www.czasopisma.pan.pl PAN POLSKA AKADEMIA NAUK www.journals.pan.pl

Archives of Environmental Protection
Vol. 44 no. 2 pp. 94–99

PL ISSN 2083-4772
DOI 10.24425/119696

DE G DE GRUYTER OPEN

Improvement of interlaboratory evaluation method of olfactometry in Japan

Takaya Higuchi[1]*, Kumiko Shigeoka[2]

[1]Yamaguchi University, Japan
[2]Japan Association on Odor Environment, Japan

*Corresponding author's e-mail: takaya@yamaguchi-u.ac.jp

Keywords: olfactometry, interlaboratory evaluation, odor index, qualified odor measurement laboratory, triangular odor bag method.

Abstract: Odor measurement is a crucial element of odor management and regulation. In Japan, nationwide interlaboratory evaluation of olfactometry using a variety of test odorants started in 2002. In the interlaboratory tests, odor index, a sensory index of odor determined by the triangular odor bag method, is measured. In 2016, interlaboratory evaluation method of olfactometry was improved. Isoamyl acetate with a concentration of 50 ppm was used as a test odor, and a total of 128 olfactometry laboratories participated in the test. In this method, test results of 11 'excellent qualified laboratories' designated by the Japan Association on Odor Environment (JAOE) were used to determine reference value and repeatability and reproducibility standard deviations of odor index. On the bases of these statistical values, measurement results of each laboratory were evaluated, including trueness and precision. Among 127 evaluated laboratories, 87 laboratories (68%) conformed to both trueness and precision criteria. In the case of 'qualified odor measurement laboratories' designated by the JAOE, 53 out of 68 laboratories (78%) conformed to both criteria. The qualified odor measurement laboratories registration system of the JAOE contributes to the improvement of the quality of olfactometry laboratories and the reliability of odor measurement in Japan.

Introduction

Odors discharged from various human activities may cause severe damage to residents. Since odor measurement is a crucial element of odor management and regulation, it is necessary to develop a reliable odor measurement method. Environmental odors consist of a wide variety of odorous compounds. This is the reason why comprehensive evaluation of odors using human sense of smell as well as instrumental analysis of individual chemicals is indispensable.

In Japan, the Offensive Odor Control Law, enacted in 1971, regulates odors discharged from business activities, and promotes preventive measures against odors to protect people's living environment and health. When the law was enacted, odor regulations based on the concentrations of odorous compounds were introduced. At present, 22 substances, such as ammonia and hydrogen sulfide, are designated as 'specific odorous substances,' and local authorities determine the regulation standard for each substance within a range established by the government. These regulations are, however, no longer sufficient to deal with a large number of odor complaints caused by unregulated substances or complex odors, since odor complaints have become more diversified. In order to improve this situation, the law was amended in 1995 and odor regulations based on 'odor index,' a sensory index of odor determined by the triangular odor bag method (TOBM), was introduced (Higuchi and Nishida 1995). Local authorities determine the odor index regulation standard within a range established by the government considering the land use, geographical conditions, odor characteristics and people's sensitivity to odors. After the amendment of the law, local authorities became entitled to adopt the odor index regulation instead of the regulations based on the concentrations of odorous compounds.

Problems related to the interpretation of measurement results, however, have been reported by the municipalities. For instance, odor index measured by a municipality differs from that measured by an odor emitting facility, and that makes the administration of legislative measure difficult. Under these circumstances, the significance of quality control system for olfactometry and standardization of measurement procedure has been recognized. On the bases of discussions about reference odor and interlaboratory comparison tests, a quality control manual for laboratory use was published in 2002 (Higuchi et al. 2002, Japan Ministry of the Environment 2002). Furthermore, nationwide interlaboratory evaluation of olfactometry using a variety of test odorants started in the same year. In the interlaboratory tests, odor index was measured three times at each laboratory in accordance with the official procedure of the TOBM, and statistical data, including reference value and repeatability and reproducibility standard deviations, were calculated and used for the evaluation.

Reference value and repeatability and reproducibility standard deviations were, however, not necessarily appropriate, since they were determined using odor index measurement results of regular seven laboratories that participated in the interlaboratory comparison tests in 2000 and 2001. In this study, a new interlaboratory evaluation method of olfactometry developed in 2016 is introduced and discussed. In this method, test results of 'excellent qualified laboratories' designated by the Japan Association on Odor Environment (JAOE) were used to determine reference value and repeatability and reproducibility standard deviations.

Triangular odor bag method

In several countries from Europe (EN 13725 2003) to North America (ASTM E679-04 2011), including Australia and New Zealand (AS/NZS 4323.3 2001), there are standardized methods used for the dynamic olfactometry analysis. These are dynamic air dilution methods for the determination of odor concentration. On the other hand, in several Asian countries, including Japan and China, the TOBM is used for odor evaluations (Brancher et al. 2017). TOBM is a static air dilution method by which odor concentration or odor index is determined. Odor concentration is the dilution ratio when odorous air is diluted by odor-free air in an odor bag until the odor becomes unperceivable. Odor index is the logarithm of odor concentration, multiplied by ten. TOBM was first developed by the Tokyo metropolitan government in 1972 (Iwasaki et al. 1972, Iwasaki et al. 1978) and notified by the Japan Environment Agency in 1995 (Japan Environment Agency 1995).

In the TOBM, the panel consists of six or more members who have passed the screening test using five odorous compounds, i.e., β-phenylethyl alcohol, methyl cyclopentenolone, isovaleric acid, γ-undecalactone and skatole (3-methyl indole). Measurements for samples taken at odor emission sources are made in three-fold dilution descending series. Three odor bags marked with the numbers 1–3 per panel member are prepared. These odor bags are filled with odor-free air passed through the activated carbon column, and plugged up with silicone rubber stoppers. Odorous air is injected into one of three odor bags using a syringe until a given dilution ratio is obtained. Each member of the panel removes the stopper and sniffs three odor bags one after another by bringing the bag close to one's nose. After sniffing three odor bags, each panel member chooses one bag that is likely to contain odorous air, and writes down the number of the bag chosen in a form. The responses given by the panel members are collected and compiled. The panel member who gave a correct response participates in the next session in which the sample is diluted three times further. The panel member who gave an incorrect response ends the test series. The test is continued until all the panel members give incorrect responses, in other words, it becomes impossible for all the panel members to identify the bag with odorous air. Then, odor concentration or odor index is calculated (Higuchi 2013).

The difference of measurement results between the dynamic olfactometry and the TOBM were examined (Ueno and Amano 2007, Ueno et al. 2009). In the case of the measurements with the same panel members, the data obtained by the TOBM corresponded to those by the dynamic olfactometry (Yes/No mode). Naddeo et al. (2016) investigated the relationship between odor index at a municipal wastewater treatment plant determined by the TOBM and the dynamic olfactometry (Yes/No mode). The results showed a strong linear correlation between odor index determined by these two methods, especially in higher concentration range.

Conventional interlaboratory evaluation method

In 2000 and 2001, interlaboratory comparisons of olfactometry were carried out to collect basic data for the establishment of quality control system and the determination of quality criteria. A total of seven olfactometry laboratories in Japan participated in the tests. These laboratories were considered to have sufficient technical skills and measurement experiences on the recommendation of the Investigative Commission. On the bases of these results, a quality control manual for laboratory use was published in 2002 (Higuchi et al. 2002, Japan Ministry of the Environment 2002).

Nationwide interlaboratory evaluation tests of olfactometry have been conducted since 2002 using a variety of odorants (Higuchi and Masuda 2004, Higuchi et al. 2007, Higuchi 2009). In recent years, more than 100 olfactometry laboratories have participated in the tests in which odor index was measured three times consecutively in a day at each laboratory except 2002. Then, statistical data of each test odor, including reference value and repeatability and reproducibility standard deviations, were calculated using measurement results of the abovementioned seven olfactometry laboratories in each year in accordance with JIS Z 8402-2 (1999). On the bases of these data, measurement results of each laboratory were evaluated, including trueness and precision, in accordance with JIS Z 8402-6 (1999). Table 1 summarizes the results of nationwide interlaboratory evaluation tests from 2002 to 2015.

Improvement of interlaboratory evaluation method

Reference value and repeatability and reproducibility standard deviations shown in Table 1 were not necessarily appropriate for interlaboratory evaluation, since they were determined on the bases of odor index measurement results of regular seven laboratories that participated in the interlaboratory comparison tests in 2000 and 2001. Odor index measurement at these seven laboratories was not intended beforehand to be used for the calculation of reference value and repeatability and reproducibility standard deviations. Furthermore, invariable technical skills at these seven laboratories were not guaranteed. Under these circumstances, new interlaboratory evaluation method of olfactometry was developed in 2016.

Method

In the new method, test results of 'qualified odor measurement laboratories' designated by the JAOE were used. 'Qualified odor measurement laboratories registration system' of the JAOE aims to improve reliability and promote dissemination of odor measurement methods in Japan by approving laboratories that can conduct appropriate odor measurement with sufficient accuracy. A qualified odor measurement laboratory is examined by the Judging Committee in the JAOE from the perspective

Table 1. Results of nationwide interlaboratory evaluation tests in Japan (2002–2015)

Year	Test odor component	a) Number of laboratory b) Reference value c) Repeatability standard deviation			d) Reproducibility standard deviation e) Mean value of all laboratories f) Standard deviation among laboratories		
		a)	b)	c)	d)	e)	f)
2002	Ethyl acetate (2000 ppm)	137	35.5*	1.7*	2.2*	33.5	3.27
2003	Ethyl acetate (2000 ppm) *m*-Xylene (94 ppm)	120	35.7	0.87	1.86	34.5	2.57
2004	Dimethyl sulfide (3 ppm) Dimethyl disulfide (3 ppm)	93	31.9	1.05	2.45	33.6	3.16
2005	Dimethyl sulfide (3 ppm)	93	32.4	1.23	3.34	31.7	3.38
2006	Source odor at sludge thickener of sewage treatment plant	86	37.0	0.94	3.29	36.4	3.61
2007	Quasi photogravure odor Toluene (100 ppm) Isopropyl alcohol (55 ppm) Ethyl acetate (60 ppm) Methyl ethyl ketone (65 ppm)	116	25.4	1.01	1.53	24.4	2.86
2008	Quasi sewage treatment plant odor Hydrogen sulfide (5 ppm) Methyl mercaptan (0.71 ppm) Dimethyl sulfide (0.27 ppm)	120	44.5	1.22	2.96	43.3	3.56
2009	1-Butanol (40 ppm)	118	32.6	0.82	2.53	32.6	2.77
2010	Ethyl acetate (50 ppm)	122	18.0**	1.3**	2.4**	18.1	2.51
2011	Dimethyl sulfide (3 ppm) Dimethyl disulfide (3 ppm)	115	37.4	0.82	2.34	35.8	2.65
2012	*n*-Butyraldehyde (1 ppm)	121	24.5	0.81	1.29	26.6	3.44
2013	Methyl isobutyl ketone (300 ppm)	126	39.0	0.67	3.43	37.5	3.02
2014	Isobutyl alcohol (35 ppm)	119	27.1	0.74	8.82	27.8	5.21
2015	Methyl ethyl ketone (1500 ppm)	125	38.2	0.66	2.36	36.6	3.04

* Determined on the bases of interlaboratory comparison test in 2000.
** Determined on the bases of interlaboratory comparison test in 2001.

of organization, technical skills, facilities and equipment, and documentation. For instance, a qualified odor measurement laboratory should have two or more olfactometry operators qualified by Japan Ministry of the Environment, an adequate testing room and sufficient equipment, and satisfactory measurement accuracy equivalent to the quality control criteria described in the quality control manual. This registration is not mandatory for official odor measurement. A total of 72 laboratories are designated as qualified odor measurement laboratories as of September 2016.

In order to select olfactometry laboratories that were considered to have sufficient technical skills and measurement experiences at that time, 'excellent qualified laboratories' were focused. A qualified odor measurement laboratory, which participated in the interlaboratory evaluation test of olfactometry four times or more within the period of validity (five years) and showed adequate results, is designated as an excellent qualified laboratory. An excellent qualified laboratory is examined by the Judging Committee in the JAOE from the perspective of measurement accuracy in the past five years. For instance, an excellent qualified laboratory should conform to trueness and precision criteria in most cases. In the interlaboratory evaluation test in 2016, qualified odor measurement laboratories, which have renewed their registration as excellent qualified laboratories over two consecutive periods of validity as of December 2016, were chosen. Then, laboratories that carried out three consecutive measurements of odor index in a day in the interlaboratory evaluation test in 2016, led by an operator who has 100 or more olfactometry experiences per year, were selected. On the bases of measurement results of these laboratories, reference value and repeatability and reproducibility standard deviations were determined, and interlaboratory evaluation of olfactometry was conducted. Fig. 1 represents a schematic of interlaboratory evaluation method of olfactometry in 2016.

In 2016, a total of 128 olfactometry laboratories participated in the interlaboratory evaluation test. A small--sized gas cylinder filled with isoamyl acetate at a concentration of 50 ppm was delivered to each laboratory. Odor index was measured three times consecutively in a day in accordance with the official procedure of the TOBM.

Results and discussion

There were 14 laboratories that had renewed their registration as excellent qualified laboratories over two consecutive periods of validity as of December 2016. Among them, 12 laboratories carried out three consecutive measurements of odor index in

a day in the interlaboratory evaluation test in 2016, led by an operator who has 100 or more olfactometry experiences per year. Eventually, one laboratory was excluded following the result of Cochran's test on outliers, and 11 laboratories remained for the determination of reference value and repeatability and reproducibility standard deviations. Odor index and statistical data of 11 laboratories are shown in Table 2. Mean value and standard deviation of odor index were 38.7 and 2.33, respectively. On the bases of data in Table 2, reference value and repeatability and reproducibility standard deviations of odor index were calculated to be 38.7, 0.79 and 2.42, respectively, in accordance with JIS Z 8402-2 (1999).

The distribution of mean odor index of 128 laboratories is depicted in Fig. 2. The minimum and maximum values are 30 and 47, respectively. Mean value is 38.5, which is very close to the reference value (38.7). On the other hand, standard deviation is 3.83, which is much larger than reproducibility standard deviation (2.42).

Among 128 laboratories, 127 laboratories conducted duplicate or triplicate odor index measurement. On the bases of the abovementioned reference value and repeatability and reproducibility standard deviations, measurement results of 127 laboratories were evaluated, including trueness and precision, in accordance with JIS Z 8402-6 (1999). As a result, the maximum permissible level of standard deviation and the permissible range of mean value in triplicate odor index measurement were calculated to be 1.4 and 38.7 ± 4.6, respectively. Evaluation results of trueness and precision of 127 laboratories are summarized in Table 3. Among 127 laboratories, 98 and 103 laboratories (77% and 81%) conformed to the criterion of trueness and precision, respectively, and 87 laboratories (68%) conformed to both. Table 4 shows evaluation results of trueness and precision of 68 qualified odor measurement laboratories that conducted duplicate or triplicate odor index measurement. In the case of qualified odor measurement laboratories, 53 laboratories (78%) conformed to both criteria, which implies that the qualified odor measurement laboratories registration system of the JAOE contributes to the improvement of the quality of olfactometry laboratories and the reliability of odor measurement in Japan.

New interlaboratory evaluation method of olfactometry introduced in this study will be applicable to other countries using not only the TOBM but also the dynamic olfactometry. The new method is not restricted by the odor measurement

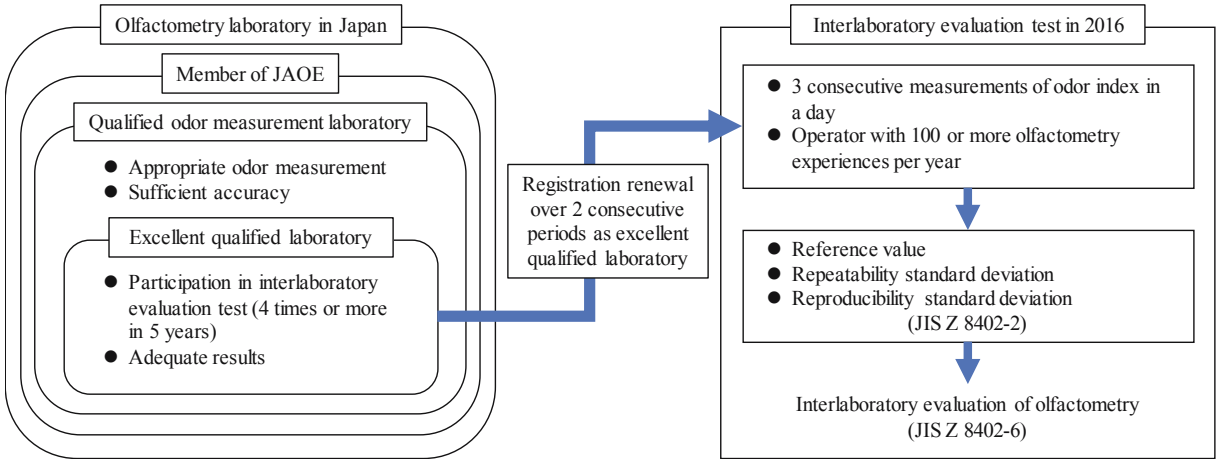

Fig. 1. Schematic of interlaboratory evaluation method of olfactometry in 2016

Table 2. Odor index and statistical data of 11 laboratories. SD represents standard deviation

Laboratory	Odor index			Mean	SD
A	41	40	40	40.3	0.72
B	40	40	40	39.9	0.00
C	40	40	41	40.3	0.72
D	34	36	35	34.9	1.25
E	42	44	45	43.7	1.25
F	37	37	37	37.4	0.00
G	37	37	39	37.8	0.72
H	37	36	37	37.0	0.72
I	40	39	39	39.1	0.72
J	37	36	37	37.0	0.72
K	39	39	37	38.2	0.72
			Mean	38.7	0.69
			SD	2.33	

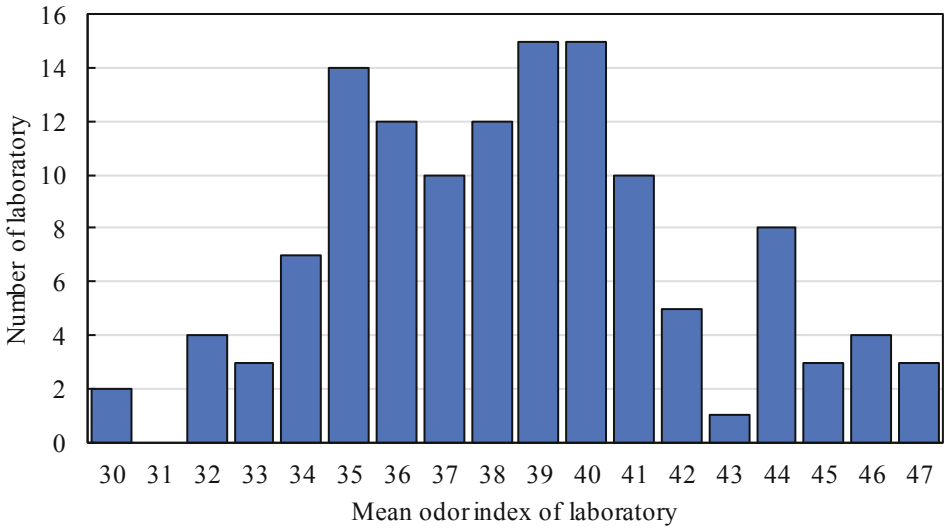

Fig. 2. Distribution of mean odor index of 128 laboratories that participated in the interlaboratory evaluation test in 2016

Table 3. Evaluation results of trueness and precision of 127 laboratories that conducted duplicate or triplicate odor index measurement

Upper: Number of laboratory		Trueness		Total
Lower: Percentage		Conformable	Unconformable	
Precision	Conformable	87 *68%*	16 *13%*	103 *81%*
	Unconformable	11 *9%*	13 *10%*	24 *19%*
Total		98 *77%*	29 *23%*	127 *100%*

Table 4. Evaluation results of trueness and precision of 68 qualified odor measurement laboratories that conducted duplicate or triplicate odor index measurement

Upper: Number of laboratory		Trueness		Total
Lower: Percentage		Conformable	Unconformable	
Precision	Conformable	53 *78%*	7 *10%*	60 *88%*
	Unconformable	4 *6%*	4 *6%*	8 *12%*
Total		57 *84%*	11 *16%*	68 *100%*

method, and the latest activities of laboratories concerning the quality control are reflected on the evaluation results. A detailed evaluation method, however, needs to be discussed considering the specific conditions to the country including the measurement procedures, the laboratory accreditation system and the interlaboratory evaluation test program.

Conclusions

Interlaboratory evaluation method of olfactometry was improved in 2016. Isoamyl acetate with a concentration of 50 ppm was used as a test odor, and a total of 128 olfactometry laboratories participated in the test. In this method, test results of 11 excellent qualified laboratories designated by the JAOE were used to determine reference value and repeatability and reproducibility standard deviations of odor index. On the bases of these statistical values, measurement results of each laboratory were evaluated, including trueness and precision. Among 127 evaluated laboratories that conducted duplicate or triplicate odor index measurement, 87 laboratories (68%) conformed to both trueness and precision criteria. In the case of qualified odor measurement laboratories, 53 out of 68 laboratories (78%) conformed to both criteria.

Determination of reference value and repeatability and reproducibility standard deviations is one of key factors to evaluate the performance of olfactometry laboratories. New

interlaboratory evaluation method of olfactometry will be applicable to other countries using not only the TOBM but also the dynamic olfactometry taking into consideration the specific conditions to the country. A continuous effort to ensure reliable and stable interlaboratory evaluation of olfactometry will be necessary for the establishment of appropriate odor measurement and evaluation system.

References

AS/NZS 4323.3 (2001). Stationary source emissions – Part 3: Determination of odour concentration by dynamic olfactometry, Standards Australia, Sydney, Australia/Standards New Zealand, Wellington, New Zealand.

ASTM E679-04 (2011). Standard practice for determination of odor and taste thresholds by a forced-choice ascending concentration series method of limits, ASTM International, West Conshohocken, USA.

Brancher, M., Griffiths, K. D., Franco, D. & De Melo Lisboa, H. (2017). A review of odour impact criteria in selected countries around the world, *Chemosphere*, 168, pp. 1531–1570.

EN 13725 (2003). Air quality – Determination of odour concentration by dynamic olfactometry, European Committee for Standardization, Brussels, Belgium.

Higuchi, T. (2009). Estimation of uncertainty in olfactometry, *Water Science and Technology*, 59, 7, pp. 1409–1413.

Higuchi, T. (2013). Determination of odour concentration by the triangular odour bag method, in: *Odour Impact Assessment Handbook*, Belgiorno, V., Naddeo, V. & Zarra, T. (Eds.). John Wiley & Sons, West Sussex, UK, pp. 43–50.

Higuchi, T. & Masuda, J. (2004). Interlaboratory comparison of olfactometry in Japan, *Water Science and Technology*, 50, 4, pp. 147–152.

Higuchi, T., Masuda, J. & Hayano, A. (2002). Establishment of quality control framework for olfactometry in Japan, *Proceedings of the WEF's International Specialty Conference. Odors and Toxic Air Emissions 2002*. (CD-ROM)

Higuchi, T. & Nishida, K. (1995). Analysis of data measured by the triangular odor bag method, in: *Odors: Indoor and Environmental Air. Proceedings of the A&WMA's International Specialty Conference*, pp. 181–192.

Higuchi, T., Ukita, M., Sekine, M. & Imai, T. (2007). A case study and recent improvements in odor management in Japan, *Water Practice*, 1, 2, pp. 1–7.

Iwasaki, Y., Ishiguro, T., Koyama, I., Fukushima, H., Kobayashi, A. & Ohira, T. (1972). On the new method of determination of odor unit, *Proceedings of the 13th Annual Meeting of the Japan Society of Air Pollution*, p. 168. (in Japanese)

Iwasaki, Y., Fukushima, H., Nakaura, H., Yajima, T. & Ishiguro, T. (1978). A new method for measuring odors by triangle odor bag method (I) — Measurement at the source, *Journal of Japan Society of Air Pollution*, 13, 6, pp. 246–251. (in Japanese)

Japan Environment Agency (1995). Determination of odor index and odor emission rate, Notification Number 63, Japan Environment Agency, Tokyo, Japan. (in Japanese)

Japan Ministry of the Environment (2002). *Olfactory Measurement Method Quality Control Manual*, Japan Ministry of the Environment, Tokyo, Japan. (in Japanese)

JIS Z 8402-2 (1999). Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method, Japanese Industrial Standards Committee, Tokyo, Japan. (Japanese version of ISO 5725-2: 1994)

JIS Z 8402-6 (1999). Accuracy (trueness and precision) of measurement methods and results – Part 6: Use in practice of accuracy values, Japanese Industrial Standards Committee, Tokyo, Japan. (Japanese version of ISO 5725-6: 1994)

Naddeo, V., Zarra, T., Kubo, A., Uchida, N., Higuchi, T. & Belgiorno, V. (2016). Odour measurement in wastewater treatment plant using both European and Japanese standardized methods: Correlation and comparison study, *Global NEST Journal*, 18, 4, pp. 728–733.

Ueno, H. & Amano, S. (2007). A comparative study between the Japanese and the European olfactometry standards (IV), *Bulletin of Tokyo Metropolitan Research Institute for Environmental Protection 2007*, pp. 45–52. (in Japanese)

Ueno, H., Amano, S., Merecka, B. & Kośmider, J. (2009). Difference in the odor concentrations measured by the triangle odor bag method and dynamic olfactometry, *Water Science and Technology*, 59, 7, pp. 1339–1342.