its regulations on the concentration in question, but due to a revision of the law in 1995, it was decided to use sensory tests (triangle odor bag method) in conjunction with the equipment. Moreover, as an additional way of measuring offensive odors, odor sensors have come onto the market, but an odor sensor that can select the target substance and one that can be used by the general public has not yet to be developed.

9.11.2 Instrumental analysis methods

(1) Overview of instrumental analysis methods [2] [3]

In many cases, offensive odor substances can be sensed as a "smell" even with extremely low concentrations. For this reason, the offensive odor substance often goes undetected if it is introduced to an analyzer as it is. Consequently, in measuring offensive odor substances, it is necessary to introduce an odor to the detector in concentrated form. Further, these are many substances mixing with the odor, so it is necessary to take the offensive odor substance alone by pretreatment, collect a sample selectively at the sampling stage, and to use a detector that has ability toslect specific substance.

The measurement of offensive odors is comprised of the following processes: sampling, concentration, preprocessing, and analysis. In some cases, collection, concentration, and preprocessing are often carried out simultaneously, or some of the operations are abridged. The measuring methods can be classified by sampling method.

① The odor is collected in a container such as a bag or bottle (glass, stainless steel, etc.) (Vessel sampling method.)

② Collection of the odor in a solution that reacts with the odorous substance (Solution absorption method.)

③ Collection of the odor in a tube filled with an adsorbent coated with a reaction agent (Reactor tube method.)

④ Collection of the odor on filter paper coated with a reaction agent (Filter paper sampling method.)

⑤ Collection of the odor in a collection tube packed with an adsorbent (Adsorption method.)

Of these sampling methods, ② to ⑤ are carried out the concentration process at the same time. A separate concentration operation is only needed with the container collection method①. ① targets the volatile components, and for the concentration method, basically a U-shaped glass tube packed with an adsorbent is cooled in a cooling medium such as liquid oxygen, and the odor substances, which have been collected in a container, are concentrated by passing it through the U-shaped glass tube (see Fig.9.11.1) [4]. This glass tube is then heated, and the odorous components are introduced to the equipment (cold-trap method). In addition, measurement is possible by combining sampling methods ② to ⑤ in the container. Methods ② to ④ all target reactive compounds gas. In the case of an acid gas, a basic reagent is added to each medium, the sample gas is passed through the medium and collected through the acid/ base reaction. The acid gas thus collected is added a strong acid, separated, and supplied for analysis. In the case of a basic gas, the opposite operation is performed. The ordinary temperature adsorption method ⑤ is suited to substances with a higher boiling point than the cold-trap method, and after passing the sample gas through a sampling tube at ordinary temperature, the substance is extracted by either heating the tube or using the solvent, and then introduced to the equipment.
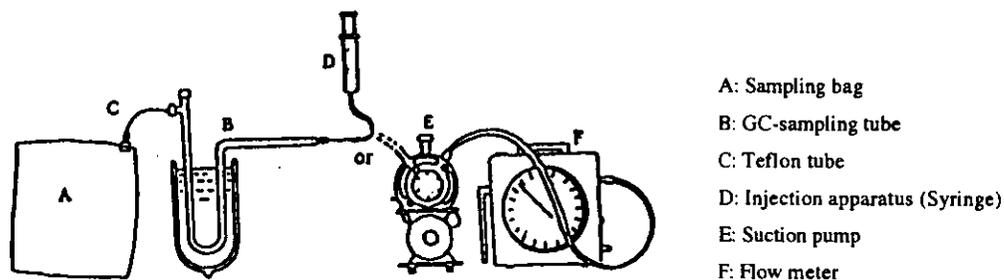

A: Sampling bag
B: GC-sampling tube
C: Teflon tube
D: Injection apparatus (Syringe)
E: Suction pump
F: Flow meter

Fig.9.11.1   Overview of the cold-trap method [4]

(2) Analytical instruments of offensive odor substances

The components of the odor are in a gaseous state, many components are mixed together, and detection sensitivity is high, for which reasons, either a gas chromatograph or a gas chromatograph-mass spectrometer is used. Such equipments are basically composed of a injection port, columns, and detector, and the sample gas that has been injected is separated into each of its component parts by the columns, and introduced to the detector for analysis. Both detectors which demonstrate ordinary responses, and detectors possessing selectivity to functional group are commercially available.   Table 9.11.1 shows them in overview.

Table 9.11.1   Overview of gas chromatograph detectors

Detector	Target analysis substance	Detection limit (pg)	Linear range
Flame ionization detector (FID)	General organic compounds	50~	10^6
Flame photometric detector (FPD)	Sulfur and phosphorous compounds	10~	10^2
Flame thermionic detector (FTD, NPD)	Nitrogen and phosphorous compounds	10~	10^4
Electron capture detector (ECD)	Organohalogen, organic metals	0.1~	10^3
Photoionization detector (PID)	Unsaturated compounds	50~	10^6
Electron conductivity detector (ELCD)	Halogen, sulfur, and nitrogen compounds	5~	10^6
Mass spectrometer (MS) scanning method	General organic compounds	10~	10^6
Mass spectrometer (MS) SIM method	General organic compounds	0.01~	10^6

(3) Analysis Methods of specified odorous substances

The Offensive Odor Control Law determines measurement methods for 22 substances starting with hydrogen sulfide as substances targeted for regulation (specified odor substances). An outline of the measurement methods for each substance is shown in Table 9.11.2.

Table 9.11.2 Outline of the measurement methods for specified odor substances

Specified odor substance	Attached tables	Classification	Collecting method (sampling method)	Concentration method	Sampling volume (minimum determination limit)	Measurement method	Apparatus used
Ammonia	1	Site boundaries Exhaust outlet	Absorption method (Boric acid solution)	Solution collection (sample solution adjustment)	50 ℓ (0.05 ppm)	Absorption spectrophotometry	Absorption spectrophotometer
Hydrogen sulfide Methylmercaptan Methyl sulfide Methyl disulfide	2	Site boundaries Exhaust outlet (excluding hydrogen sulfide)	Sampling bag (bag collection)	Cold-trap/heated introduction method	1 ℓ (0.0002 ppm) 1 ℓ (0.0002 ppm) 1 ℓ (0.0005 ppm) 1 ℓ (0.0005 ppm)	Gas chromatography	Gaschromatograph analyzer with flame photometric detector (FPD)
Trimethylamine	3	Site boundaries Exhaust outlet	Absorption method	Solution collection Alkali decomposition Cold-trap/heated introduction method	50 ℓ (0.0005 ppm)	Gas chromatography	Gas chromatograph analyzer with flame ionization detector (FID)
Acetaldehyde Propion aldehyde n-Butyl aldehyde Isobutyl aldehyde n-Valer aldehyde Isovaler aldehyde	4	Site boundaries Exhaust outlet (excluding acetaldehyde)	Sampling bag Cartridge method	2, 4-DNPH collection and sample adjustment	50 ℓ (note)	Gas chromatography	Gas chromatograph analyzer with flame thermionic detector (FTD)
			Sampling bag (bag collection)	Adsorption/heated introduction method	2 ℓ (0.0005 ppm)	Gas chromatograph-mass spectrometer	Gas chromatograph-mass spectrometer which has electron shock ionization (EI method) (SIM method)
Isobutanol	5	Site boundaries Exhaust outlet	Sampling bag (bag collection)	Cold-trap/heated introduction method, Adsorption/heated introduction method	1 ℓ (0.01 ppm)	Gas chromatography	Gas chromatograph analyzer with flame ionization detector (FID)
Ethyl acetate Methyl isobutyl ketone	6	Site boundaries Exhaust outlet	Sampling bag (bag collection)	Cold-trap, Adsorption (heated introduction method)	1 ℓ (0.01 ppm)	Gas chromatography	Gas chromatograph analyzer with flame ionization detector (FID)
Toluene Styrene Xylene	7	Site boundaries Exhaust outlet (excluding styrene)	Sampling bag (bag collection)	Cold-trap Adsorption (heated introduction method)	1 ℓ (0.01 ppm)	Gas chromatography	Gas chromatograph analyzer with flame ionization detector (FID)
Propionic acid n-Butyric acid n-Valeric acid Isovaleric acid	8	Site boundaries	Adsorption method	Alkali beads collection, Formic acid injection/heated introduction method	25 ℓ (0.005 ppm) 25 ℓ (0.005 ppm) 25 ℓ (0.005 ppm) 25 ℓ (0.005 ppm)	Gas chromatography	Gas chromatograph analyzer with flame ionization detector (FID)

(Note): Acetaldehyde (0.005 ppm). Propion aldehyde (0.005 ppm). Isobutyl aldehyde (0.0005 ppm). n-Butyl aldehyde (0.005 ppm). n-Valer aldehyde (0.002 ppm). Isovaler aldehyde (0.002 ppm).

* "Attached tables" indicate separate tables for measurement methods of specified offensive odor substances (Environment Agency report), and 1, 2... signifies table 1, table 2..., etc.

(4) Other instrumental analysis methods

The measuring methods shown in (3) require equipment, preparation, and an experienced surveyor, and establishing of the sufficient measuring system is difficult. For this reason, the use of detection tubes that can be employed in a wide variety of fields such as work environment measurements and so forth in offensive odor analysis as a simple measuring method is currently under discussion. Of the specified odorous substances, detection tubes for use in the work environment have been improved for five substances: ammonia, methylmercaptane, hydrogen sulfide, acetaldehyde, and styrene, making them available for actual use. The specifications of the detection tubes for use of odorous substances are shown in Table 9.11.3 [5]. Moreover, sampling by using these detection tubes use large quantities of sample gas, and the tubes are connected to both a suction pump and an integrated flowmeter (a dry test meter).

Table 9.11.3 Specifications of the detection tubes for offensive odor use [5]

Target substance	Manufact -urer	Detection range (ppm)	Sampling gas volume	Reaction principle	Interfering gas	Discoloration state
Ammonia	G. Co.	0.5~5.0	750 mℓ	$2NH_3+H_2SO_4 \rightarrow (NH_4)_2SO_4$	Discoloration of amines and diamines at 2 ppm or more. High error margin coexisting with 1/15 or more of NH_3.	Pink→Yellow
	K. Co.	0.3~5.0	500 mℓ	$2NH_3+H_3PO_4 \rightarrow (NH_4)_2HPO_4$	Amines	Pink→Yellow
Hydrogen sulfide	G. Co.	0.01~0.2	750 mℓ	$H_2S+HgCl_2 \rightarrow HSHgCl+HCl$	No effect on CH_3SH, SO_2, NO_2, NH_3	Yellow→Purple
	K. Co.	0.02~0.2	1500 mℓ	$H_2S+HgCl_2 \rightarrow HSHgCl+HCl$	CH_3SH has no effect at 0.02 ppm or below.	Yellow→Pink
Styrene	G. Co.	0.2~4.0	1500 mℓ	Concentration polymerization due to fuming sulfuric acid smoke emission	Patchy generation of a yellowish-brown color with butadiene 2 ppm, slight discoloration with tenfold or more of alcohol, ketone, ester, and aldehyde.	White→yellow
	K. Co.	0.4~4.0	2000 mℓ	Concentration polymerization due to fuming sulfuric acid	No effect at 10 ppm or less with each of acetone, benzene, toluene, xylene, or ethyl acetate.	White→yellow

9.11.3 Sensory test methods [6][7]

Sensory test methods involving offensive odors are methods of measuring offensive odors using the human olfaction. The human olfaction has the advantage of catching all smells. Sensory test methods involving offensive odors are applied suitably as follows: methods that determine the dilution rate of odors (odor concentration, odor index) through methods of assigning a numerical value, and methods that determine the intensity of an odor. The triangle odor bag method is used as a way of determining the dilution rate, and methods using the six-state odor intensity scale are used as ways of determining the strength of an odor.

(1) Triangle odor bag method

As methods by which the odor is gradually diluted to determine the dilution rate at which the human olfaction can no longer detect the odor, the following have all been reported: the scentometer method, the olfactormeter method, and the syringe injection method, but the triangle odor bag method, which solves the flaws in the syringe injection

method, is most widely used in Japan, and due to a revision in the Offensive Odor Control Law in 1995, has been introduced as a new method of measuring offensive odors.

The triangle odor bag method panels are passed 3 ℓ of odor bags filled with one odor and two odorless bags, and they select the odor-filled bag from among them by an operation shown in Fig.9.11.2. If the answer is correct, the same operation is repeated with an odor-filled bag that has been further diluted, and this experiment is repeated until an incorrect answer is given, by which specific method the dilution rate (odor concentration, odor index) is determined. The dilution method from a threefold series downwards. The methods for calculating the dilution index from the triangle odor bag method is shown in Fig.9.11.3.

Moreover, specimens are collected by either plastic bag (Mylar bag, Tedlar bag, etc.), or glass bottle.
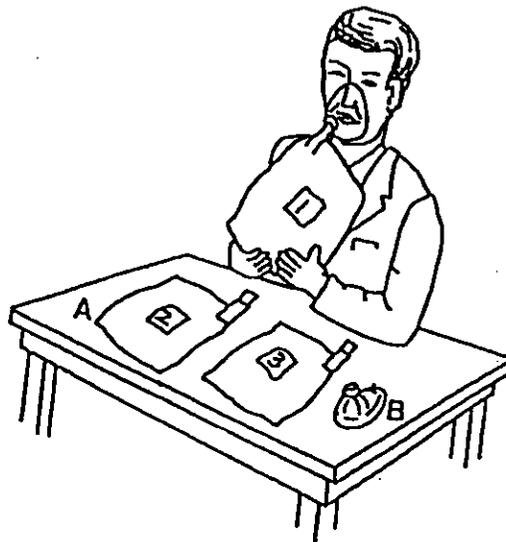

Fig.9.11.2　Triangle odor bag method operation [7]

Dilution rate	30	100	300	1,000	3,000	10 million	Threshold value for each panel	Cutting of Max. and Min. values
log. values	1.48	2.00	2.48	3.00	3.48	4.00		
Panels A	/	/	○	○	×		3.24	
B	/	/	○	×				Cut
C	/	/	○	○	○	○		Cut
D	/	/	○	○	○	×	3.74	
E	/	/	○	○	×	3.24		
F	/	/	○	○	○	×	3.74	

Fig.9.11.3　Method of calculating the triangle odor bag method [6]

(2) Six-stage odor intensity

The measurement of odor intensity is a method of assigning numerical values based on a measurement that shows in tabular form how the strength of an odor is sensed when the surveyor directly inhales that smell in the

296

environment. The measurement method is to plot on a graph as shown in Fig.9.11.4 [8] the strength of an odor directly smelled at ten-second intervals by three or more surveyors at each survey site. This operation is repeated continuously for five minutes at the same survey site. The mean value of the surveyors is calculated for each time period, and the strength of the odor at the measuring site is evaluated.
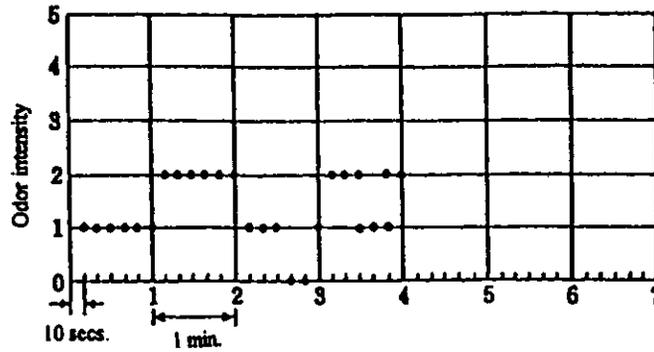

Fig.9.11.4   Six-stage odor intensity scale [8]

Calculating the odor index

(1) Environmental specimens

The odor index is calculated according to the following formula.   However, if the mean correct rate concerning the initial dilution ratio is less than 0.58, the odor index values are displayed as less than 10 log.M.

$$Y = 10 \log \left(M \times 10^{\frac{\gamma_1 - 0.58}{\gamma_1 - \gamma_0}} \right)$$

With this formula, the mean correct rate is expressed when Y is the odor index, M is the initial dilution ratio, γ_1 is the mean correct rate relating to the initial dilution ratio, γ_0 is the initial dilution ratio times 10.

(2) Outlet vent specimens

A.   The threshold values for each panel relating to the dilution ratio for the specimen odor are calculated according to the following formula.

$$X_i = \frac{\log M_{1i} + \log M_{0i}}{2}$$

In this formula, X_i expresses the threshold value for a given panel relating to the dilution ratio of the sample odor, M_{1i} is the maximum value from among the dilution ratio relating to the relevant odor bags when the panel in question has been selected with an odor bag attached, and M_{0i} is the dilutant value relating to an attached odor bag when either selection is dysfunctional or when an odorless bag is selected from the panel in question.

B.   Of the X_i calculated for each panel, one of the maximum and minimum values each are excluded, the values other than the two excluded ones are added together, and the values obtained are excluded from the values reduced by two from the number of people on the panel.

C.   The calculation is made using the following formula.

$Y = 10 X$

With this formula, Y expresses the odor index, and X is the value calculated in B. above.