Confidence in Evaluation of High Purity of Samples

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1) Introduction

Traditionally, pure water and chemicals consumed by the electronics industry have been controlled for a particle contamination level of 0.2μm. However, the era now calls for a tightened level of 0.1μm, or an even higher 0.05μm. Further, advancement in filtration technology has reduced solid materials contained in liquids and a trend for purity is toward a heightened level. Particle counters' sensitivity to particle diameters have improved in response to users' demands. Too much effort, however, has been concentrated on bringing the detectable particle diameter down at the expense of a detectable area in a flow of a sample (an area of a sample where laser beam irradiation is focused) becoming smaller. Consequently, detection efficiency is getting smaller and so is the number of detectable particles.

What is the reason for the large variation in data taken from the same samples with particle counters of various makes? What is meant by 'zero particles' in data? Our study proceeded with emphasis placed on these points based on field measurements and specifications of particle counters from various manufacturers. The result of an evaluation of a sample when particle counters with an extremely poor detection efficiency are used is reported here. Also reported here are points needing particular attention to enable appropriate evaluation of samples.

2) Findings from experiment and measurements

5 particle counters were used for the experiment. Of them, 2 are RION's products, and the rest are other manufacturers'. Figure 1 shows the piping system and table 1 shows specifications of the particle counters used. Measurements were taken 4 times, each lasting for 10 minutes, using DI- water and tap water diluted with DI-water. Tables 2 through 5 show measurements of DI-water. Data shown are as counted. When calculating concentration, account must be taken for detection efficiency. As seen in tables 2 to 5, the lower detection efficiency, the smaller the count. In particular, when particle diameters were 0.2μm or larger, 21 was the average with the KL-20 counter while zero was shown for the rest of counters. Zero was counted by counters B and C regardless of particle diameters. Evaluation of samples required fact finding efforts to learn if no particles really existed or if those counters were accidentally incapable of detecting any particles because their detection efficiency was low.

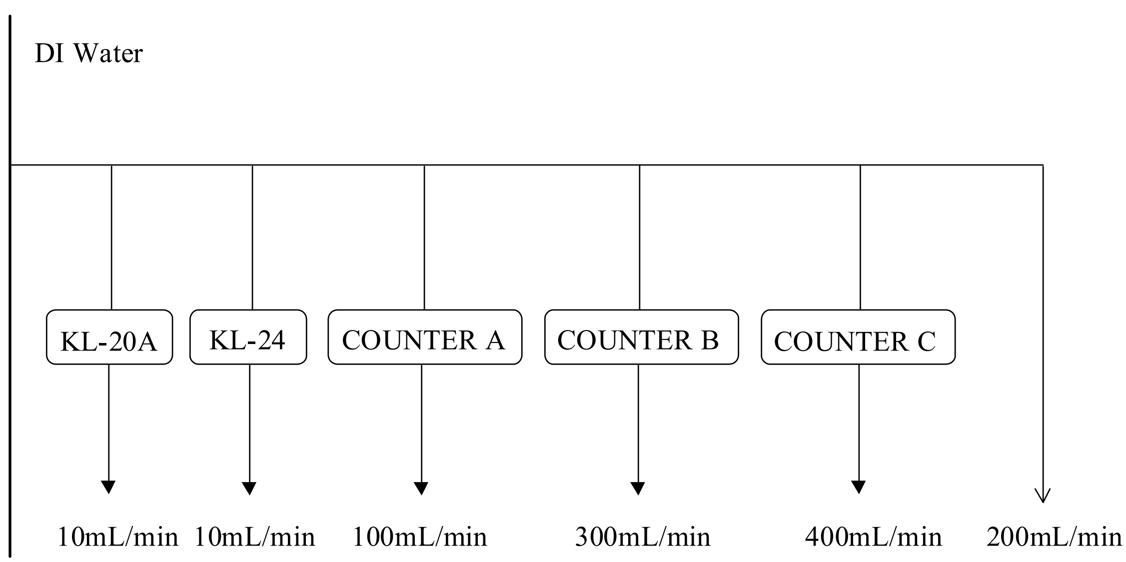

Fig. 1. Sample distribution system for comparison purposes.

Table 1. Specifications of particle counters used for experiments

MODEL	KL-20A	KL-24	COUNTER A	COUNTER B	COUNTER C
Sensitivity (mm)	0.2	0.1	0.05	0.1	0.08
Detection Efficiency (%)	100	17	0.25	0.56	0.00417
Flow Rate (mL/min)	10	10	100	300	400
Sample Rate (mL/min)	10	1.7	0.25	1.68	0.017
Measuring Time for 1mL (s)	6	35.3	240	35.7	3600

Table 2. Measurements taken from KL-20

	0.2µm	0.3µm	0.5µm	1µm	2µm
1	18	11	1	0	0
2	24	11	0	0	0
3	27	10	0	0	0
4	16	8	0	0	0
Total	85	40	1	0	0
Average	21.2	10	0.25	0	0

Table 3. Measurements taken from KL-24

	0.1µm	0.15µm	0.2µm	0.3µm	0.5µm
1	3	0	0	0	0
2	7	2	0	0	0
3	5	0	0	0	0
4	7	1	0	0	0
Total	22	3	0	0	0
Average	5.5	0.75	0	0	0

Table 4. Measurements taken from COUNTER A

	0.05µm	0.1µm	0.15µm	0.2µm
1	2	0	0	0
2	1	0	0	0
3	1	1	0	0
4	1	0	0	0
Total	5	1	0	0
Average	1.25	0.25	0	0

Table 5. Measurements taken from COUNTER B, C.

	0.08µm	0.1µm	0.15µm	0.2µm
COUNTER B	-	0	0	0
COUNTER C	0	0	0	0

Figure 2 is a graph showing the particle concentration calculated, with detection efficiency taken into consideration, from average values of measurements taken by each counter. It appears in this graph that measurements taken by each of the 5 counters are all different despite the fact that the sample used was identical for all. Figure 3 covers the case where a highly concentrated sample (tap water + pure water) was used. Good agreement among all the 5 particle counters was noticeable with this sample of high concentration.

3) Statistical construction

We have learned from figures 2 to 3 that measurement of identical samples using 5 particle counters can be totally different depending upon the concentration. Now, we will discuss the cause and its construction.

We assume that the Poisson's distribution applies to the probability of appearance of particles in samples of low concentration (of about 0 to 10 particles) such as DI-water. $M \times S = \lambda$ (particles) can be anticipated to be contained in a sample of S(ml) taken from a material having a real average particle concentration of M (particles/ml). However, it is natural to see the observed value X disperse. The Poisson's distribution is to

$$P(x;\lambda) = e^{-\lambda}\left(\frac{\lambda^{x}}{x!}\right) \quad (1)$$

indicate the extent of this dispersion. Appearance probability of the Poisson's distribution can be obtained from equation (1). Probability P where observed value X may be obtained from the population λ is available from equation (1).

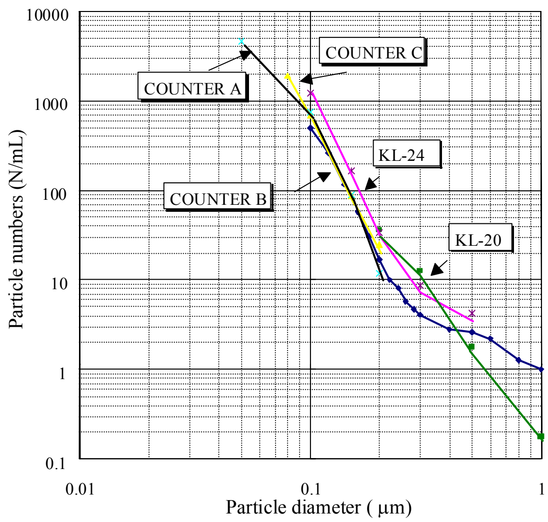

Fig. 2. Measurement of particles in DI water.

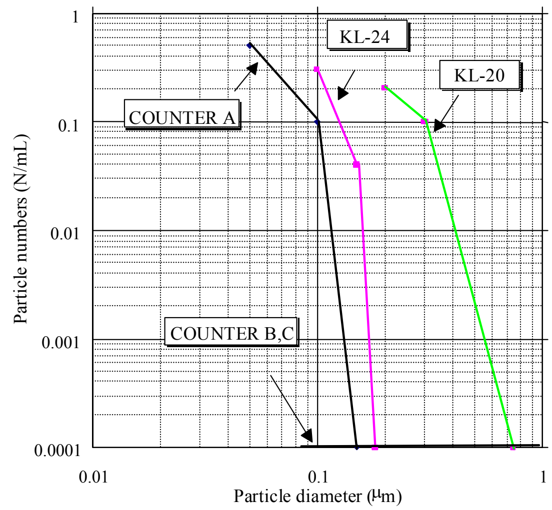

Fig. 3. Measurement of particles in city water.

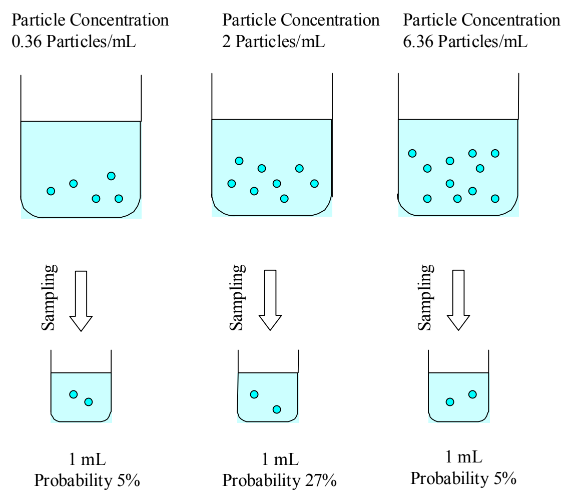

Fig. 4. Concentration of samples and appearance probability.

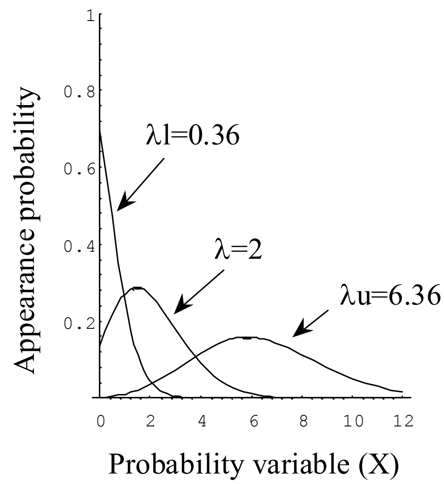

Fig. 5 Upper and lower limits on Poisson distribution.

When observed value X is obtained, λ 1 that satisfies equation (2) is the lower confidence limit of populationλ . This is the sum of probabilities that is larger than the observed value X.

$$\sum_{X=x}^{\infty} P(x;\lambda l) = \frac{\varepsilon}{2} \qquad (2)$$

λ u that satisfies equation (3) is referred to as the upper confidence limit and is the sum of probabilities that is smaller than the observed value X.

$$\sum_{X=0}^{x} p(x;\lambda u) = \frac{\varepsilon}{2} \qquad (3)$$

Figure 4 is a model drawing to be used to figure out the real concentration of a sample when a observed value of 2 (particles/ml) is obtained. Despite the different concentrations of the 3 samples, individual probabilities may produce an observed value of 2. An example is that the probability of the existence of 2 or more particles in a sampled volume of 1ml of liquid of 0.36 concentration (0.36 particles/ml) is 5%. Similarly, the probability of containing a maximum of 2 particles in 1ml sampled from liquid of 6.36 (particles/ml) concentration is 5%. It stands to reason that probability is highest at 27% for the case where 2 particles are contained in 1ml sampled from liquid containing a concentration of 2 (particles/ml). Under the situation where a certain observed value is anticipated to appear at 5% probability as with the cases above, the low concentration end and high concentration end are referred to as the 95% lower confidence limit and 95% upper concentration limit, respectively. Accordingly, an observed value of 2 (particles/ml) indicates that the concentration of a sample falls between 0.36 (particles/ml) and 6.36 (particles/ml) and that confidence coefficient (one tailed test) is 95%. What is meant by this is that if confidence of 95% is required, the real value lies between 0.36 and 6.36 (particles/ml). This is referred to as a confidence interval.

Table 6. Confidence interval with a 95% confidence level.

Observed value	Interval Estimation	
0	0	3
1	0.05	4.47
2	0.36	6.36
3	0.82	7.75
4	1.37	9.15
5	1.97	10.51
6	2.61	11.97
7	3.28	13.15
8	3.98	14.44
9	4.7	15.7
10	5.43	16.96

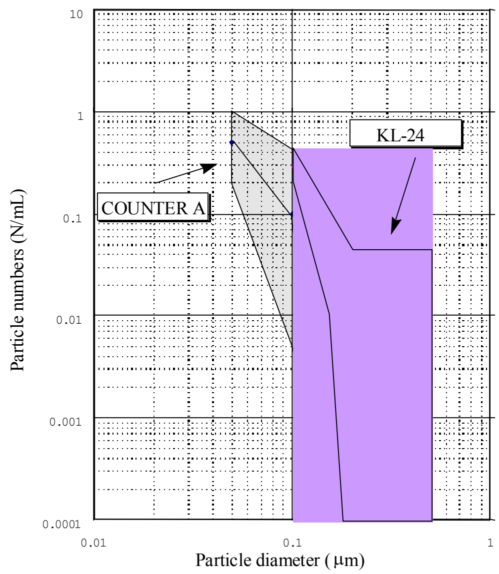

Fig. 6. Comparison of confidence intervals of counter A and KL-24 when DI-water is measure.

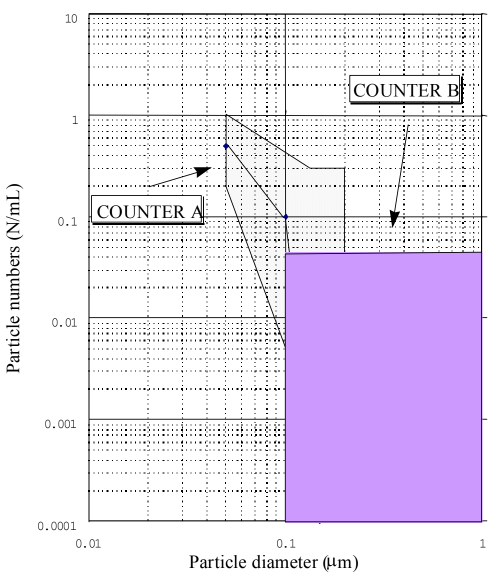

Fig. 7. Comparison of confidence intervals of counter A and counter B when DI-water is measure.

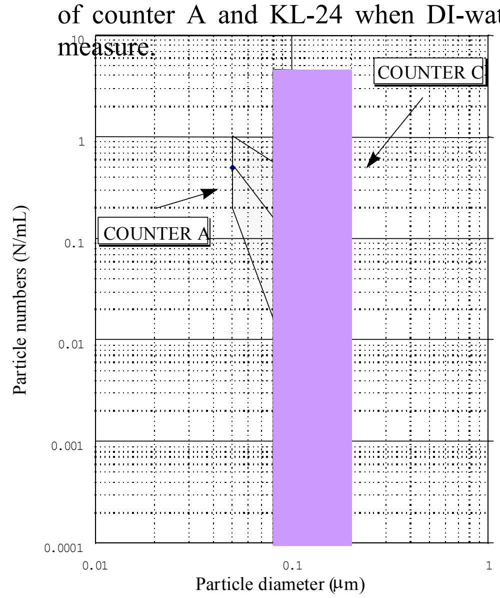

Fig.8. Comparison of confidence intervals of counter A and counter C when DI-water is measure

What will the confidence interval be when an observed value is 0 (particles/ml)? The lower confidence limit in this case is naturally 0. The upper confidence limit is 3 as will be obtained from equation (3). This means that an observation of 0 must be not interpreted as the particle concentration of the sample being 0 (particles/ml). Figure 5 is a graph of appearance probability which is observed from a population. Table 6 indicates observed values obtained and estimated interval for 95% of one tailed test. Extending this idea, we will attempt to determine the upper and lower confidence limits of measurement of DI-water.

Figures 6 to 8 compare confidence intervals of observed values obtained using respective particle counters. Confidence intervals are hatched there. Data that originally appeared to be all individual and different is now transformed into an easily understandable form by introducing the concept of the confidence interval.

Refer to figure 8 for a good example. A measured value of 0, if it is obtained using a particle counter of extremely low detection efficiency, does not necessarily mean the real particle concentration of the sample is zero. Instead, it is likely that quite a few particles are contained. This appears to be contradictory. We must bear in mind that the values from COUNTER C were 0 over the total particle diameter range. Samples, however, in a statistical sense, must be evaluated in a range of higher concentration than COUNTER A that allowed a value to be observed.

Proper evaluation of measurements taken in low concentration ranges is impossible with observed values and average only. Consideration of the degree of accuracy of observed value is always necessary. More

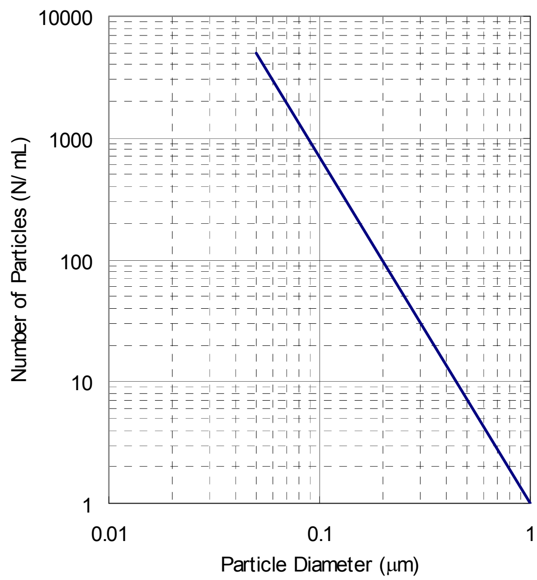

Fig. 9. Particle diameter and concentration.

Table 7. Detection efficiency and counted value.

	0.05μm	0.1μm	0.2μm	0.5μm
100%	6400	800	30	5
10%	640	80	3	0.5
1%	64	8	0.3	0.05
0.10%	6.4	0.8	0.03	0.005

accurate evaluation requires the range of a confidence interval to be narrower (higher confidence). To obtain data with a narrow confidence interval, capability of detecting many of materials introduced in particle counters is requisite. In other words, detection efficiency must be high. Accurate evaluation of samples is difficult even with the smallest detectable particle diameters, if detection efficiency is low. Figure 9 shows an assumed distribution of particle concentration in a sample with another assumption placed that the particle concentration is in inverse proportion to the 3rd power of a particle diameter. Table 7 is count values of a sample that would have been measured with particle counters of various detection efficiencies.

As learned from the table, a particle counter capable of measuring 0.05μm with detection efficiency of 1% will count less than a particle counter with detection efficiency of 100% for particle sensitivity to 0.2μm can count. The counted value will naturally be 1/100 with 0.2μm particles, resulting in a large reduction in confidence in measured values. It is regrettable to state that particle counters procured from the market and used at the time of this experiment exhibit detection efficiency of only about 0.25% for a particle diameter of 0.05μm, as shown in table 1. The count for 0.2μm in this instance is 0.25 particles, which is highly possible to be counted as 0. The implication of this is that chances are high that 100 particles of 0.2μm particles contained in a sample may be counted as 0. Thus, the use of a particle counter of this type absolutely requires an utmost level of caution.

The above discussion has proved that it is not necessarily correct to believe that the smaller the diameter a particle counter used for purity evaluation can measure the higher the purity that can be measured. Another approach by using a particle counter with higher sensitivity to particle diameters and low detection efficiency (a particle counter with low counting sensitivity) poses an increased risk of loss of confidence in diameters such as 0.2μm or 0.3μm that are the diameters of real interest for control purposes. Prudence, including sufficient consideration of particle diameters and concentration, is a matter of prime importance required at the users side when choosing a particle counter model.

4) Conclusion

Adequacy for introduction of the Poisson's distribution is a future subject to be verified experimentally. At this moment, the discussions we have made can be summarized as follows:

a) The ratio of samples to be picked to the entire amount to be evaluated. Or, whether or not statistical consideration of frequency, time and methods to be employed is given to the amount of samples.

b) The fact, as a problem solely with particle counters, that some particle counters are designed with a focus placed only on sensitivity to particle diameters, without considering an effective sampling amount. This requires considerable corrections in the conversion factor and moving average and shows the capability limit (confidence in measurement accuracy in low concentration) of measuring instruments.

c) Users tend to place importance only on measurable particle diameters, with least knowledge about the issues mentioned above. A fact exists that neither sufficient study has been made, nor standards established for study of the meaning and interpretation of data collected from particle counters, and evaluation methods of objects to be measured. This leads to misunderstanding that a 0 counting of the smaller particles means the purity of a sample is higher.

With regard to particle contamination, a level of high purity should be required around a work and an acceptable level of particle contamination of pure water and chemicals was to have been decided. If so, the meaning of the data must have been considered seriously. However, the current situation is such that there is no consensus in the industry for this field concerning standards and point of view. Consequently, much confusion has resulted.

Essentially, a consensus (of standards for evaluation of purity) should come before identification of specifications. We, the authors, wish to have a consensus established. It is our expectation to have opinions and ideas about evaluation of data, standards for evaluation of purity of liquids and specification requirements for particle counters from an extended range of people concerned.

5) Acknowledgment

We would like to express our heartfelt gratitude to device manufacturers' personnel who offered us support to the fullest extent during the experiments conducted to compile this report.