ANNEX (5)

OUTLINE OF ACCURACY CONTROL SYSTEM (QA/QC) FOR ENVIRONMENT MONITORING DATA IN JAPAN

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GENERAL REQUIREMENT FOR ACCURACY CONTROL

- (1) Are monitoring points adequate?
- (2) Is the analysis method well suited?
- (3) Is the targeted accuracy correct?
- (4) Is the accuracy control method kept well?
- (5) Are sampling methods and their number of times appropriate?

SEQUENCE OF WORK OPERATION FOR ACCURACY CONTROL

- (1) To know the kind and magnitude of error in the analysis
- (2) To assess whether the error is admissible or not
- (3) To search for the cause in case of inadmissible
- (4) To improve by removing the cause from the analytical procedures
- (5) To investigate remedial measures by introducing more accurate technology
- (6) To routinely prepare the documents containing the procedures for maintaining reliability

What the Accuracy Control Should Be

- In long-range monitoring, the possibility of fluctuation of accuracy and precision becomes higher with the change of various factors such as renewal of analytical instruments and replacement of laboratory staff.
- To adequately maintain accuracy control is an essential issue in determining the feasibility of monitoring, because scientific evaluation of the monitoring results is conducted through the analytical data containing the error.

Can humans avoid error?

- Quality Analysis is done by humans. who make every time mistake. Humans are always involved the risk of making mistakes.
- There are two (2) kinds of views whether humans are born inherently good or evil.
- Humans have five (5) senses, especially use visual sense during the analytical procedure.
- There are many mistakable numbers in handwriting filed notes.
- Laboratory staff have to tackle with instruments difficult to operate.

How to Minimize the Occurrences of Errors

- To know the range of analytical results. (Monitoring point-wise Max and Min and concentrations pollutants in natural resources like normal river water, normal soil etc.)
- To always keep the suspicious mind for the analysis results
- To pay attention to the different outcome. (Color of samples and chemical reaction)
- To correctly set-up the analytical instrument.
- To check the slope of calibration curve of each parameter.
- To confirm the existence of transcription error of field note.
- To check the condition of each analytical instrument.

Average Value and Standard Deviation

Precision measures the variation among measurements and may be expressed in different terms.

Standard Deviation(s):

$$s = \sqrt{E(x - \overline{X})^2 / n - 1}$$

E = sum $\quad$ $\overline{x}$ = mean

x = measurements $\quad$ n = number of measurements

Relative Standard Deviation (RSD):

- Calculate the mean $(\overline{x})$.
- Calculate the standard deviation (s).
- Calculate the coefficient of variant (CV).
  CV = standard deviation(s)/mean $(\overline{x})$.
- Calculate the Relative Standard Deviation (RSD).

$$RSD = CV \times 100$$

Relative Percent Difference (RPD): RPD is the difference between the duplicate values divided by the average of the duplicate values and multiplied by 100.

$$RPD = [(A - B)/(A + B/2)] \times 100$$

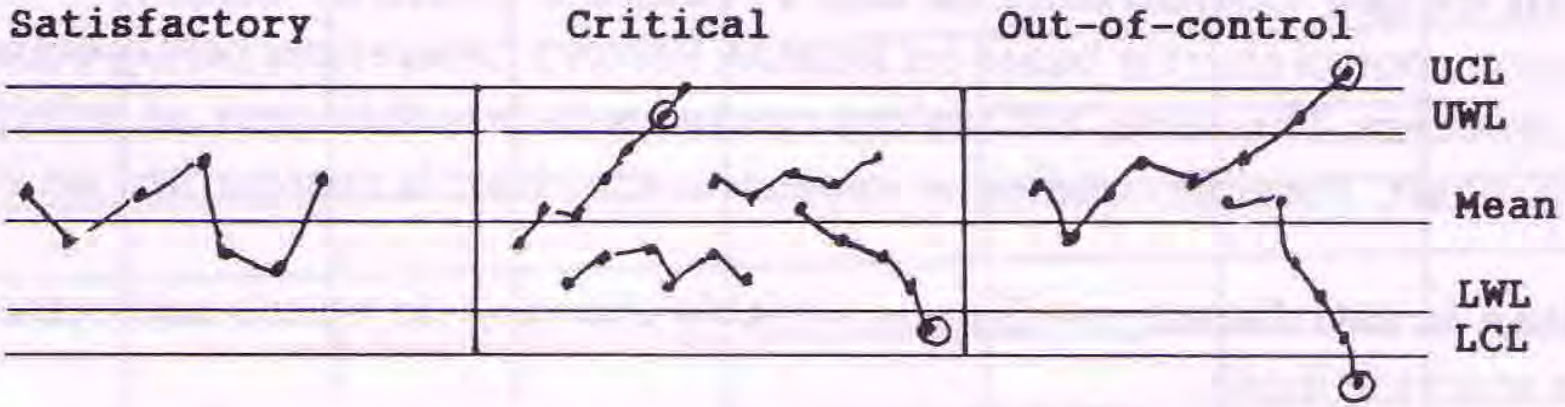
or shortly

$$RPD = [(A - B)/(A + B)] \times 200$$

Samples for Accuracy Control Management

- In environmental analysis, sometimes, accuracy is managed by coefficient of variation (CV%) values obtained by multiple analyses of samples.
- However, the results are used only for the index of accuracy regarding the daily analysis values; hence, the accuracy of continuous fluctuation of analysis results and the mean value necessary for the long-term monitoring are not assured. Further, even if there are cases where mean values and standard deviations obtained by analyzing the standard solution are managed, it is impossible to evaluate the error which comes from the difference of matrix constitution between the standard solution and the samples.
- Accordingly, it is ideally desirable to simultaneously analyze the sample used for the accuracy control with properties equal to the actual samples. Prior to the start of monitoring, it is recommendable to store and preserve the sub-sectioned one made by homogenizing the samples obtained from the monitoring site as the sample for accuracy control.

X-R Control Chart



Satisfactory - Data is variable showing no trends and remaining within the warning limits

Critical - Any point outside the Upper and Lower Warning Limits (UWL and LWL)
Seven (7) successive points in the same direction causing either an upward or downward trends
Ten (10) successive points on the same side of the average value of the chart

Out-of-Control - Any points outside the Upper and Lower Control Limits (UCL, LCL)

Control Limits for Accuracy

- Collect accuracy data (% recovery) for a particular measurement.
- Calculate the mean (x) and standard deviation (s) for these recovery values, and determine the warning and control limits.
- Adding 2 standard deviations from the means gives the upper warning limit and subtracting 2 standard deviations from the means gives the lower warning limit.
- Adding three (3) standard deviations to the mean and subtracting three (3) standard deviations from the mean gives the upper and lower limits, respectively.

Upper Warning Limit, UWL : $\bar{x} + 2s$

Lower Warning Limit, LWL : $\bar{x} - 2s$

Upper Control Limit, UCL : $\bar{x} + 3s$

Lower Control Limit, LCL : $\bar{x} - 3s$

Classification of Errors

- 1. Constant Error
- (a) Systematic Error: Error caused by defectiveness of instrument and analytical method.
- (b) Human Error: Error caused by excess/miss-estimation of area/scale markings due to the habitual practice of laboratory staff.
- If the cause can be found, the constant error can be sometimes compensated because it shares a constant ratio and magnitude in the analysis. However, when the analyzed values are affected by chromatic interference of concomitant substances, it is difficult to compensate using the simple equation.
- 2. Gross Error
- Gross error is defined to be the error caused by carelessness like mistakes on unit, *lapsus calami*, etc., and it is possible to be found by consecution of the analytical procedure and calculation results.
- 3. Accidental Error
- Aside from constant and gross errors, an error may occur accidentally. Accidental error is defined to be the error caused by many unknown factors and it is very difficult to avoid it even if the instrument is highly sensitive and analysts pay attention to the analysis procedure. Such an error can be used for the statistical analysis.

Addition & Recovery Test

- Addition & recovery test is defined to be a method used for testing that a given quantity is added to the analytic sample for the confirmation on whether it has been accurately analyzed or not. For example, when 10 ng/g of HCB is added to the sediment sample of which concentration of HCB (analysis value) is 10 ng/g and analyzed value is obtained as 19 ng/g, the sediment sample's recovery rate is estimated to be 90%.
- To obtain the correct recovery rate, it is essential that the target substances could be obtained as authentic reagents, and addition is done under the actual condition of the target substances.
- Based on the additional recovery testing, it is possible to confirm the error (multiplier error) existent at constant ratio. If the linearity of calibration curve is confirmed in advance, addition & recovery test can compensate such multiplier error.

Operational Blank Test

- When target substances contaminate the instrument, glassware and solvents, positive error is given. If the analytical procedure has been adequately carried out, the analyzed value has a constant positive error in many cases. This can be compensated by operational blank test.

SRMs COMMERCIALLY ABAILABLE IN JAPAN

No.	SRMs	Contents	Parameters	Supplier
11	Dry Fish Meal Powder	20g	TBT, TPT	Japanese National Environmental Institute
12	Marine Sediment	30g	TBT, TPT	Ditto
1939a	Polychlorinated Biphenyls in River Sediment A	50g	PCB	US Standard Technology Bureau
1941a	Organics in Marine Sediment	50g	PCB, PAH, Organic-Chlorine Pesticides	Ditto
1944	New York-New Jersey Waterway Sediment	50g	PCB, PAH	Ditto
1974a	Organics in Mussel Tissue (Frozen)	3 pieces	PCB, PAH, Organic-Chlorine Pesticides	Ditto
JSAC 0421, JSAC 0.422	Soil	60g	DBD, DBF, co-PCB	Japan Society for Analytical Chemistry
JSAC 0421, JSAC 0.422	Fly Ash	50g	DBD, DBF, co-PCB	Ditto
JSAC 0421, JSAC 0.422	Soil	60g	Cymazine, Dildline	Ditto
JSAC 0421, JSAC 0.422	River Sediment	60g	DBD, DBF, co-PCB	Ditto
JSAC 0421, JSAC 0.422	Marine Sediment	60g	DBD, DBF, co-PCB	Ditto

Outline of Proficiency Test

- A proficiency test (PT) scheme comprises the regular distribution of test materials to participating laboratories for independent testing. The results are returned to the organizer of the scheme who makes an analysis of the results and reports the analysis results to all the participants.
- It is well known that the results of proficiency tests conducted by the participating laboratories and obtained from the same analytical method vary widely considering that their values are normal distribution with a center line of average value.
- Due to these results, the average value of the proficiency test could not be certified as less erroneous; therefore, if the results of a certain laboratory accord the average value, it is difficult to say that laboratory's data are accurate. On the contrary, if the laboratory's data are always equal to the constant position of normal distribution, the accuracy could be considered as authentic.
- Further, if the position of distribution of that laboratory's data often fluctuates, it is supposed that there are some problems in the accuracy of analysis. In case of separate analysis among several laboratories, it is may be possible to manage the accuracy among these laboratories by the proficiency test.

Sample and Parameter of Japanese Proficiency Test Conducted During Recent Years

Year	Samples	Parameters	Remarks
1998	Adjusted Water Samples-1	Fluorine, Boron, Nitrate/Nitrite, Lead and Selenium	
	Adjusted Water Samples-2	Pesticides	
	Dust and Sediment	Dioxin	
1999	Adjusted Wastewater Samples	Nitorgen Compounds (Nitrate, Nitrite, Ammonia and T-N)	
	Adjusted Water Samples	Uranium, Endocrine Disrupters and Pesicides	Sample No.1, 2, 3
	Soil Samples	Dioxin and Coplerner PCB	
2000	Adjusted Water Samples-1	Antimony, Nikel, Mercury and Cadmium	
	Adjusted Water Samples-2	Stylene dimer, Stylene Trimer and Estradiol	
	Adjusted Water Samples-3	Dioxin and Coplerner PCB	
	Sediment Samples	Dioxin and Coplerner PCB	Taken sample in the lake
2001	Adjusted Water Samples	COD, T-N and T-P	
	Endocrine Disrupters	Phthalic acid-di-n-butyl and Nonyl-pehnol	
	Dioxin Compounds	Dioxin and Coplerner PCB	
2002	Adjusted Soil Samples	COD, T-N and T-P	
	Endocrine Disrupters	Phthalic acid-di-n-butyl and Nonyl-pehnol	
	Adjusted Air Samples	Benzen, Trichloro-ehylene, Tetrachloro-ehylene, Dichloro-methane	
	Dust Samples	Dioxin and Coplerner PCB	

Outline of Japanese Proficiency Test Conducted by Ministry of Environment

Item	Correspondence	Supplementary Explanation
Execution Body	Ministry of Environment	Actual working is proceeded by JEHC
Objective of Proficiency Test	1. To confirm the variation among the environmental Laboratories in the whole country.	
	2. To improve the analytical technology in the laboratory staff with recognition of own analytical techniques.	
	3. To improve the analytical technology and accuracy after examine of merits and demerits of each analytical method, and to secure the credibility of the environmental monitoring data.	
Entry Laboratories	1998: Totally 492 Laboratories (Public: 79, Private: 413) ,Collect Rate: 94.3%	Water Samples
	1999: Totally 514 Laboratories (Public: 90, Private: 424), Collect Rate: 92.3%	Water Samples
	2000: Totally 476 Laboratories (Public: 78, Private: 390), Collect Rate: 93.23%	Water Samples
	2001: Totally 522 Laboratories (Public: 99, Private: 423), Collect Rate: 95.8%	Water Samples
	2002: Totally 477 Laboratories (Public: 94, Private: 383), Collect Rate: 96.2%	Water Samples
Examination of Submitted Documents	Some entry laboratories did not attatch calibration curve and chromatogram.	
Interview Survey	To confirm the reason why unsatisfactory analysis results has been obtained, the interview survey is conducted for each laboratory.	Survey items: adopted method, analytical process, standard solution used, analytical equipment used, ratio between blank test and detected value, etc.
Site Visit Survey	To confirm the further reason why unsatisfactory analysis results has been obtained, site visit survey is conducted at the laboratory that submitted unsatisfactory analysis results which has not been identified the reason through the interview survey.	Totally five (5) laboratories were investigated in 2002 by site survey.
Statistical Arrangement	Various statistical arrangement has been conducted in the analytical results.	

Error Control Management

- Errors caused by uncertainty of paperwork that mainly consist of the mix-up of samples and mistakes in recording and calculations often occur. Among them, carelessness is mainly attributed to errors, but it is meaningless to magnify the carelessness.
- The most important measure is to establish a system that is effective for the automatic prevention of errors with work as small as possible. To minimize mistakes in transcribing, it is necessary to plan skipping the transcription.
- Moreover, to avoid miscalculation, it is indispensable to cogitate or explain the calculation process and equation to make them understandable.
- Also, formats of analytical reports should be prepared with detailed countermeasures to prevent generating mistakes.

Conditioning of Analytical Instrument

- Analytical equipment used should be conditioned to enable the analysis of samples under the sensitivity required by each analytical method. At the same time, it is necessary to confirm situations with or without chromatic interference and matrix effect that may cause analytical errors, and whether or not it is possible to adjust/avoid them.
- Reliability as well as sensitivity, selectivity, linearity and stability of the instrument also should be confirmed.

Performance Check of VIS/UV Spectrophotometer

- Spectrophotometers should be retain their wavelength accuracy for the life of the instrument under normal operating conditions. To confirm the performance of the spectrophotometer, the wavelength accuracy must be periodically checked as follows (One of the methods):

(1) Wave length Calibration Check

Good results may be produced by measuring the absorbance of a cobalt chloride solution (22 to 23g of $CoCl_2$, dissolve and dilute to 1 L with 1% HCL solution) on 500, 505, 510, 515 and 520nm wavelengths. The wavelength calibration check is satisfying when maximum absorbance occurs between 505 and 515 nm.

(2) Linearity Check

Linearity check of each instrument is given by the measurement of the absorbance at 510 nm of the stock and the 1:1 diluted cobalt chloride solution. The absorbance of the 1:1 diluted solution ahould be half of the stock value in correct operation.

Performance Check of GC

- The GC is multipurpose instrument; however, specific detectors and column are needed to analyze certain compounds.
- The detector response to different analytical parameters and standards may vary due to the condition of the analytical column,detector or the chromatograph.
- Therefore, in order to insure the performance of the GC, integrated areas and response factors should be recorded in performance check sheets for the standards of specified analytes. If these results vary more than ± 20%, corrective action is needed.

Performance Check of AAS

- Performance check of the AAS should be checked each time a different metal that is analyzed as part of the analytical procedure.
- The performance check is an indicator of any deterioration of either the lamps or the spectrophotometer and shows the optical condition of the instrument.
- It is measured by a “sensitivity check standard”, with which a concentration is given by the method for each metal.
- The absorbance of this standard should be 0.200.
- If it differs by more than ± 10%, the instrument is not performing correctly and has to be corrected.

Performance Check and Calibration of Balance

- Balances are very delicate instruments. The proper use and care the balances is imperative. The following comprehensive rules should be followed to protect and keep this important laboratory equipment in excellent condition.
- Balance should be on a heavy, shockproof table, with adequate working area, and a drawer for the balance accessories. They should be located away form traffic area and protected from sudden drafts and humidity changes.
- In balance, it is necessary to keep desiccant inside to protect from humidity.
- Temperature should be room temperature.
- Special precaution should be taken to avoid spillage of chemicals on the pan or inside the balance.
- It is necessary to check to make sure the balance is in a level condition, and the balance should be adjusted to zero with zero adjustment prior to use.
- When the balance is not in use, the beam should be raised, the weights returned to the beam, objects removed from the pan, and weighing compartment closed.

Instrument Detection Limit (IDL) Recommended by the Textbook

- IDL can be calculated based on the extent of data resulting from the repetitive application of standard solution using the minimum concentration of the standard solution for calibration. If possible, 7 or more standard deviation(s) shall be obtained by repetitive test using the standard solution with *S/N ratio of 5-15.*
- IDL can be calculated by the following equation:

  $IDL = s \times t^*(n-1, 0.01)$

  Where,

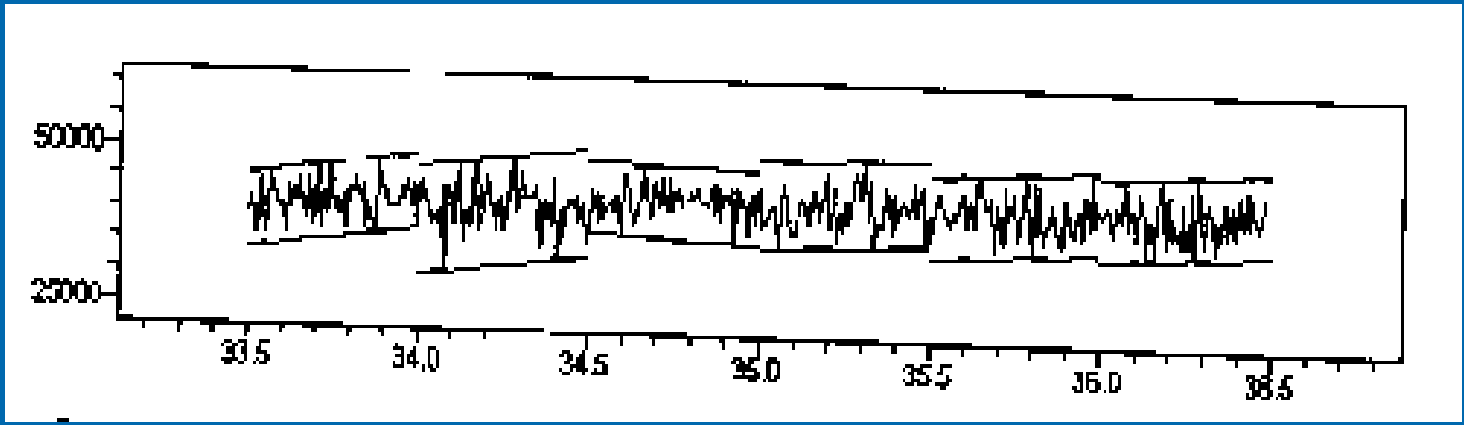
  $t^*(n-1, 0.01)$ is the value of the degree of freedom $(n-1)$ of which the t value or risk ratio is 1% (one-sided). Further, in case the testing number is $n = 7$, the $t^*(n-1, 0.01)$ value should be 3.143.

Student's t-variant

Number of Repetitions	Degree of Freedom (n-1)	t(n-1, 0.01), One-Sided
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821

Calculation of Noise Level

- The S/N ratio is the ratio of the signal to the noise level cannot directly found by a numeric equation. The answer is sought by repeatedly calculating two (2) parallel line lines that fulfill the condition.



- The above figure is an image of the circumstances when finding the noise level from 33.5 minutes to 36.5 minutes in 0.5-minute steps. First, the range is divided into 0.5 minute intervals and parallel lines are found in each section that fulfill the following conditions. The line in the upper position shall be above all of the points of the chromatogram. The line in the lower position below all of the points of the chromatogram. The distance between the two (2) lines in the intensity direction shall be minimized. The average distance between the various parallel lines in the noise level shall be calculated.

Practical Information for S/N Ratio

- There are two (2) kinds of instruments, one is not computerized (only paper chart output), the other one is computerized (possible to control on display of computer)
- Even if apparent nose can be seen in the paper chart output or display of computer, it is possible to see the noise by increasing the sensitivity. In case of LC solution in computerized instruments, digital value of noise can be obtained on upper right of the signal monitor of instrument by moving of cursor. After joining upper and lower end of noise by cursor, level value can be measured as uV. If the uV value of noise can be obtained, it is possible to calculate S/N ratio by dividing.
- It takes a certain time to stabilize the instrument like GC, therefore, measurement of S/N ratio is very much related to the point of time. However, it is possible to calculate S/N ratio any time when the condition of analysis is assured. For the purpose of practical use, it is enough to measure S/N ratio after switching on of instrument.

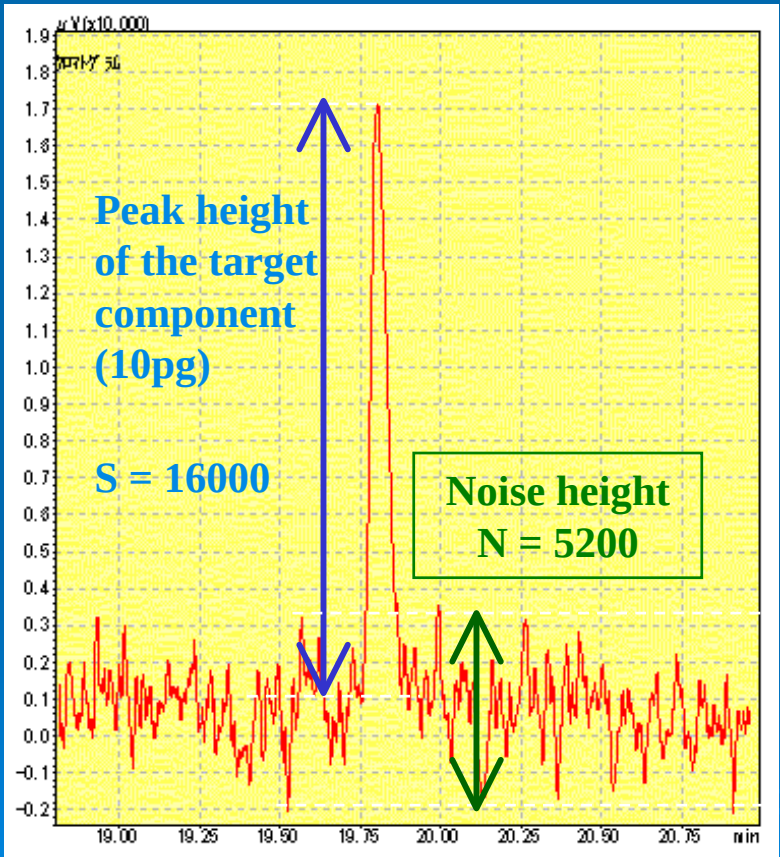
Readjustment of Analytical Instrument

- If abnormal values or outliners are observed among the results of repetition analysis, it is necessary to readjust the analytical equipment and to try the repetitive testing again.
- Further, the concentration value converted into the samples should be calculated from the sampling quantity, final fill-up fluid volume and injection volume into the equipment, and its value should be confirmed to be less than the target detection limit of each analytical method.
- If the converted concentration value does not satisfy the target detection limit, the reason should be found and resolved by readjusting the analytical equipment.

Minimum Detectable Quantity and Limit Value of Quantitative Determination

Minimum detectable quantity（Detection limit） ... Usually, value of S/N=2-3

Limit value of quantitative determination ... Usually, S/N=10-20



S/N = 16000 / 5200
= 3.1

In the case of a left peak, S / N ratio of 10pg are calculated as 3.1.

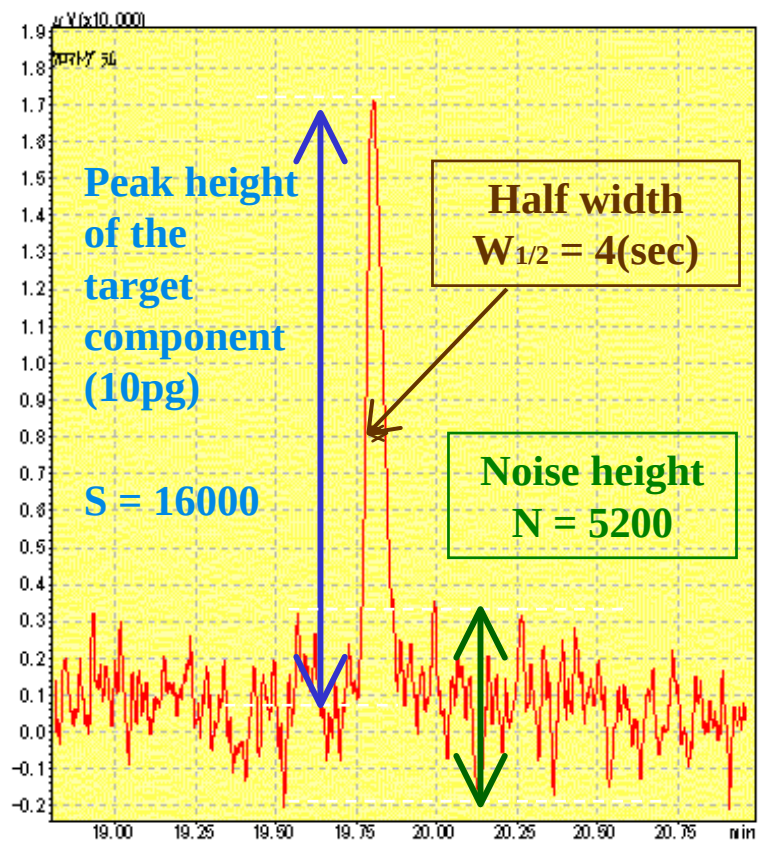
For calculating the quantity of component when S/ N= 2,

5200 / 16000 x 10(pg) x 2 = 6.5(pg)

The detection limit (in case of S/N= 2) of this component is calculated as 6.5pg.

Minimum Detectable Quantity（MDQ) of Detector

Since the peak height of of the component changes with the peak width even if it is the same quantity (area), the minimum detectable quantity which shows the specification of detector is expressed with the quantity of component per second at S/N= 2.



5200 / 16000 x 10(pg) / 4(sec) x 2 = 1.6(pg/sec)

The minimum detectable quantity per second of this component (in case of S/N= 2) is calculated as 1.6pg/sec.

Moreover, when the element which has response to detector like FID (C), FTD (N or P), and FPD (S or P or Sn) is known, it is expressed with the quantity of response elements per second.

For example, supposing a left peak is Tributyl Phosphate($(C_4H_9)_3PO_4$ (MW:266) and detector is FPD(AW of P :31),

1.6 (pg/sec) x 31 / 266 = 0.19 pgP/sec

The minimum detectable quantity of this FPD for P element in Tributyl Phosphate (in case of S/N= 2) is calculated as 0.19 pgP/sec.

Operation and Maintenance of Analytical Instrument

- To confirm whether the performance of each instrument is kept or not, evaluation items regarding the performance of instrument such as PTRI (Programmed Temperature Retention Index), degree of tailing, separation number (TZ: Trennzahl), resolution, IDL and so on should be set up, and periodically confirmed for the purpose of rectifying the change of performance of instrument.
- When deterioration of instrument is observed, it is necessary to adjust the instrument.

Four (4) Different Grades of Laboratory Water (ASTM)

Grade of Water	Maximum Toatal Solids (mg/l)	Maximum EC (uS/cm)	pH
Type I	0.1	0.06	-
Type II	1.0	1.00	-
Type III	1.0	1.00	6.2 -7.0
Type IV	2.0	5.00	5.0 - 8.0

Reagent Grade Water Used in Laboratory

- Type I : Water has no detectable concentration of the compounds or element to be analyzed at the detection limit (IDL) of the analytical method. Type I water in test methods requiring minimum interference, bias and maximum precision.
- Type II : Water is intended to provide the user with water in which the presence of bacteria can be tolerated. It is used to prepare reagents, dyes, or staining.
- Type III: Water may be used for glassware washing, preliminary rinsing of glassware, and as a feed-water for production of higher quality grade water.
- Type IV: Water is used for another purpose except for Type I, II, III.

Quality Check of Laboratory Pure Water

Parameter	Monitoring Frequency	Permissible Limit
EC (μ S/cm)	D	1 - 2 uS/cm
pH	D	5.5 - 7.5
TOC (mg/l)	A	< 1.0
NH_3-N (mg/l)	M	<0.1
Free Chloride (mg/l)	M	<0.1
A: Annually, M: Monthly, D: Daily		

Standard Material (Solution)

- It is recommendable to use a standard material (solution) assured by the trace ability wherever possible to assure the reliability, because analyzed value is obtained based on concentration. If impossible to obtain a standard material, it is necessary to substitute it using high-grade reagents with quality of more than 98% purity for semi-micro analysis.
- Detailed information such as name of supplier, lot, source, conditioning method and date of manufacture of the standard material (solution) should be adequately recorded. When the standard solution is stored, it is indispensable to note the expiration date, and to confirm the change of concentration before using.

Internal Standard Material

- Internal standards (IS) are used for organic analyses by GC/MS, some GC analyses, and some metals analyses by ICP/MS.
- An internal standard is as analyte included in each standard and added to each sample or sample extract/digestate just before sample analysis.
- Internal standards mimic the analytes of interest but not interfere with the analysis.
- The selection of standard materials, as well as their stage of addition and quantities, should depend on each analytical method. The minimum requirements for the selection of standard materials are as follows:
  (i) distinguishable with target substances; (ii) nonexistent in the sample matrix; (iii) stable during the analytical process; (iv) same behavior as target substances;
  (v) high detection sensitivity, etc.

What is Surrogate Material ?

- The meaning of Surrogate is “used to describe a person or thing that takes place of, or is used instead of st/sth else. (ex, She saw him as a sort of surrogate father.)
- Surrogates are used for organic analysis, and used to evaluate method performance in each sample.
- A surrogate standard is a compound of a known amount added to each sample before extraction.
- Surrogates mimic the analytes of interest and are compounds unlikely to be found in environmental samples, such as fluorinated compounds or stable isotopically labeled analogs of the analytes of interest.

Preparation of Calibration Curve

- The standard solution for calibration curve should be prepared as follows: (i) minimum concentration should be almost twice as IDL; (ii) preparation of five (5) different standard solutions within the linear range; and (iii) addition of surrogate material to each standard solution.
- These are adopted as the standard solution sequence, and it is necessary to repeatedly analyze at least three (3) times, and to calculate RRF (Relative Response Factor) inherent to each instrument used.
- RRF can be obtained based on the relation between the concentration ratio of target substances/correspondent internal standard materials (surrogate materials) and the response ratio (peak area ratio) using the following equation:

$$RRF = (Cis/Cs) \times (As/Ais)$$

- Where,

Cis: Concentration of internal standard material in the standard solution.

Cs: Concentration of target substance in the standard solution.

As: Response value of target substance in the standard solution.

Ais: Response value of internal standard material

Allowable Error for Standard Solution

- If the relative standard deviation of each RRF obtained by repeated analysis of standard solution sequence is within 5%, its average value is equal to the value of RRF in the inherent instrument used. Further, this could be adopted as criteria for the judgment on calibration curve available for the quantitative analysis. When the fluctuation exceeds 5%, readjustment of instrument and re-measurement should be done. On the other hand, when there is a transition of operative condition or conditioning of new standard solution, RRF should be newly calculated by repeated analysis of standard solution in the same sequence.
- At the start of analysis of actual samples, it is necessary to confirm that the new RRF value obtained by the analysis using the standard sequence consisting of 2 to 3 kinds of concentration is less than 20% compared to the criteria value of RRF. After starting the analysis of actual samples, periodical analysis of the standard solution with the same concentration as envisaged for actual samples is required, and its RRF value should be confirmed to be less than 20% of fluctuation range. Further, it is necessary to confirm that the fluctuation range of relative retention with the standard solution is less than ±5%.

Operational Blank Test

- Operational blank test is also called “Blank Test”, and it is conducted to confirm any contamination caused by the sample preparation or sample injection procedure to the analytical instrument, to set up the analytical condition without problems, and to maintain the reliability of analytical data.
- Analytical procedure is as prescribed in each analytical method, and it is necessary to confirm whether or not target parameters can be detected using conditioned samples prepared only without sample matrix. If target parameters are detected, it is needed to grasp the concentration as well as with or without other obstruction contents, and to record their values for reference as occasion arises.
- If the values of operational blank tests are large, the reliability of analysis value becomes deteriorated due to not only the increase of the detection limit but also the high possibility of emergence of abnormal values caused by human error. Accordingly, values of the operational blank test should be maintained at less than the target detection limit in order not to affect the analysis data. Frequency of the operational blank test is recommended to be once per 10 samples, or once a day (Number of Samples: <10).

Method Detection Limit (MDL)

- Using the samples of which concentration is near the detection limit, analysis should be done through the prescribed method, and the given analysis results should be converted into concentration. This analytical procedure should be repeated more than seven (7) times. MDL can be obtained using values calculated by the aforementioned procedures, as follows:

  $MDL = s \times t^*(n-1, 0.01)$

  Where,

  $t^*(n-1, 0.01)$ is the value of the degree of freedom $(n-1)$ of which the t value or risk ratio is 1% (one-sided). Further, in case the testing number is $n = 6$, the $t^*(n-1, 0.01)$ value should be 3.14.

Confirmation of Calculation Results of MDL

- The MDL value obtained here should be confirmed as to whether or not it satisfies the target detection limit of each analytical method. If unsatisfied, it is necessary to re-adjust the analytical instrument. Further, it is possible to adjust by increasing the sample size or further concentrating the final fill-up quantity of samples injected into the instrument; however, the procedure should be documented.
- MDL varies depending on the instrument used and the procedures adopted; therefore, when such conditions have changed, the MDL should be calculated to confirm the target detection limit as circumstances demand.

Selection of Samples used for Calculation of MDL

- Samples used for the calculation of MDL should be selected among the ones where target/interfering substances are contained as small as possible.
- When their concentrations are unknown, it is necessary to prepare the samples with the same quantity as actual samples, and to analyze them using GC/MS and other equipment after prescribed pre-treatment and conditioning of sample solution.
- If their concentrations are less than five (5) times as target detection limit including operational blank test value, and interfering substances are also non-detected, it can be used as samples for MDL calculation.

Analysis of Conditioned Samples

- Conditioned samples should be analyzed according to the prescribed method throughout all of the procedures, including extraction, pre-treatment, conditioning of the solution and measurement. Analytical sample quantity should be the same as the actual samples and repetition should be at least seven (7) times.
- The results can be used as the basic data for the calculation of MDL.

Method Qualification Limit (MQL)

- The method quantification limit (MQL) can be calculated, as follows:

  $MQL = MDL \times 3$

- Values of less than MDL are qualitative, more than MDL and less than MQL are semi-quantitative, and more than MQL is quantitative for the evaluation of magnitude relation of concentration. However, it is necessary to consider that even qualitative and semi-quantitative analysis results obtained under a well-managed accuracy control system can be used as the effective information.

Testing Method for Addition & Recovery Rate

- Addition & recovery rate is obtained by the relation between addition quantity and analyzed value through the following procedures: (i) the standard solution prepared for the target substances and surrogate materials should be added to the samples in order to adjust the concentration of them in the samples at about ten times as the detection limit; (ii) the same pre-treatment, conditioning of sample solution and measurements as the analytical method should be conducted.
- If the value obtained from the operational blank test is large and target substances are contained, trial tests should again be conducted with increased additional quantities of standard materials so that the testing for additional recovery rate is not affected. The rough standard of permissible level of additional recovery rate is from 70% to 120%. In case of the dilution method of radioisotope, the permissible level of recovery rate of surrogate materials is within the range of 50% to 120%.

Feedback of the Results of Testing for Addition & Recovery Rate

- If the recovery rate widely deviates from the permissible level, it is required to try taking samples again, following the extraction procedures, after investigation of the causes.
- The testing for additional recovery rate should be conducted prior to the analysis of actual samples. Further, when the recovery rate has the possibility to vary due to the change of supplier or the lot of equipment and chemical reagents used, it is necessary to conduct the testing for additional recovery rate.

Stability of Instrument

- It is essential to periodically analyze the stability of the instrument at the middle of standard solution sequence, and to confirm whether or not the sensitivity of each target substance or internal standard material (surrogate material) widely varies compared to the time when calibration curve was made.
- When relative sensitivity corresponding to intensity ratio of target substances and the internal standard materials fluctuates by more than ±20%, re-measurement is necessary after removal of the causes.

Duplicates Samples

- To keep the comprehensive reliability for sampling, pre-treatment procedures and analysis using instrument, more than two (2) samples prepared under the same condition should be analyzed. Such analysis is called “Double Analysis”.
- Recommendable frequency of double analysis is once per 10 samples. It is necessary to confirm that the difference between the values of more than two (2) samples analyzed is less than 30% compared to the average value of analysis results.
- In case of appearance of large values, re-measurement should be done after removal of the causes.

Travel Blank Test

- Travel blank test is carried out to confirm whether contamination is present or not throughout the analytical process from preparation of sampling to measurement. Except for the sampling procedure, analytes should be prepared under completely the same condition and analyzed under the same procedures as the actual samples, and their analyzed values are dealt as “Travel Blank Values”.
- Travel blank test should not be done every time; however, to keep the reliability of sampling, the data of travel blank test should be well examined in advance and managed to enable indication as occasion arises.

Management of Abnormal/Missing Values

- When unsatisfactory cases are found like large values of operational blank test, large difference between the double analysis values and abnormal values of the travel blank tests, re-measurement should be done because analysis data are considered to be unreliable and missing values.
- Re-measurement not only involves manpower, a long time and cost, but also hinders analysis and affects the evaluation of the entire investigation due to the different sampling periods. Therefore, it is essential to check in advance, and to pay attention to the emergence of abnormal and missing values.
- Further, if abnormal and missing values are obtained, it is necessary to sufficiently examine the process of their emergence, and to keep them on record in order to avoid their re-occurrence.

RECORDING OF OPERATION

- (1) Method of Taking Samples, Storage and Transportation
- ・Identification, adjustment and operation of instrument and glassware.
- ・Condition of target samples (sampling method, sampling locations, sampling date, etc.)
- ・Climatic conditions
- ・Condition of handling and storage of sampling vessels, etc.
- ・Method of transportation
- (2) Information Related to Samples
- ・Water Quality: pH, concentration of organic pollutants, SS, etc.
- ・Sediment: External view, odor, water contents, ignition loss, etc.
- ・Biological Samples: Species, growth condition, lipid contents, etc.
- (3) Method and Condition regarding Conditioning of Samples
- ・Water Quality: With or without filtration and its method, etc.
- ・Sediment: With or without removal of pore water and its method, etc.
- ・Biological Samples: Sampling position and its method, etc.
- (4) Method of Pre-Treatment
- ・Modification, change for the better, improvement factor and so on
- ・Other remarkable items
- (5) Records regarding Operational Condition and Calibration of Instrument
- ・Suppliers of equipment, product number, performance condition, etc.
- ・Record of operation and maintenance
- (6) Various Kinds of Values Obtained in the Course of Analysis
- ・Sample size for the analytical procedures, extract quantity, condensation ratio, etc.
- ・Setting condition of each instrument, etc.

REPORTING REGARDING ACCURACY CONTROL

- (1) Sample identification including taking samples, transportation and storage.
- (2) Analytical procedures such as date of analysis, method number for the analytical method used, condition of pre-treatment, generated raw data, calculation process, analytical calibration/standardization/frequency, corrected/reported data, and name of the analysis staff.
- (3) Determination of IDL (Instrument Detection Limit).
- (4) Determination of MDL (Method Detection Limit).
- (5) Determination of Detection Limit at the sample analysis.
- (6) QC check samples preparation, QC requirements, QC routine checks related to the analysis such as operation blank test, double analysis, travel blank test, testing for additional recovery rate, data validation/reduction and so on.
- (7) Others (preparation of reagents, standards, electronic data documentation).

THANK YOU VERY MUCH !!

ANNEX (6)

EXPRESSION OF UNCERTAINTY FOR MEASUREMENT IN CALIBRATION

CTI Engineering International Co., Ltd.
KUNIO ISHIKAWA

CONTENTS OF TECHNICAL TRANFER ON UNCERTAINTY

MAIN CONTENTS

What is the Uncertainty in Laboratory

- To meet the requirement prescribed in ISO/IEC Guide 25, the testing laboratories shall estimate the uncertainty of measurement.
- Estimated uncertainty of measurement shall be indicated in the analysis report or certification of results.
- When the uncertainty is estimated, all the factors related to the uncertainty shall be considered.

ESTIMATION OF UNCERTAINTY OF MEASUREMENT

- (1) Testing laboratories shall have and shall apply procedures for estimating uncertainty of measurement. In certain cases the nature of the test method may preclude rigorous, metrologically and statistically valid calculation of uncertainty of measurement. In these cases the laboratory shall at least attempt to identify all the components of uncertainty and make a reasonable estimation, and shall ensure that the form of reporting of the result dose not give a wrong impression of the uncertainty. Reasonable estimation shall be based on knowledge of the performance and validation data.
- (2) A calibration laboratory, or a testing laboratory performing its own calibrations, shall have and shall apply a procedure to estimate the uncertainty of measurement for all calibrations and types of calibrations.

Uncertainty in Chemical Analysis

- (1) Uncertainty related to calibration of zero point, balance and instruments.
- (2) Uncertainty related to purity and guaranteed performance of chemical reagents and standard solution.
- (3) Uncertainty related to analytical procedure such as contamination, loss, sublimation or imperfection of extraction.
- (4) Uncertainty related to resolution and deviation of read of analog instruments.
- (5) Deviation of sampling, pre-treatment and instruments.
- (6) Uncertainty related to volume of volumetric vessels.

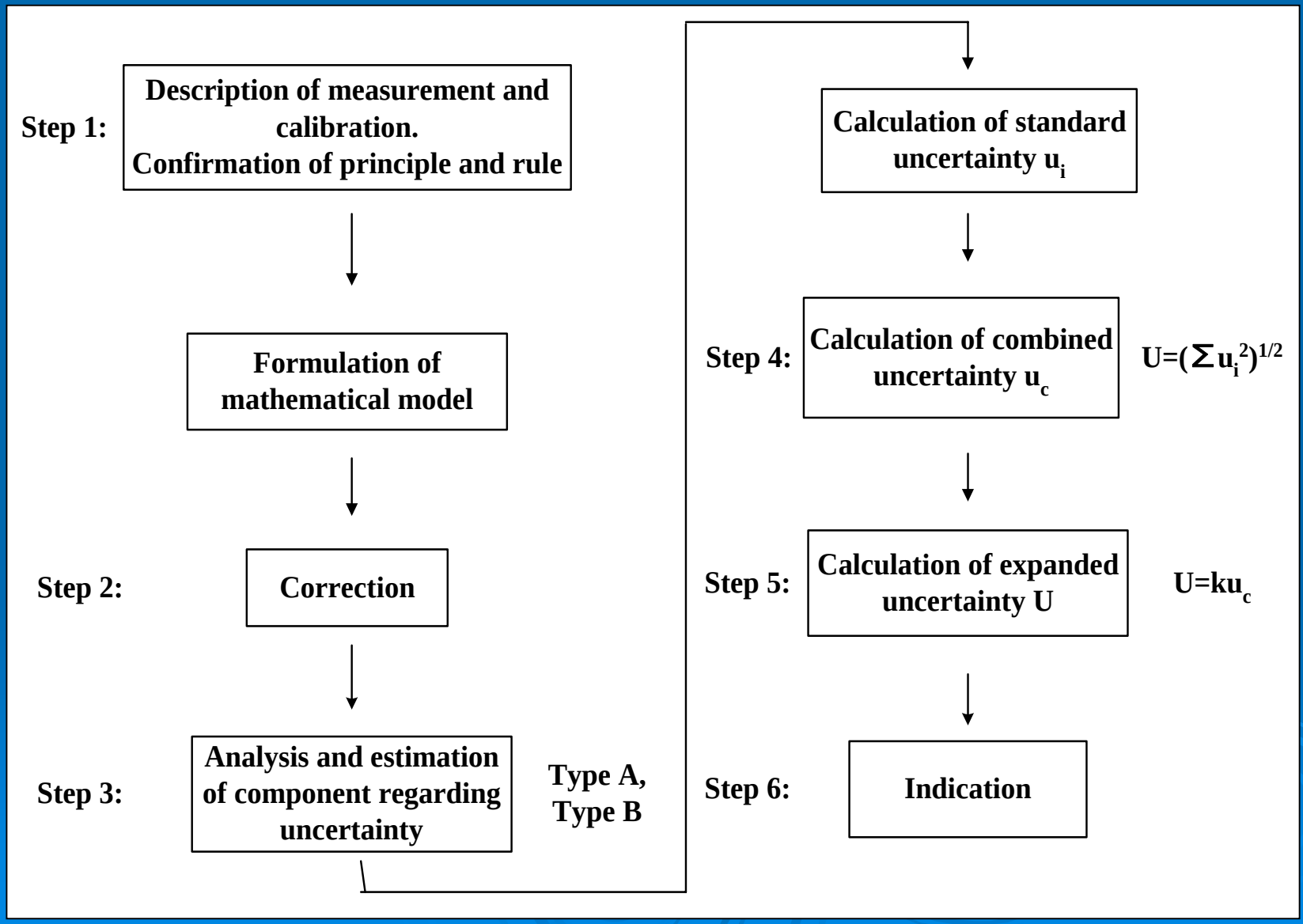
Uncertainty of Standard Reference Material

- (1) Uncertainty related to unevenness of material.
- (2) Measuring error.
- (3) Measuring method of laboratory and staff.
- (4) Uncertainty related to experience and judgment.

COMPONENTS OF UNCERTAINTY

- (1) When estimating the uncertainty of measurement, all uncertainty components which are of important in the given situation shall be taken into account using appropriate methods of analysis
- (2) To assess whether the error is admissible or not
- (3) To search for the cause in case of inadmissible
- (4) To improve by removing the cause from the analytical procedures
- (5) To investigate remedial measures by introducing more accurate technology
- (6) To routinely prepare the documents containing the procedures for maintaining reliability

Procedure for Estimation of Uncertainty



Type of Evaluation

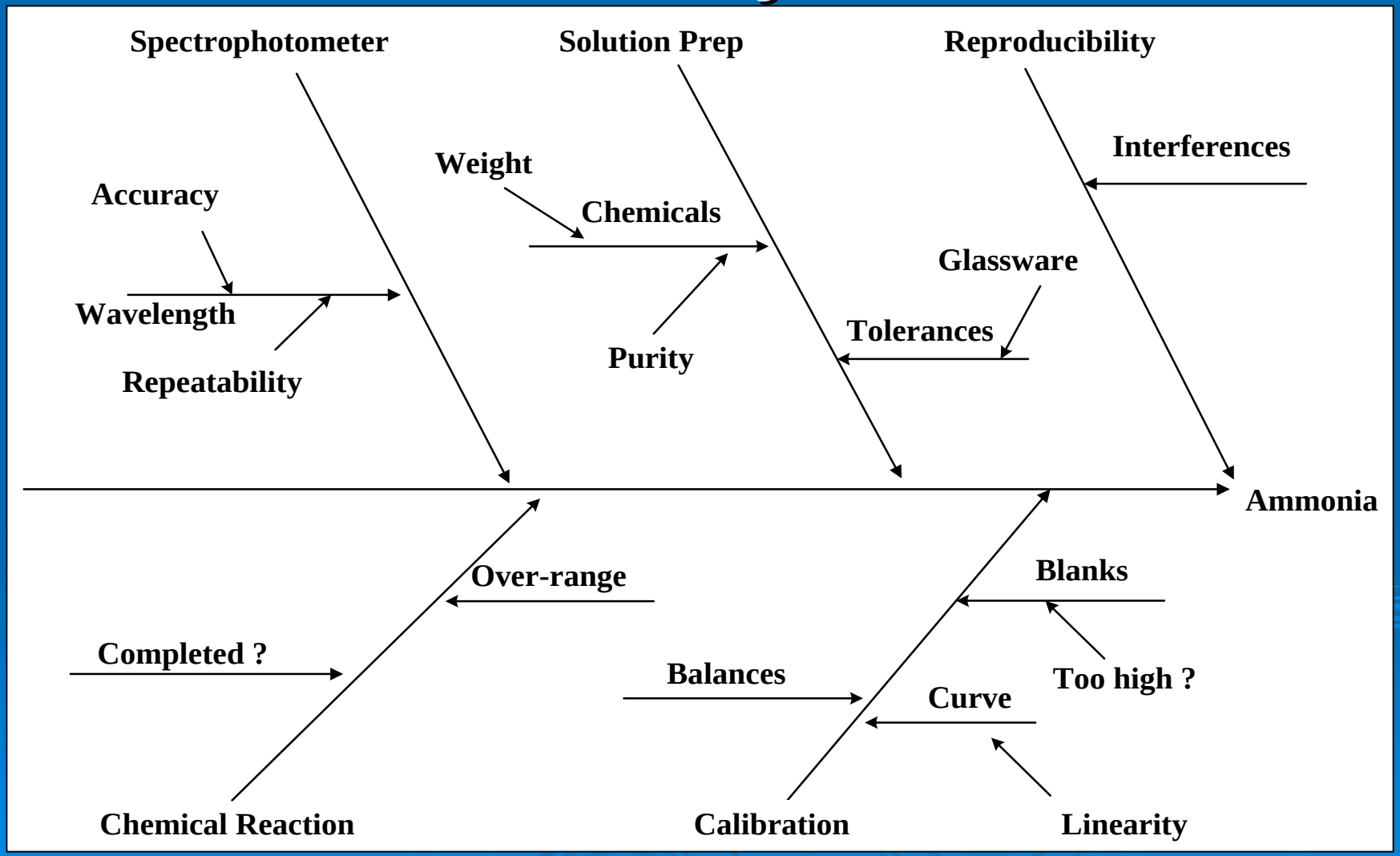
- **Type A evaluation**

  Method of evaluation of uncertainty by the statistical analysis of series of observation.

- **Type B evaluation**

  Method of evaluation of uncertainty by means other than the statistical analysis of series of observation.

Fishbone Diagram for Identification of Uncertainty Sources



Calculation Step of Uncertainty

- Average and SD (standard deviation) of 10 times weighing measurement = 49.9263±0.036g.
- Uncertainty of weighing measurement = 0.036g.
- Uncertainty = SD.
- Relative uncertainty = uncertainty/average value
- = 0.036g/ 49.9263g = $7.2*10^{-5}$

- Tolerance of 50 ml burette = ±0.05 ml
- In case of above, uncertainty = 0.05/√6 = 0.020 ml.

Parameters to be selected

- Candidates of parameters to be selected are as follows: Suspended solid (SS), BOD, Coliform, Lead (Pb), T-Phosphorus, Sulfate (SO_4^{2-}), Nitrate & Sulfide.
- Among them, at least 1 parameter will be selected for actual calculation of uncertainty.
- After calculation of uncertainty, it will be possible to apply another parameters in the same manner.

THANK YOU VERY MUCH !!

ANNEX (7)

Calculation Sheet Sample of Uncertainty for: pH

Step 1: Instruments used

Note:

Clear statement of what is being measured, including relationship between the instruments and the input qualities (e.g. measured quantities, constant, calibration standard values, etc.) upon which it depends. Where possible include corrections for known systematic effects. The specification information should be given in the relevant Standard Operation Procedure (SOP) or other method.

Input the name of instruments used

Analysis of pH in clean and wastewater samples.

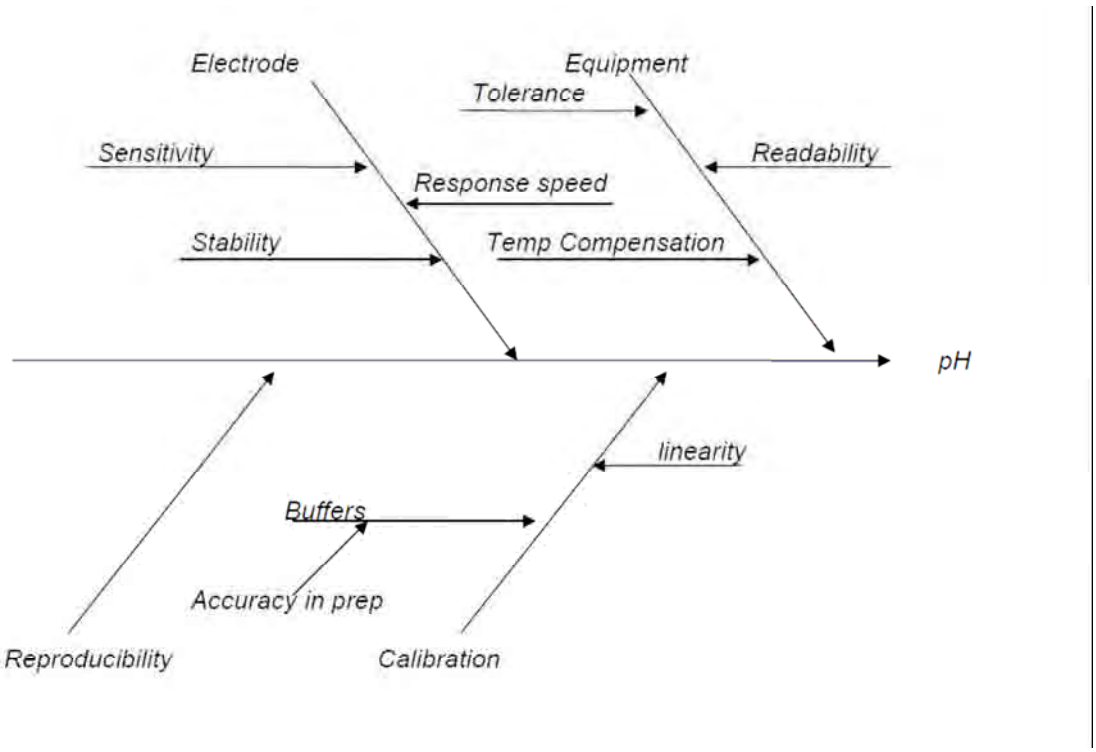
For analysis in the range 4-8 pH units, the equipment used is a ***Metrohm Autotirator*** (for sample changing facilities) with a combined junction ph electrode, calibrated over the range 4-7 pH units.

For analysis over 8 pH units, the equipment used is a ***Mettler Delta 320*** with a combined junction pH electrode, calibrated over the range 7-10 pH units.

Step 2: Identify Uncertainty Sources

Note:

List the possible sources of uncertainty. This will include sources that contribute to the uncertainty on the parameters specified in step, but may include other sources and must include sources arising from chemical assumptions.



Among the uncertainty sources, significant uncertainty components can be selected as follows: all the uncertainty components are covered by the bias and precision testing undertake.

Step 3: Quantify Uncertainty Components

Note:

Measure or estimate the size of the uncertainty component associated with each potential source of uncertainty identified. It is often possible to estimate or determine a single contribution to uncertainty associated with a number of separate sources. It is also important to consider whether available data accounts sufficiently for all sources of uncertainty, plan additional experiments and studies carefully to ensure that all sources of uncertainty are adequately accounted for.

From precision work on autotitrator, standard deviation of 10 river samples is 0.0309pH units
Uncertainty for this is 0.0309

Sewage effluents and AQC solution give a lower uncertainty, so the higher value will be considered.

From NS30 work on Mettler meter, standard deviation of 20 river samples is 0.055pH units
Uncertainty for this is 0.055

Sewage effluents and AQC solution give a lower uncertainty, so the higher value will be considered.

The Mettler pH meter giving the higher uncertainty, this value will be use din Step 4 overleaf.

For Aquacheck, the bias uncertainty for 10 samples all matrices and values is 0.0038

Step 4: Calculate Combined Uncertainty

The information obtained in step 3 will consist of quantifies contributions to overall uncertainty, whether associated with individual sources or with the combined effects of several sources. The contributions have to be expressed as deviations, and combined according to the appropriate rules, to give a combined uncertainty.

The appropriate coverage factor should be applied to give an expanded uncertainty.

Combined Uncertainty $= \sqrt{(0.055^2 + 0.0038^2)}$

$= 0.0551$

Expanded Uncertainty *(k = 2 because there are more than 6 degrees of freedom)*

$= 0.0551 \times 2$

$= 0.1102$

Result can be reported as $x \pm (0.1102*x)$

Staff Name: _____

Date: _____

Calculation Sheet Sample of Uncertainty for: Conductivity

Step 1: Instruments used

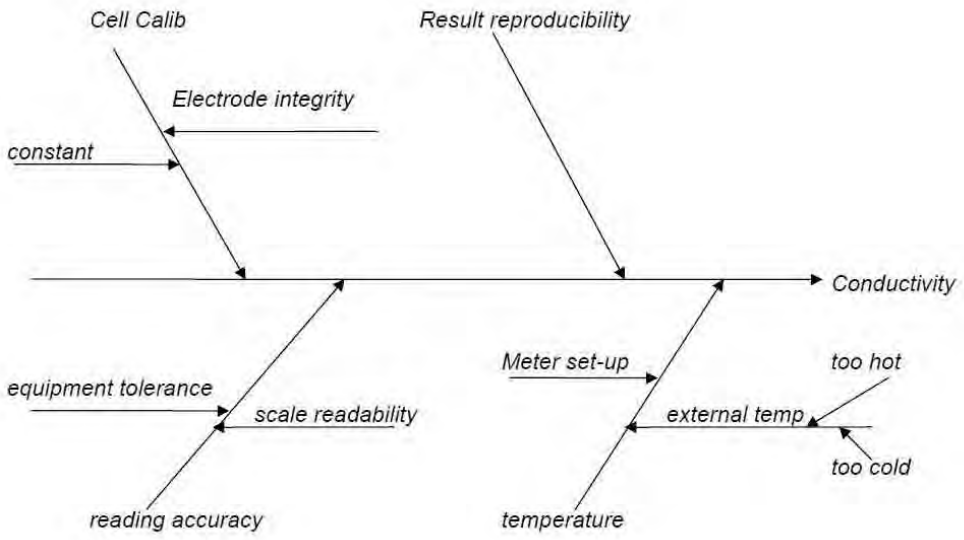
Note:
Clear statement of what is being measured, including relationship between the instruments and the input qualities (e.g. measured quantities, constant, calibration standard values, etc.) upon which it depends. Where possible include corrections for known systematic effects. The specification information should be given in the relevant Standard Operation Procedure (SOP) or other method.

Input the name of instruments used

Electrical conductivity of waters and wastewaters using *Jenway conductivity meter*, with temperature compensation to 20 ℃.
Meter is set up using a cell with a known cell constant.

Step 2: Identify Uncertainty Sources

Note:
List the possible sources of uncertainty. This will include sources that contribute to the uncertainty on the parameters specified in step, but may include other sources and must include sources arising from chemical assumptions.



Among the uncertainty sources, significant uncertainty components can be selected as follows: meter accuracy, temperature coefficient and results reprocibility.

Step 3: Quantify Uncertainty Components

Note:
Measure or estimate the size of the uncertainty component associated with each potential source of uncertainty identified. It is often possible to estimate or determine a single contribution to uncertainty associated with a number of separate sources. It is also important to consider whether available data accounts sufficiently for all sources of

uncertainty, plan additional experiments and studies carefully to ensure that all sources of uncertainty are adequately accounted for.

Meter accuracy stated as +/-0.5% }
} *from equipment manual*
Temperature coefficient stated as +/-2% / C }

From precision / validation work, 18 sample give a standard deviation of 3.38%

From Aquacheck results, 10 samples give a bias of 36.001%

Equipment Uncertainty = $\sqrt{(0.005^2 + 0.02^2)} = 0.0206$

Precision uncertainty = $0.0338/\sqrt{18} = 0.0080$

Bias uncertainty = $0.36/\sqrt{10} = 0.1138$

Step 4: Calculate Combined Uncertainty

The information obtained in step 3 will consist of quantifies contributions to overall uncertainty, whether associated with individual sources or with the combined effects of several sources. The contributions have to be expressed as deviations, and combined according to the appropriate rules, to give a combined uncertainty.
The appropriate coverage factor should be applied to give an expanded uncertainty.

Combined Uncertainty = $\sqrt{(0.0206^2 + 0.0080^2 + 0.1138^2)}$
= 0.1159

Expanded Uncertainty (k = 2 because there are more than 6 degrees of freedom)
= 0.1159 x 2
= 0.2319

Result can be reported as $x \pm (0.2319*x)$

Staff Name: _____

Date: _____

ANNEX (8)

Annex (8)

Uncertainty of Measurement of Analysis of Lead in Water by Flame AAS

DINAMA Laboratory

12/9/2006

Identification of Analysis Procedure

Sample treatment

1. 1 Lt of sample To homogenize
2. To weigh in empty Erlenmeyer (P)
3. To add approximately 50 gr of water (density: d=m/v)
4. To take the weight of the Erlenmeyer more the sample (P1)
5. To add 10 mL of HNO_3 (the change in the added quantity does not influence too much)
6. To put on the plate
7. It is allowed to cool and the final weight takes (P2). Measure the final density (d=m/v)

Preparation of standard solution for calibration curve

8. Pb 1,000mg/l stock solution
9. 1g of stock solution usisn Balance
10. 10 times dilution, 10g of pure water using balance, Pb 100 mg/l
11. N_1 and N_2g of Pb 100mg/l using balance
12. 200 and 33.3 times dilution (Adding pure water) using balane, Min & Max Conc

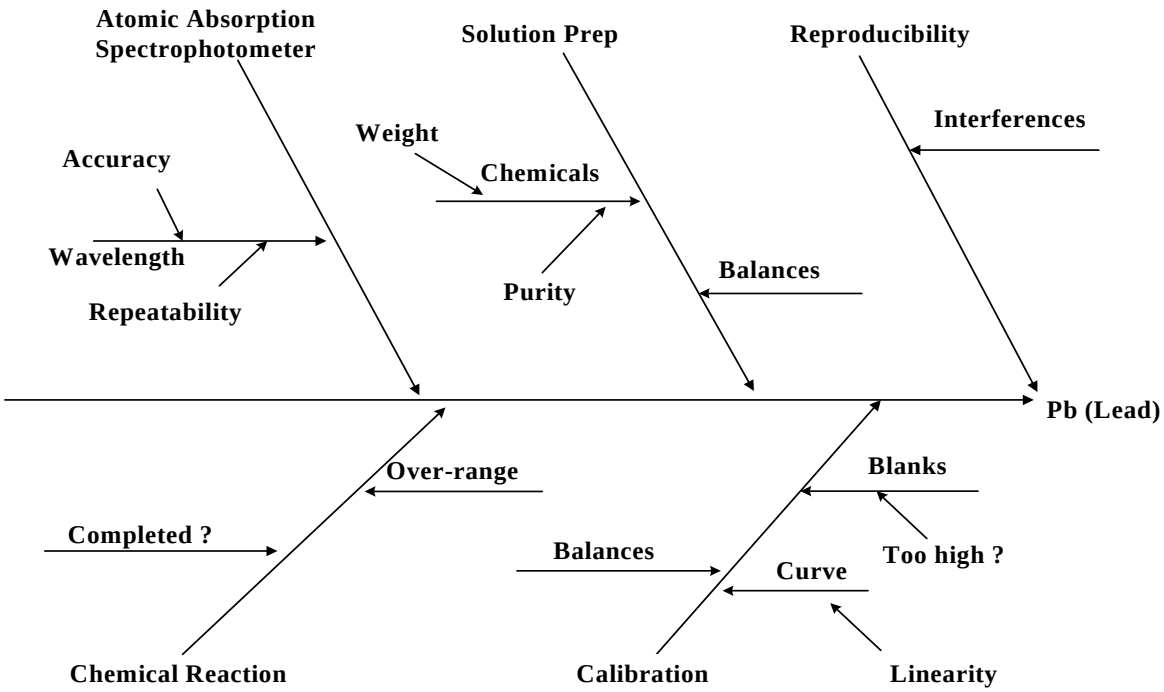
Consideration of AAS photometric accuracy

13. AAS equipment

Measuring calibration curve and samples using AAS

14. Calibration and samples

Annex (8)



Calculation of Uncertainty of Lead (Pb) in Water

Step-1 Sample Treatment

Among aforementioned process (No.1 to 7), process No.2,4,7 can be selected as the uncertainty components. And their SD are as follows: usisg balance=0.0023 and using micro-pippet= 0.00405

Combined uncertainty of step-1

$$(u_c) = \sqrt{0.0023^2 + 0.0023^2 + 0.0023^2 + 0.00405^2 + 0.0023^2} = 0.0075$$

Step-2 Standard Preparation

From monoelemental standards of approximately 1,000mg/L, a intermediate multielementary standard is prepared with approximately 100mg/L of every metal. This intermediate solution has a validity of 6 months.

Among aforementioned process (No.8 to 12), process No.8,9,10,11,12 can be selected as the uncertainty components. And their SD are as follows: original standard (1,000 $\pm$ 10mg/l Pb,)= $0.01/\sqrt{3}$ =0.00578 and usisg balance=0.0023.

Combined uncertainty of step-2

$$u_c(C_{1\text{-}2})/C_{1\text{-}2} = \sqrt{0.00578^2 + 0.0023^2 + 0.0023^2 + 0.0023^2 + 0.0023^2} = 0.0074$$

Normal range used for the calibration curve indicates the linearity, and their concentration is from 0.5 to 3 mg/l. Furether, the uncertainty of preparation of standard solution used for calibration curve is the same value between minimum and maximun concentration. Because weighing and dilution process is completely same.

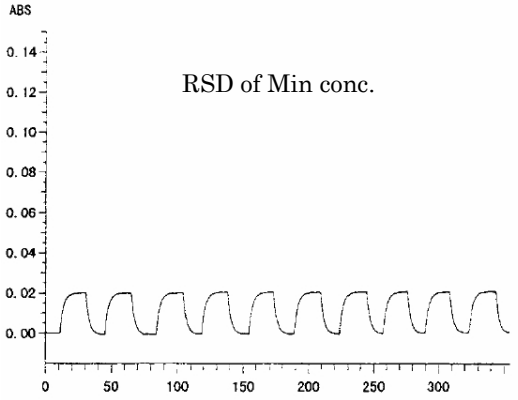
Annex (8)

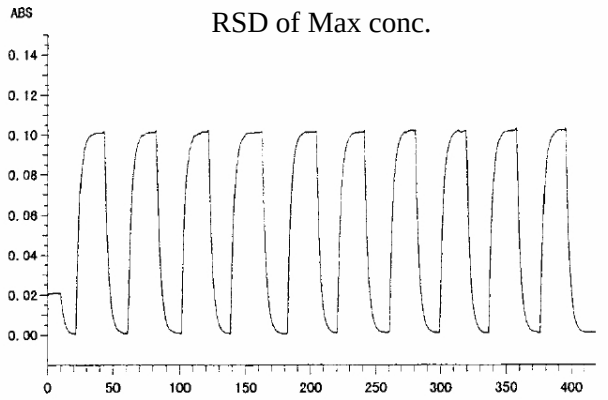
Step-3 Calibration curve of AAS

Consideration of AAS photometric accuracy

Usually, absorbance of AAS has linearity under the span of 0 to 0.1. AAS photometric accuracy should be considered following points: base line (drift), back ground absorbance, bending of working curve, flame condition and detection limit. Among these points, followings can be selected as the major uncertainty componebt of AAS photometric accuracy:

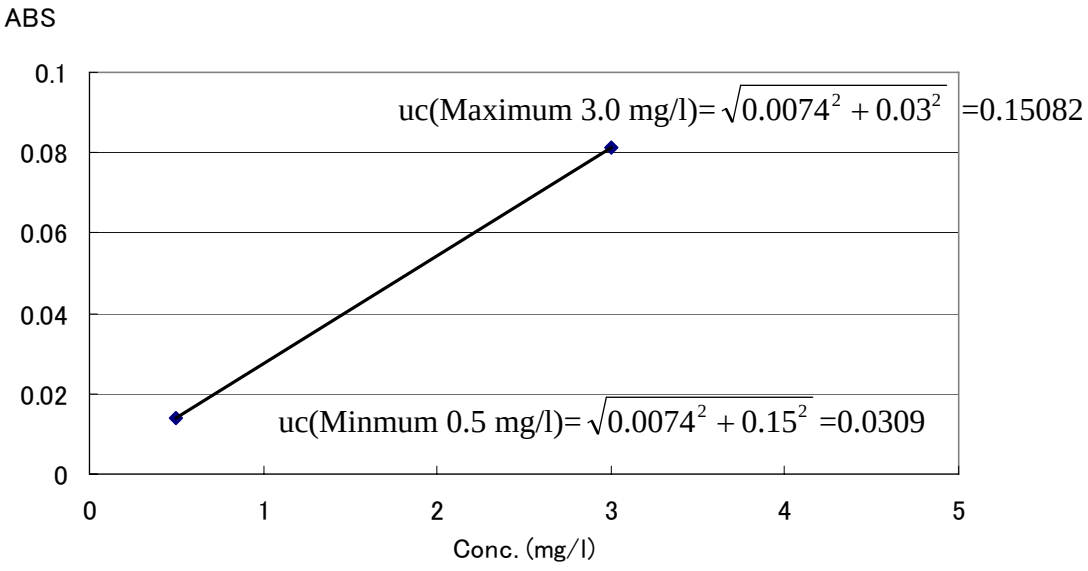
Item	u as RSD	Method
Reproducibility of Min conc. Of calibration curve	0.03	Repeated measuring as shown in the figure below.
Reproducibility of Max conc. Of calibration curve	0.15	Ditto
Min conc. (0.5 mg/l Pb)	0.0074	Results of step-2
Max conc. (3.0 mg/l Pb)	0.0074	Ditto





Estimation of expanded uncertainty of calibration curve

Calibration curve of Pb can be assured linearity within the range of 1 mg/l to 10 mg/l, hence, it can be prepared using the concentartion of ups and downs. Further, expanded uncertainty of calibration curve can be estimated as shown in th figure below.



Average Uc = (0.0309+0.1508)/2 = 0.0909

Overall expanded uncertainty

Overall expanded uncertainty ($U_{expanded}$) can be calculated as follows

$$U_{expanded} = k \times x \sqrt{(step - 1)^2 + (AverageUc - step2,3)^2}$$

Expanded Uncertainty (k=2 because there are more than 6 degree of freedom)

$$U_{expanded} = 2 \times x \sqrt{0.0075^2 + 0.0909^2} = 1.824 \times 10^{-1} \times x$$

ANNEX (9)

Annex (9)

DIRECCIÓN NACIONAL DE MEDIO AMBIENTE

DEPARTAMENTO DE NORMALIZACIÓN TÉCNICA- LABORATORIO

Sistema de Gestión de la Calidad Certificado según Norma UNIT-ISO 9001:2000

INFORME DE RESULTADOS

Montevideo, 12 de septiembre de 2006

Nº Muestra	10536
Solicitante	Dpto. Calidad de Aguas
Referencia	JICA
Muestreador	JM y NG
Punto de muestreo	F1
Fecha de Muestreo	27/07/2005
Fecha de Ingreso al Laboratorio	27/07/2005

Parámetro	Unidad	Valor	Técnica	SOP
DBO5	mg O2/L	10	Electrométrico	SOP 08
DQO	mg O2/L	86	Colorimétrico R Cerrado	SOP 09
Grasas y Aceites	mg/L	40	Gravimétrico	SOP 01
S. T fijos	mg/L	1.0E+3	Gravimétrico	SOP 21
S. T vol.	mg/L	6.0E+2	Gravimétrico	SOP 21
S. Totales	mg/L	1.6E+3	Gravimétrico	SOP 21
S.Susp.fijos	mg/L	14	Gravimétrico	SOP 20
S.Susp.totales	mg/L	28	Gravimétrico	SOP 20
S.Susp.vol.	mg/L	15	Gravimétrico	SOP 20
Turbidez	NTU	22	Nefelométrico (NTU)	SOP 22
Sulfuro	mg/L	< 0.05	T. Potenciométrico	SOP 52
Amonio	mgNH4-N/L	20	Electrométrico	SOP 03
Fósforo total	mg P/L	5.4	Colorimétrico	SOP 13
Nitrato	µg NO3-N/L	< 50	Electrométrico	SOP 16
Nitrito	µg NO2-N/L	27	Colorimétrico	SOP 15
Etil paration	µg/L	< 0.010	GC-ECD	
Metil Paration	µg/L	< 0.010	GC-ECD	
Mirex	µg/L	< 0.004	GC-ECD	

Nota: La fecha de realización del análisis se indica en las rutas de análisis, por el número de análisis. SOP: Procedimiento Estandarizado de Operaciones.

Analistas:

Lic. Sandra Castro Scarone

Jefa De Depto. Normalización Técnica - Laboratorio

ANNEX (10)

Annex (10)

Example of Check List: Conformity with General Requirement (Some Part)

Requirement for Accreditation	Citation from Laboratory Documents	Comment
3.05.2 Do the important equipment and standards have the independent indentification number? Does include follows in Inventory? a) Name of equipment? b) Name of manufacturer c) Date of installation and starting use? d) Location installed? e) Condition at installation? f) Operation manual of manufacturer? g) Maintenance manual? h) Total record of maintenance and calibration? i) Detail record of calibration? 3.05.3 When computer is used for the direct control and importing data, it is confirmed the appropriateness of the entire system?.		

Example of Check List: Specific information on Applicant (Laboratorey) (Some Part)

3.04 Accomodation and environmental condition

Plesase attach the layout plan:

If correspondent, please indicate the rule for testing environmental condition related to the testing method:

How these conformity are monitored? :

3.05 Equipment and Standard Material

Equipment List:

Please attach the equipment inventory including type, range of usage, condition of calibration, etc.

Desirable order: (a) Praimary equipment, (b) Major equipment, (c) Secondary equipment

Equipment List

Name of Equipment/Type	Latest date		Interval of calibration or maintenance
	Calibration	Maintenance	

Example of Check List: Information on Testing Mehtod of Applicant (Laboratorey) (Some Part)

Required items for accreditation	Laboratory documents (ex. Quality Manual Chapter 1.2)	Comments
3.04 Environmental codition 3.04.1 Minute analysis? What kinds of procedures are adopted for preventing contamination to samples? Fields test is conducted? What kinds of procedures are adopted for preventing mixing in the inert matter to samples? All of the related environmental condition is monitored? 3.06. Testing, traceability and calibration Does Record of calibration and maintenance of equipment include follows? a) Identification of each equipment b) Date of calibration c) Results of all of the calibration d) Name of calibration staff e) Detail information on malfunction of performance of equipment		

ANNEX (11)

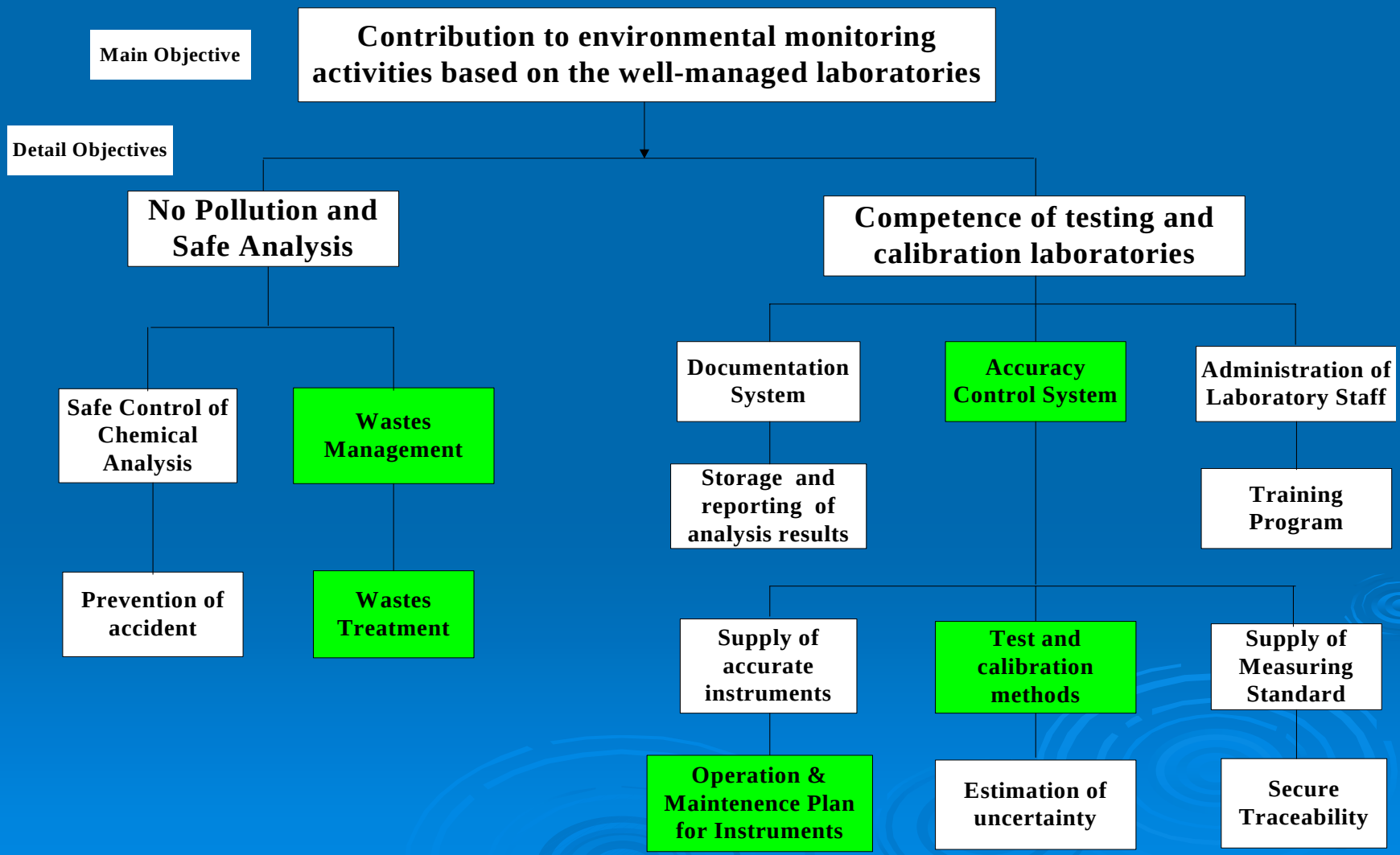
OUTLINE OF LABORATORY MANAGEMENT

CTI Engineering International Co., Ltd.
KUNIO ISHIKAWA

CONTENTS OF PRESENTATION

1. INTRODUCTION

Items included in the Laboratory Management



2. ACCURACY CONTROL SYSTEM

GENERAL REQUIREMENT FOR ACCURACY CONTROL

- (1) Are monitoring points adequate?
- (2) Is the analysis method well suited?
- (3) Is the targeted accuracy correct?
- (4) Is the accuracy control method kept well?
- (5) Are sampling methods and their number of times appropriate?

SEQUENCE OF WORK OPERATION FOR ACCURACY CONTROL

- (1) To know the kind and magnitude of error in the analysis
- (2) To assess whether the error is admissible or not
- (3) To search for the cause in case of inadmissible
- (4) To improve by removing the cause from the analytical procedures
- (5) To investigate remedial measures by introducing more accurate technology
- (6) To routinely prepare the documents containing the procedures for maintaining reliability

What the Accuracy Control Should Be

- In long-range monitoring, the possibility of fluctuation of accuracy and precision becomes higher with the change of various factors such as renewal of analytical instruments and replacement of laboratory staff.
- To adequately maintain accuracy control is an essential issue in determining the feasibility of monitoring, because scientific evaluation of the monitoring results is conducted through the analytical data containing the error.

Can humans avoid error?

- Quality Analysis is done by humans. who make every time mistake. Humans are always involved the risk of making mistakes.
- There are two (2) kinds of views whether humans are born inherently good or evil.
- Humans have five (5) senses, especially use visual sense during the analytical procedure.
- There are many mistakable numbers in handwriting filed notes.
- Laboratory staff have to tackle with instruments difficult to operate.

How to Minimize the Occurrences of Errors

- To know the range of analytical results. (Monitoring point-wise Max and Min and concentrations of pollutants in natural resources like normal river water, normal soil etc.)
- To always keep the suspicious mind for the analysis results
- To pay attention to the different outcome. (Color of samples and chemical reaction)
- To correctly set-up the analytical instrument.
- To check the slope of calibration curve of each parameter.
- To confirm the existence of transcription error of field note.
- To check the condition of each analytical instrument.

Average Value and Standard Deviation

Precision measures the variation among measurements and may be expressed in different terms.

Standard Deviation(s):

$$s = \sqrt{E(x - \overline{X})^2 / n - 1}$$

E = sum $\quad$ $\overline{x}$ = mean

x = measurements $\quad$ n = number of measurements

Relative Standard Deviation (RSD):

- Calculate the mean $(\overline{x})$.
- Calculate the standard deviation (s).
- Calculate the coefficient of variant (CV).
  CV = standard deviation(s)/mean $(\overline{x})$.
- Calculate the Relative Standard Deviation (RSD).

$$RSD = CV \times 100$$

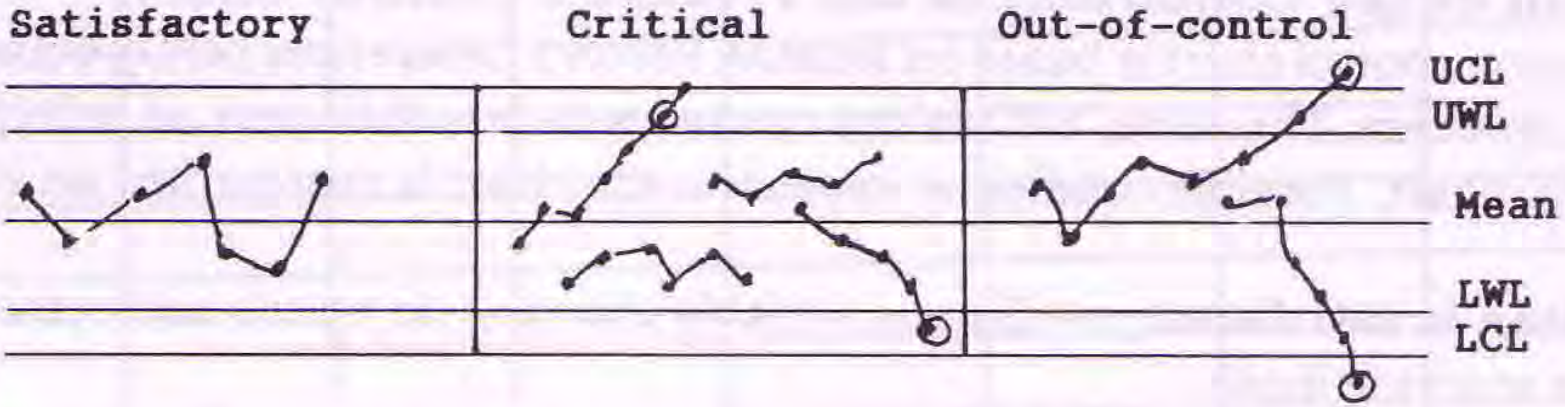
Relative Percent Difference (RPD): RPD is the difference between the duplicate values divided by the average of the duplicate values and multiplied by 100.

$$RPD = [(A - B)/(A + B/2)] \times 100$$

or shortly

$$RPD = [(A - B)/(A + B)] \times 200$$

X-R Control Chart



Satisfactory - Data is variable showing no trends and remaining within the warning limits

Critical - Any point outside the Upper and Lower Warning Limits (UWL and LWL)
Seven (7) successive points in the same direction causing either an upward or downward trends
Ten (10) successive points on the same side of the average value of the chart

Out-of-Control - Any points outside the Upper and Lower Control Limits (UCL, LCL)

Classification of Errors

- 1. Constant Error
- (a) Systematic Error: Error caused by defectiveness of instrument and analytical method.
- (b) Human Error: Error caused by excess/miss-estimation of area/scale markings due to the habitual practice of laboratory staff.
- If the cause can be found, the constant error can be sometimes compensated because it shares a constant ratio and magnitude in the analysis. However, when the analyzed values are affected by chromatic interference of concomitant substances, it is difficult to compensate using the simple equation.
- 2. Gross Error
- Gross error is defined to be the error caused by carelessness like mistakes on unit, *lapsus calami*, etc., and it is possible to be found by consecution of the analytical procedure and calculation results.
- 3. Accidental Error
- Aside from constant and gross errors, an error may occur accidentally. Accidental error is defined to be the error caused by many unknown factors and it is very difficult to avoid it even if the instrument is highly sensitive and analysts pay attention to the analysis procedure. Such an error can be used for the statistical analysis.

SRMs COMMERCIALLY ABAILABLE IN JAPAN

No.	SRMs	Contents	Parameters	Supplier
11	Dry Fish Meal Powder	20g	TBT, TPT	Japanese National Environmental Institute
12	Marine Sediment	30g	TBT, TPT	Ditto
1939a	Polychlorinated Biphenyls in River Sediment A	50g	PCB	US Standard Technology Bureau
1941a	Organics in Marine Sediment	50g	PCB, PAH, Organic-Chlorine Pesticides	Ditto
1944	New York-New Jersey Waterway Sediment	50g	PCB, PAH	Ditto
1974a	Organics in Mussel Tissue (Frozen)	3 pieces	PCB, PAH, Organic-Chlorine Pesticides	Ditto
JSAC 0421, JSAC 0.422	Soil	60g	DBD, DBF, co-PCB	Japan Society for Analytical Chemistry
JSAC 0421, JSAC 0.422	Fly Ash	50g	DBD, DBF, co-PCB	Ditto
JSAC 0421, JSAC 0.422	Soil	60g	Cymazine, Dildline	Ditto
JSAC 0421, JSAC 0.422	River Sediment	60g	DBD, DBF, co-PCB	Ditto
JSAC 0421, JSAC 0.422	Marine Sediment	60g	DBD, DBF, co-PCB	Ditto

Error Control Management

- Errors caused by uncertainty of paperwork that mainly consist of the mix-up of samples and mistakes in recording and calculations often occur. Among them, carelessness is mainly attributed to errors, but it is meaningless to magnify the carelessness.
- The most important measure is to establish a system that is effective for the automatic prevention of errors with work as small as possible. To minimize mistakes in transcribing, it is necessary to plan skipping the transcription.
- Moreover, to avoid miscalculation, it is indispensable to cogitate or explain the calculation process and equation to make them understandable.
- Also, formats of analytical reports should be prepared with detailed countermeasures to prevent generating mistakes.

Conditioning of Analytical Instrument

- Analytical equipment used should be conditioned to enable the analysis of samples under the sensitivity required by each analytical method. At the same time, it is necessary to confirm situations with or without chromatic interference and matrix effect that may cause analytical errors, and whether or not it is possible to adjust/avoid them.
- Reliability as well as sensitivity, selectivity, linearity and stability of the instrument also should be confirmed.

Performance Check of VIS/UV Spectrophotometer

- Spectrophotometers should be retain their wavelength accuracy for the life of the instrument under normal operating conditions. To confirm the performance of the spectrophotometer, the wavelength accuracy must be periodically checked as follows (One of the methods):

(1) Wave length Calibration Check

Good results may be produced by measuring the absorbance of a cobalt chloride solution (22 to 23g of $CoCl_2$, dissolve and dilute to 1 L with 1% HCL solution) on 500, 505, 510, 515 and 520nm wavelengths. The wavelength calibration check is satisfying when maximum absorbance occurs between 505 and 515 nm.

(2) Linearity Check

Linearity check of each instrument is given by the measurement of the absorbance at 510 nm of the stock and the 1:1 diluted cobalt chloride solution. The absorbance of the 1:1 diluted solution ahould be half of the stock value in correct operation.

Performance Check and Calibration of Balance

- Balances are very delicate instruments. The proper use and care the balances is imperative. The following comprehensive rules should be followed to protect and keep this important laboratory equipment in excellent condition.
- Balance should be on a heavy, shockproof table, with adequate working area, and a drawer for the balance accessories. They should be located away form traffic area and protected from sudden drafts and humidity changes.
- In balance, it is necessary to keep desiccant inside to protect from humidity.
- Temperature should be room temperature.
- Special precaution should be taken to avoid spillage of chemicals on the pan or inside the balance.
- It is necessary to check to make sure the balance is in a level condition, and the balance should be adjusted to zero with zero adjustment prior to use.
- When the balance is not in use, the beam should be raised, the weights returned to the beam, objects removed from the pan, and weighing compartment closed.

Four (4) Different Grades of Laboratory Water (ASTM)

Grade of Water	Maximum Toatal Solids (mg/l)	Maximum EC (uS/cm)	pH
Type I	0.1	0.06	-
Type II	1.0	1.00	-
Type III	1.0	1.00	6.2 -7.0
Type IV	2.0	5.00	5.0 - 8.0

Reagent Grade Water Used in Laboratory

- Type I : Water has no detectable concentration of the compounds or element to be analyzed at the detection limit (IDL) of the analytical method. Type I water in test methods requiring minimum interference, bias and maximum precision.
- Type II : Water is intended to provide the user with water in which the presence of bacteria can be tolerated. It is used to prepare reagents, dyes, or staining.
- Type III: Water may be used for glassware washing, preliminary rinsing of glassware, and as a feed-water for production of higher quality grade water.
- Type IV: Water is used for another purpose except for Type I, II, III.

Standard Material (Solution)

- It is recommendable to use a standard material (solution) assured by the trace ability wherever possible to assure the reliability, because analyzed value is obtained based on concentration. If impossible to obtain a standard material, it is necessary to substitute it using high-grade reagents with quality of more than 98% purity for semi-micro analysis.
- Detailed information such as name of supplier, lot, source, conditioning method and date of manufacture of the standard material (solution) should be adequately recorded. When the standard solution is stored, it is indispensable to note the expiration date, and to confirm the change of concentration before using.

Duplicates Samples

- To keep the comprehensive reliability for sampling, pre-treatment procedures and analysis using instrument, more than two (2) samples prepared under the same condition should be analyzed. Such analysis is called “Double Analysis”.
- Recommendable frequency of double analysis is once per 10 samples. It is necessary to confirm that the difference between the values of more than two (2) samples analyzed is less than 30% compared to the average value of analysis results.
- In case of appearance of large values, re-measurement should be done after removal of the causes.

Management of Abnormal/Missing Values

- When unsatisfactory cases are found like large values of operational blank test, large difference between the double analysis values and abnormal values of the travel blank tests, re-measurement should be done because analysis data are considered to be unreliable and missing values.
- Re-measurement not only involves manpower, a long time and cost, but also hinders analysis and affects the evaluation of the entire investigation due to the different sampling periods. Therefore, it is essential to check in advance, and to pay attention to the emergence of abnormal and missing values.
- Further, if abnormal and missing values are obtained, it is necessary to sufficiently examine the process of their emergence, and to keep them on record in order to avoid their re-occurrence.

RECORDING OF OPERATION

- (1) Method of Taking Samples, Storage and Transportation
- ・Identification, adjustment and operation of instrument and glassware.
- ・Condition of target samples (sampling method, sampling locations, sampling date, etc.)
- ・Climatic conditions
- ・Condition of handling and storage of sampling vessels, etc.
- ・Method of transportation
- (2) Information Related to Samples
- ・Water Quality: pH, concentration of organic pollutants, SS, etc.
- ・Sediment: External view, odor, water contents, ignition loss, etc.
- ・Biological Samples: Species, growth condition, lipid contents, etc.
- (3) Method and Condition regarding Conditioning of Samples
- ・Water Quality: With or without filtration and its method, etc.
- ・Sediment: With or without removal of pore water and its method, etc.
- ・Biological Samples: Sampling position and its method, etc.
- (4) Method of Pre-Treatment
- ・Modification, change for the better, improvement factor and so on
- ・Other remarkable items
- (5) Records regarding Operational Condition and Calibration of Instrument
- ・Suppliers of equipment, product number, performance condition, etc.
- ・Record of operation and maintenance
- (6) Various Kinds of Values Obtained in the Course of Analysis
- ・Sample size for the analytical procedures, extract quantity, condensation ratio, etc.
- ・Setting condition of each instrument, etc.

REPORTING REGARDING ACCURACY CONTROL

- (1) Sample identification including taking samples, transportation and storage.
- (2) Analytical procedures such as date of analysis, method number for the analytical method used, condition of pre-treatment, generated raw data, calculation process, analytical calibration/standardization/frequency, corrected/reported data, and name of the analysis staff.
- (3) Determination of IDL (Instrument Detection Limit).
- (4) Determination of MDL (Method Detection Limit).
- (5) Determination of Detection Limit at the sample analysis.
- (6) QC check samples preparation, QC requirements, QC routine checks related to the analysis such as operation blank test, double analysis, travel blank test, testing for additional recovery rate, data validation/reduction and so on.
- (7) Others (preparation of reagents, standards, electronic data documentation).

Inventory for Analytical Equipment

- (1) Based on the inventory data prepared, major instruments actually equipped should be listed-up in each laboratory basis;
- (2) Major instruments should be grouped according to kind of instrument and application;
- (3) Official inventory consists of instrument name, model number/name, manufacturer name, target parameters/application, key point of maintenance, current operational condition, priority of repairing, person in charge of operation and maintenance, etc;
- (4) Operational condition can be classified into following four (4) categories: good condition and frequently used, no problem and can be used, necessary to replace spare parts or to be repaired and completely broken or no use.

Equipment and its Software

- Equipment and its software used for testing, calibration, and sampling shall be capable of achieving the accuracy required and shall comply with specification relevant to the tests and/or calibrations used.
- Calibration programmers shall be established for key quantities or values of the instruments where these properties have a significant effect on the results.
- Before being placed into service, equipment shall be calibrated or checked to establish that it meets the laboratory's specification requirements and complies with the relevant standard specification.

Form of Logbook for each Equipment

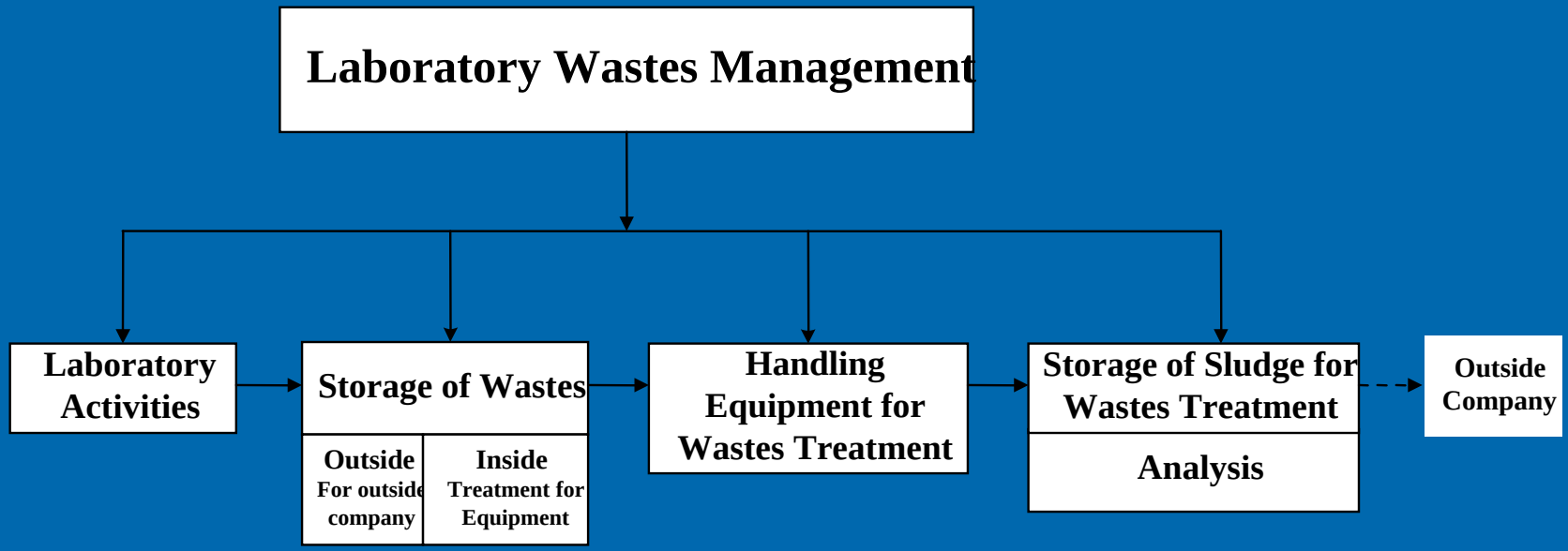
No.	Date	Operator	Analyzed Parameters	Kind of Sample	Operational Condition and Checking Items	Output (File Name)	Remarks

Laboratory Personnel in charge of O&M

- Equipment shall be operated by authorized personnel.
- Deployed responsible personnel should constantly take care of the analytical equipment, and periodically report the current status of the equipment to the manager.
- All the checking data and repairing works should be recorded in the logbook. And always stock of spare parts and expendables should be recorded in the ledgers.
- It is recommendable to consider the setting condition of the analytical equipment. If the inadequate setting condition is found, it is essential to improve the setting condition.
- Instruction and manual on the use and maintenance of equipment shall be available for use by the appropriate laboratory personnel.

3. Laboratory Wastes Management

Whole System for Laboratory Wastes Management



Classification
Stock of Cotainer
Logbook (Volume, Date, Who, from Where)

Preaparation: Necessary container
Keep condition of wastes container
(Labeling, Safe keeping)
Logbook (Volume, Date, Who, from Where)

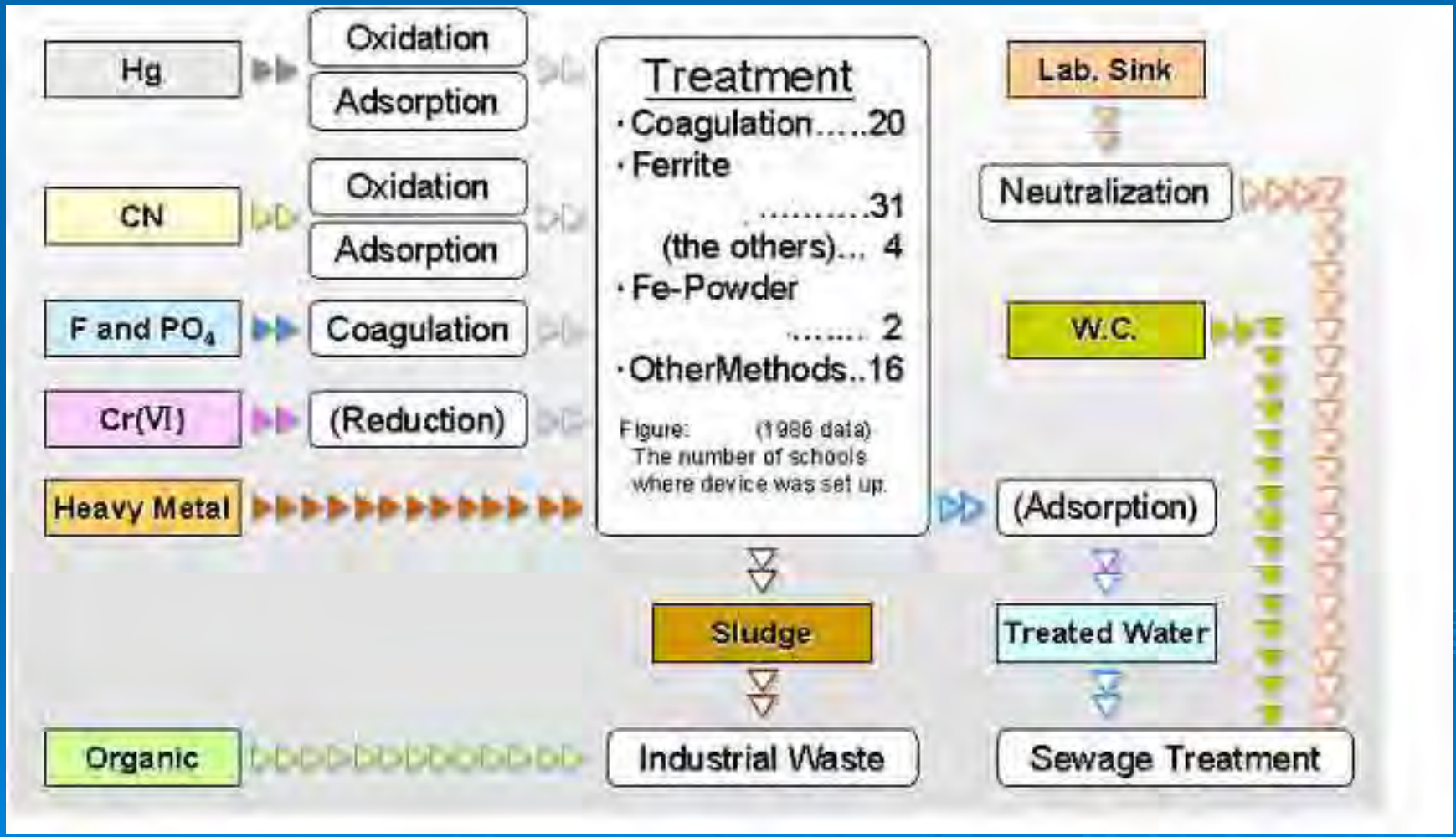
Treatment
Who will operate it?
(House keeping staff)
Preparation of chemicals for operation
Logbook (Volume, Date, Who, from Where)

Confirmation to outside company
Making report for wastes management activities
Preparation of chemicals
Analysis treated wastewater
Logbook (Volume, Date, Who, from Where)

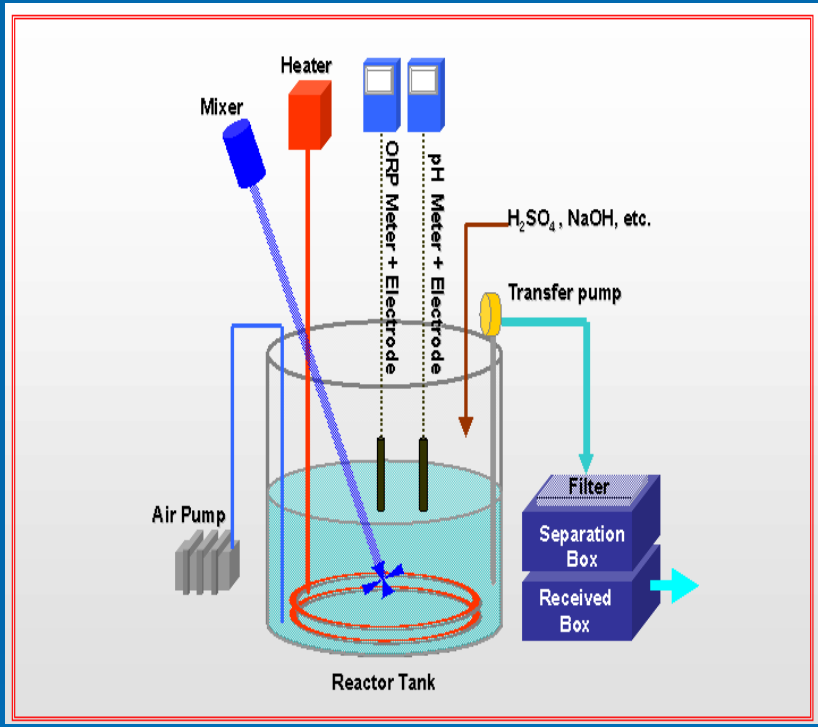
Procedure for Collection of Wastes

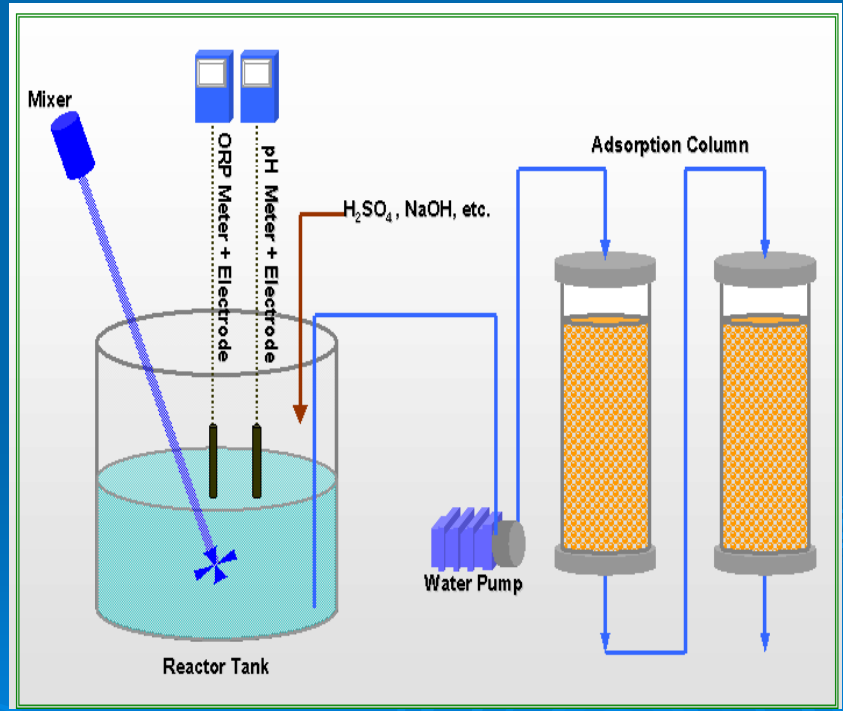
- Collection of liquid wastes should be implemented through the categorization of liquid wastes produced by environmental laboratories.
- In practice, the collection of waste is conducted in container with following requirements:
- (1) Use plastic container that is corrosive resistant
- (2) Volume of the container should be conformed with the category of the waste.
- (3) Container must ensure safety
- (4) Labeled in accordance to the category of waste
- (5) Should include instructions for storage or each category or waste, for example: “store at a pH less than 7”, etc.

Selection of Treatment Methods



Basic Style of Device for Treatment





Discharging Treated Wastes

Wastes Minimization

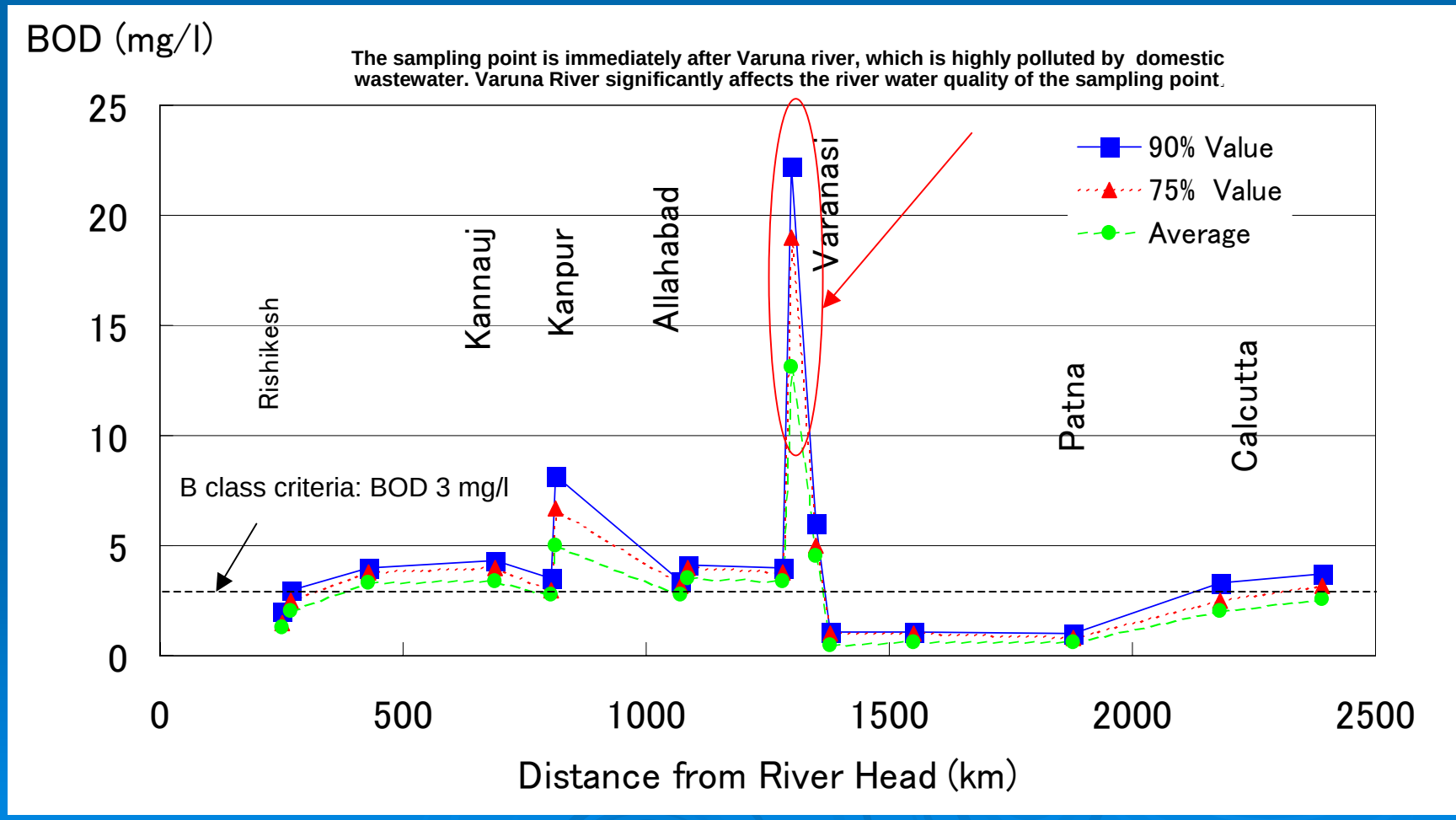
- (1) Consideration on Sample Volume
- (2) Treatment to reduce hazards
- (3) Substitutions of less hazardous materials
- (4) Procedural changes to minimize generation
- (5) Improved laboratory management practices

4. Analytical Key-points for Basic Parameters

Data Evaluation

- 1. Understanding the Real Meaning of Basic Parameters
- 2. Statistical Analysis
- 2.1 Mean, Minimum, Maximum Data
- 2.2 Percentile Value
- 3. Comparison of Data
- 3.1 Environmental Standards
- 3.2 Normal Distribution in the Measurement (including data of another countries)
- 3.3 Checking Co-relation between Parameters
- 4. Graphical Presentation
- 4.1 Longitudinal Water Quality Change in Rivers
- 4.2 Annual, Monthly Change in the Monitoring Points
- 5. Pollution Sources
- 5.1 Inventory of Pollution Sources
- 5.2 Distribution of Pollution Sources regarding Monitoring Points
- 6. Simulation Study
- 6.1 Calculation of Pollution Loads
- 6.2 Future Prediction of WaterQuality

EXISTING RIVER WATER QUALITY
GANGA MAIN STEM, - ORIGIN TO CALCUTTA -



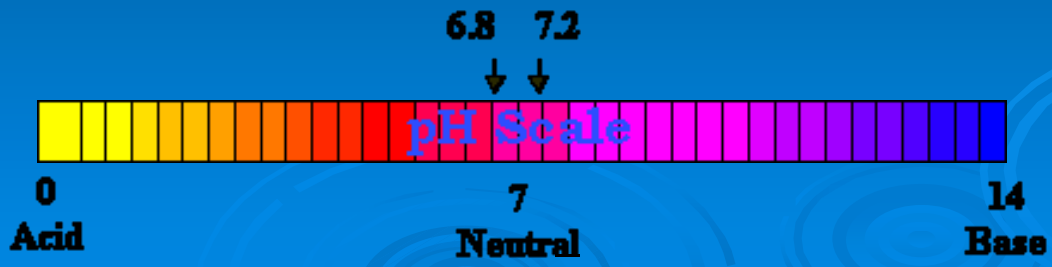
Meaning of BOD Value

- BOD means the dissolved oxygen which will be consumed by aerobic microorganisms in water.
- It is expressed by the amount of dissolved oxygen consumed at 20℃ for 5 days after the sample has been treated.
- BOD is one of the most important parameters used for the evaluation of organic pollution of river water quality.
- To keep the self-purification effect in the river course, it is required to maintain 4 – 5 mg/l of BOD.

Meaning of pH Values

- (1) pH is a measure of how acidic the water is.
- (2) pH = -log a_H

  where a_H is the "activity" of hydrogen ions in the solution. So pH is simply a measure of the hydrogen ions (H^+; protons)
- In a sense, all that most aquarists need to know is that pH is a measure of the hydrogen ions in solution, and that the scale is logarithmic. That is, at pH 6 there is 10 times as much H^+ as at pH 7, and that at pH 6 there is 100 times as much H^+ as at pH 8.
- The centimeter is a unit measure of length. The gram is a unit measure of weight. Similarly, pH is the unit measure we use to say how much free or active acid is in a substance. The pH scale goes from 0 to 14. A pH of 0 means a very high acid activity; a pH of 14 means a very low acid activity. In between these two extremes is a pH of 7. This is the pH of pure water



Meaning of Fecal Coliform

- Among the coliform bacteria, there are not only natural origins but also zoo-origins.
- To evaluate the hygienic condition, it is necessary to analysis fecal coliform number as well as total coliform number.
- Fecal coliform group consists of Escherichia genus, Klebsiella genus, Enterobactor genus, Citrobacter etc..
- Among the fecal coliform group, Escherichia genus is specified as an origin of fecal matter.
- It is very difficult to completely analyze E. coli.

Basic Information on the Bacterial Contamination

1. Coliform bacteria are used as the index of the hygienic quality of water for several beneficial uses and for many foods. About one-quarter of the 100 to 150 grams of feces produced per person per day is bacterial cells.

2. It is reported that coliform organisms are at an output of 300 billion per capita per day. Further, $100*10^9$ MPN/100ml of coliform bacteria contains in a fresh domestic wastewater in Japan.

3. The intestinal bacteria dies according to flowing process in a stream. In case of warm-weather condition, 90% of coliform organisms die within two days, and 99% of ones die within five days.

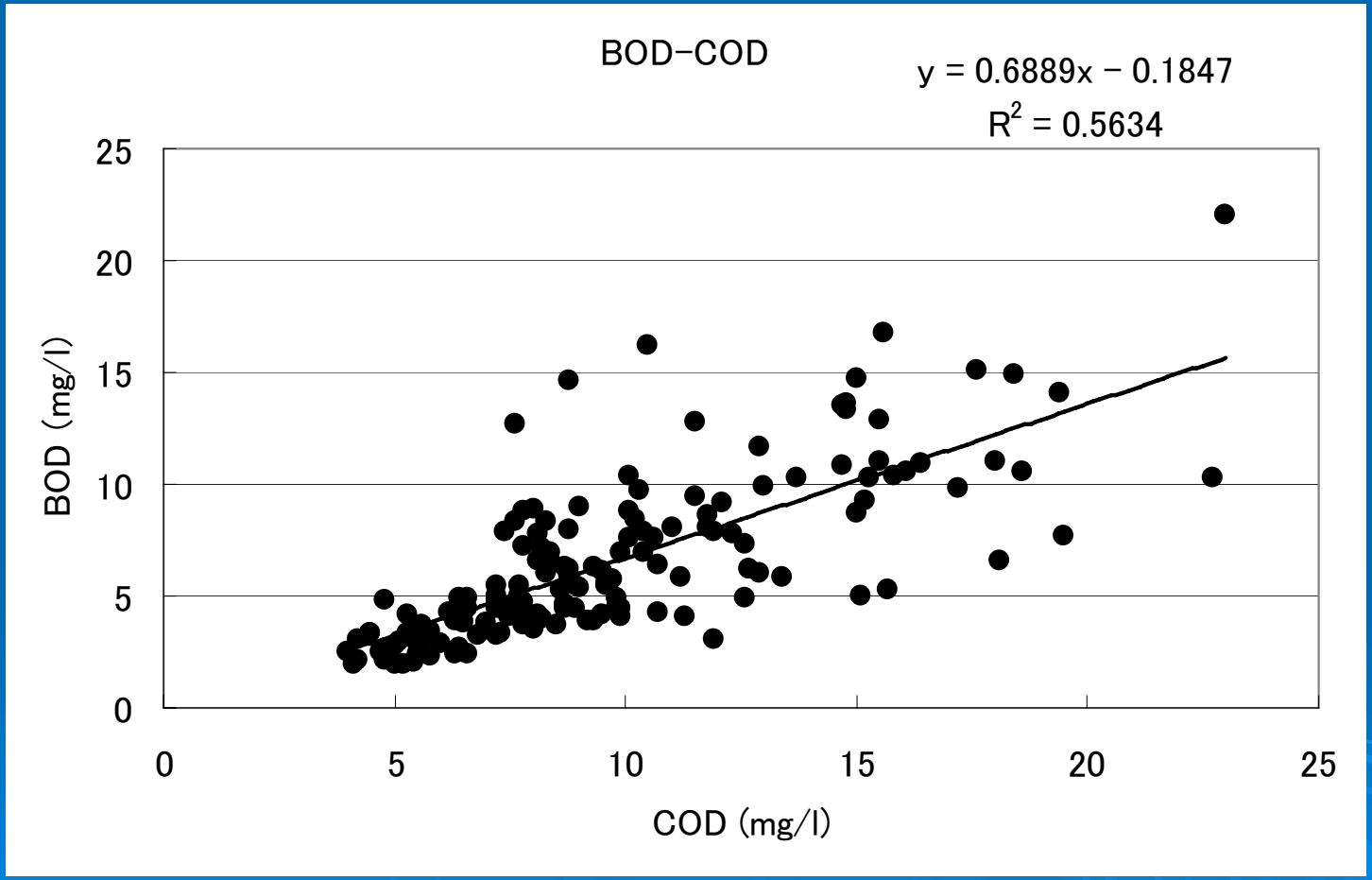
4. Coliform number varies depending on the organic pollution of river.

More detailed Information should be collected by actual monitoring

Co-relation among Basic Parameters

- There is a certain co-relation between basic parameters focused on organic pollution of the river water.
- Basic parameters of organic pollution such as BOD, COD, Coliform number, Electro-conductivity and DO, should be accurately analyzed for evaluation of degree of river water quality pollution.
- Values of BOD, COD, Coliform number and NH_3-N, Electro-conductivity are low in the clean river stretch, and DO Value is high.
- On the other hand, above-mentioned parameters indicate opposite trend in the polluted river stretch.
- Co-relation among basic parameters can be used for accuracy control of the analysis data in some senses.

Co-relation Between BOD & $COD_{(Mn)}$ (Ayase River in Tokyo)



General Requirement for pH Analysis

- For best accuracy, a pH meter should be standardized using a standard solution whose value is near that of the test solution. However, standardizing with the pH = 6.86 standard constitutes a good compromise when the test solutions cover a broad range of pH values.
  - A pH meter may be standardized as follows:
- 1. Rinse electrodes with distilled (or deionized) water and blot dry.
  2. Place electrodes in pH standard buffer solution.
  3. Adjust pH meter temperature dial to the temperature of the standard solution.
  4. Turn pH meter to "operate."
  5. Adjust pH meter to the pH value of the standard, using the "standardize" control. THE pH METER IS NOW STANDARDIZED.
  6. Turn pH meter to "standby".
  7. Remove electrodes from standard and rinse with water.
  - The pH Measurement Procedure
- Once the pH meter is standardized, the measurement procedure is as simple as this:
- 1. Rinse electrodes with distilled (or deionized) water and blot dry.
  2. Place electrodes in test solution.
  3. Adjust pH meter temperature dial to the temperature of the test solution.
  4. Turn pH meter to "operate."
  5. Read the pH of the test solution on the pH meter directly.
  6. Turn pH meter to "standby."
  7. Remove electrodes from test solution and rinse with water.

General Requirement for BOD Analysis

- The BOD test shall be carried out immediately after sampling. When immediate test is impossible, it is necessary to preserve the sample in refrigerator, and to carry out the test as soon as possible.
- The BOD test generally includes large error due to the delicate analytical process, feature of biological testing, contamination of glassware and so on.
- It must be paid attention to bubbling of air in the culture bottle that affects errors through all the analysis process of BOD, therefore, siphon should be used for operation.

THANK YOU VERY MUCH !!

References Cited

- (1) Accuracy Control

  ・Monitoring and Survey Manual, Part II Analysis Method, Chapter 2 Accuracy Control of Measurement, Japanese Ministry of Environment.

  ・Environmental Sampling and Analysis for Technicians, MARIA CSUROS.

- (2) Laboratory Wastes Management

  ・Guideline prepared in JICA PROJECT FOR STRENGTHENING THE DECENTRALIZED ENVIRONMENTAL MANAGEMENT SYSTEM IN INDONESIA

- (3) Analytical key-point for Basic Parameters

  ・Analysis Manual for River Water Quality, Japanese Ministry of Land & Transportation, and others.

ANNEX (12)

JAPAN INTERNATIONAL COOPERATION AGENCY (JICA)

MINISTRY OF HOUSING, USE OF LAND AND ENVIRONMENT
THE ORIENTAL REPUBLIC OF URUGUAY

THE PROJECT ON CAPACITY DEVELOPMENT FOR WATER QUALITY MANAGEMENT IN MONTEVIDEO AND METROPOLITAN AREA

OUTLINE OF ACCURACY CONTROL SYSTEM FOR ENVIRONMENTAL MONITORING DATA IN JAPAN

TEXTBOOK

August 2006

CTI ENGINEERING INTERNATIONAL CO., LTD.

OUTLINE OF ACCURACY CONTROL SYSTEM FOR ENVIRONMENTAL MONITORING DATA ADOPTED IN JAPAN

TABLE OF CONTENTS

1. INTRODUCTION

When accuracy control is extensively interpreted, and adequate information is presented in order to comprehend the trend of change of concentration of pollutants in the environment, it is required to consider the following:

(1) Are monitoring points adequate?

(2) Is the analysis method well suited?

(3) Is the targeted accuracy correct?

(4) Is the accuracy of method kept well?

(5) Are sampling methods and their number of times appropriate?

Accuracy control is defined as the management of analytical procedures using various methods including statistical analysis in order to always report the analysis results obtained from analytical data with precision and accuracy. It consists of a sequence of work operations aiming at the following: (i) To know the kind and magnitude of error in the analysis; (ii) To assess whether the error is admissible or not; (iii) To search for the cause in case of inadmissible; (iv) To improve by removing the cause from the analytical procedures; (v) To investigate remedial measures by introducing more accurate technology; and, (vi) To routinely prepare the documents containing the procedures for maintaining reliability. The meaning of accuracy is how close the analytical data are to the true values, and the precision is used for the judgment on the degree of deviation obtained by repetition analysis. Both are distinctively used. When the described accuracy and precision is assured in long-range, the analytical method is considered reliable. For a monitoring study, it is necessary to analyze extremely small amounts of contents in complex samples like environmental water and sediment in long-range, maintaining reliability. In long-range monitoring, the possibility of fluctuation of accuracy and precision becomes higher with the change of various factors such as renewal of analytical instruments and replacement of laboratory staff. To adequately maintain accuracy control is an essential issue in determining the feasibility of monitoring, because scientific evaluation of the monitoring results is conducted through the analytical data containing the error.

2. GENERAL REQUIREMENTS OF THE ACCURACY CONTROL SYSTEM

2.1 Precision Control Management

(1) Average Value and Standard Deviation

The degree of deviation based on repeatedly carried out measurements is called precision, and it is possible to indicate it using the value of average and standard deviations. Generally, the distribution of repeated measured values is considered to be normal distribution on the mean value. In the normal distribution group, about two-thirds of all measured values is distributed in the range from mean value to both sides of inflection points. The distance from mean value to inflection point is called standard deviation, and it can be called measurement with high accuracy, since standard deviation is smaller. The analyzed concentrations indicate various values in every sample; therefore, there are many cases that show unserviceable methods using

the standard deviation as mean value and index to the accuracy. Generally, the ratio of mean value versus standard deviation, namely, coefficient of variation (CV%) is used in many cases.

(2) Samples for Accuracy Control Management

In environmental analysis, sometimes, accuracy is managed by CV values obtained by multiple analyses of samples. However, the results are used only for the index of accuracy regarding the daily analysis values; hence, the accuracy of continuous fluctuation of analysis results and the mean value necessary for the long-term monitoring are not assured. Further, even if there are cases where mean values and standard deviations obtained by analyzing the standard solution are managed, it is impossible to evaluate the error which comes from the difference of matrix constitution between the standard solution and the samples. Accordingly, it is ideally desirable to simultaneously analyze the sample used for the accuracy control with properties equal to the actual samples. Prior to the start of monitoring, it is recommendable to store and preserve the sub-sectioned one made by homogenizing the samples obtained from the monitoring site as the sample for accuracy control.

(3) x-R Control Chart Method

The x-R control chart is to be prepared by plotting the mean values and differences obtained by analyzing the samples two (2) times for the accuracy control using the same method at the same time with a series of actual analysis of samples. Fluctuation of the mean value reflects factors such as change of standard solution, contamination of instrument and reagents, change of sensitivity of measuring instrument, and renewal of measuring technique; while, the fluctuation of difference reflects the precision of analysis operation of pipetting in the day, etc., and the stability of the analytical equipment, etc. It is called the stable state when the mean value settles down in the range where x and R is fixed in this control chart. On the control chart, this stable stage should be controlled by drawing two (2) management sample lines on the position equal to three (3) times (more than 99% of samples are included) of standard deviation, and centering the mean values of average value (x). When analysis values are longer within the limit line, certain conditions shall be considered in the series of analysis. On the other hand, when deviant values from this range are obtained, it is necessary to take measures because some abnormal conditions may have occurred.

(4) Allowable Limit of Accuracy

The aforementioned allowable limit is obtained through calculation of the analysis results in order to assure the accuracy of the analysis value; however, it is out of relation to the requirement regarding availability of data. The allowable error in long-term monitoring for trace contents of pollutants should be determined for the purpose of grasping the long-term fluctuation of the pollutant in the environment. Further, needless high precise measurements and analyzes with accuracy larger than the permissible limit should be avoided.

2.2 Accuracy Control Management

It is very difficult to completely find out the true value of concentration of pollutants in water and sediment even if the analysis is carefully carried out. Accuracy is defined as the degree of deviation of the analyzed value from the true values of target substances. The difference between the true value and the analyzed value is called the error. Error is classified into the following three (3) kinds according to the various causes:

- Constant Error

  (a) Systematic Error: Error caused by defectiveness of instrument and analytical method.

  (b) Human Error: Error caused by excess/miss-estimation of area/scale markings due to the habitual practice of laboratory staff.

  If the cause can be found, the constant error can be sometimes compensated because it shares a constant ratio and magnitude in the analysis. However, when the analyzed values are affected by chromatic interference of concomitant substances, it is difficult to compensate using the simple equation.

- Gross Error

  Gross error is defined to be the error caused by carelessness like mistakes on unit, *lapsus calami*, etc., and it is possible to be found by consecution of the analytical procedure and calculation results.

- Accidental Error

  Aside from constant and gross errors, an error may occur accidentally. Accidental error is defined to be the error caused by many unknown factors and it is very difficult to avoid it even if the instrument is highly sensitive and analysts pay attention to the analysis procedure. Such an error can be used for the statistical analysis.

(1) Addition & Recovery Test

Addition & recovery test is defined to be a method used for testing that a given quantity is added to the analytic sample for the confirmation on whether it has been accurately analyzed or not. For example, when 10 ng/g of HCB is added to the sediment sample of which concentration of HCB (analysis value) is 10 ng/g and analyzed value is obtained as 19 ng/g, the sediment sample's recovery rate is estimated to be 90%. To obtain the correct recovery rate, it is essential that the target substances could be obtained as authentic reagents, and addition is done under the actual condition of the target substances. Based on the additional recovery testing, it is possible to confirm the error (multiplier error) existent at constant ratio. If the linearity of calibration curve is confirmed in advance, addition & recovery test can compensate such multiplier error.

(2) Operational Blank Test

When target substances contaminate the instrument, glassware and solvents, positive error is given. If the analytical procedure has been adequately carried out, the analyzed value has a constant positive error in many cases. This can be compensated by operational blank test.

(3) Standard Reference Material (SRM)

Standard Material is intended for use in developing and validating analytical methods for the determination of each parameter. Currently, SRMs with validated concentrations are commercially available in Japan (See Table-2). SRMs are prepared by the procedure that solid samples taken from various environments are mixed and sub-sectioned after crushing. Validated concentration is decided from comprehensive standpoints using average values of parallel analyses conducted in authoritative institutions or many reliable laboratories under the orthodox standard method, because their absolute contents are unknown.

However, when SRMs are targeted, it is doubtful that certain methods can absolutely analyze their contents; therefore, validated values are widely ranged in many cases. The actual environmental samples cover a lot of elements such as water, soil, air, powder, dust, biological samples, etc.; hence, every kind of SRM should be prepared. On the other hand, it is impossible in fact to obtain SRMs that have completely the same feature (matrix) as the analytes like sediment because grain size widely ranges from sand to clay. Therefore, it is recommendable to think that it is impossible to calibrate instruments by using SRMs. SRMs are not versatile, hence, when laboratory staff take turns, it is recommendable for them to adopt the confirmation and management of accuracy control used in the first operation stage of analysis. For example, when the x-R control chart slightly changes, it is very difficult to distinguish whether the change was derived from analytical procedure or from the deterioration of standard solution. If SRMs are used, it is easy to distinguish both reasons. The Japanese National Environmental Institute started to prepare and deliver SRMs from 1980.

2.3 Management of Detection Limit Control

The analytical methods used for the long-term monitoring of environmental pollutants are established for the purpose of obtaining analysis results with sufficient accuracy as prescribed, and are based on the presupposition that the detection limit of the analytical method is sufficiently small. However, it is sometimes difficult to detect the target parameters because their concentrations are extremely low. The detection limit is sometimes dealt as figures during the statistical treatment; hence, it is probable that the fluctuation of the detection limit affects the evaluation of monitoring results (accuracy). Accordingly, it is essential to manage the uniform detection limit throughout the monitoring period as described in later sections.

Table-2 SRMs Commercially Available in Japan

No.	SRMs	Contents	Parameters	Supplier
11	Dry Fish Meal Powder	20g	TBT, TPT	Japanese National Environmental Institute
12	Marine Sediment	30g	TBT, TPT	Ditto
1939a	Polychlorinated Biphenyls in River Sediment A	50g	PCB	US Standard Technology Bureau
1941a	Organics in Marine Sediment	50g	PCB, PAH, Organic-Chlorine Pesticides	Ditto
1944	New York-New Jersey Waterway Sediment	50g	PCB, PAH	Ditto
1974a	Organics in Mussel Tissue (Frozen)	3 pieces	PCB, PAH, Organic-Chlorine Pesticides	Ditto
JSAC 0421, JSAC 0.422	Soil	60g	DBD, DBF, co-PCB	Japan Society for Analytical Chemistry
JSAC 0421, JSAC 0.422	Fly Ash	50g	DBD, DBF, co-PCB	Ditto
JSAC 0421, JSAC 0.422	Soil	60g	Cymazine, Dildline	Ditto
JSAC 0421, JSAC 0.422	River Sediment	60g	DBD, DBF, co-PCB	Ditto
JSAC 0421, JSAC 0.422	Marine Sediment	60g	DBD, DBF, co-PCB	Ditto

2.4 Proficiency Test

A proficiency test (PT) scheme comprises the regular distribution of test materials to participating laboratories for independent testing. The results are returned to the organizer of the scheme who makes an analysis of the results and reports the analysis results to all the participants. It is well known that the results of proficiency tests conducted by the participating laboratories and obtained from the same analytical method vary widely considering that their values are normal distribution with a center line of average value. Due to these results, the average value of the proficiency test could not be certified as less erroneous; therefore, if the results of a certain laboratory accord the average value, it is difficult to say that laboratory's data are accurate. On the contrary, if the laboratory's data are always equal to the constant position of normal distribution, the accuracy could be considered as authentic. Further, if the position of distribution of that laboratory's data often fluctuates, it is supposed that there are some problems in the accuracy of analysis. In case of separate analysis among several laboratories, it is may be possible to manage the accuracy among these laboratories by the proficiency test.

The Japanese Ministry of Environment has been conducting proficiency tests, as shown in the table attached to ANNEX. Based on the results, the main outputs were used for the improvement of accuracy. Surveys were conducted and their results were used for improvement of participated laboratories' accuracy by feedback information, as described below:

(1) Interview Survey was conducted on laboratories concerned, for the purpose of confirming the reason why unsatisfactory analysis results were obtained.

(2) Site Visit Survey were carried out on laboratories that submitted unsatisfactory analysis results with reasons unidentified through the interview survey, for the purpose of confirming further reasons why the unsatisfactory analysis results were obtained.

(3) Various statistical arrangements were made on the analysis results.

2.5 Error Control Management

Errors caused by uncertainty of paperwork that mainly consist of the mix-up of samples and mistakes in recording and calculations often occur. Among them, carelessness is mainly attributed to errors, but it is meaningless to magnify the carelessness. The most important measure is to establish a system that is effective for the automatic prevention of errors with work as small as possible. To minimize mistakes in transcribing, it is necessary to plan skipping the transcription. Moreover, to avoid miscalculation, it is indispensable to cogitate or explain the calculation process and equation to make them understandable. Also, formats of analytical reports should be prepared with detailed countermeasures to prevent generating mistakes.

3. EVALUATION OF PERFORMANCE OF ANALYTICAL EQUIPMENT AND OPERATION AND MAINTENANCE

3.1 Conditioning of Analytical Instrument

Analytical equipment used should be conditioned to enable the analysis of samples under the sensitivity required by each analytical method. At the same time, it is necessary to confirm situations with or without chromatic interference and matrix effect that may cause analytical

errors, and whether or not it is possible to adjust/avoid them. Reliability as well as sensitivity, selectivity, linearity and stability of the instrument also should be confirmed.

3.2 Instrument Detection Limit (IDL)

IDL can be calculated based on the extent of data resulting from the repetitive application of standard solution using the minimum concentration of the standard solution for calibration. If possible, 7 or more standard deviation(s) shall be obtained by repetitive test using the standard solution with S/N ratio of 5-15. Calculation method of actual S/N ratio is shown in ANNEX.

IDL can be calculated by the following equation:

$$IDL = s \times t^*(n-1, 0.01)$$

Where,

$t^*(n-1, 0.01)$ is the value of the degree of freedom $(n-1)$ of which the t value or risk ratio is 1% (one-sided). Further, in case the testing number is $n = 7$, the $t^*(n-1, 0.01)$ value should be 3.143. (For details, see Table-1.)

If abnormal values or outliners are observed among the results of repetition analysis, it is necessary to readjust the analytical equipment and to try the repetitive testing again. Further, the concentration value converted into the samples should be calculated from the sampling quantity, final fill-up fluid volume and injection volume into the equipment, and its value should be confirmed to be less than the target detection limit of each analytical method. If the converted concentration value does not satisfy the target detection limit, the reason should be found and resolved by readjusting the analytical equipment.

3.3 Operation and Maintenance of Analytical Instrument

To confirm whether the performance of each instrument is kept or not, evaluation items regarding the performance of instrument such as PTRI (Programmed Temperature Retention Index), degree of tailing, separation number (TZ: Trennzahl), resolution, IDL and so on should be set up, and periodically confirmed for the purpose of rectifying the change of performance of instrument. When deterioration of instrument is observed, it is necessary to adjust the instrument. Periodical operation and maintenance of analytical instrument should be conducted according to the frequency as shown in Table-2 attached in ANNEX.

4. RELIABILITY MANAGEMENT OF ANALYSIS RESULTS

4.1 Standard Material (Solution)

It is recommendable to use a standard material (solution) assured by the trace ability wherever possible to assure the reliability, because analyzed value is obtained based on concentration. If impossible to obtain a standard material, it is necessary to substitute it using high-grade reagents with quality of more than 98% purity for semi-micro analysis. Detailed information such as name of supplier, lot, source, conditioning method and date of manufacture of the standard material (solution) should be adequately recorded. When the standard solution is stored, it is indispensable to note the expiration date, and to confirm the change of concentration before using. Storage and preparation frequency of selected and standard solutions are shown in Table-3 attached in ANNEX.

4.2 Internal Standard Materials, Surrogate Materials

Internal standard materials or surrogate materials are used as additional standard materials indispensable for the internal standard method. The internal standard materials should be added to samples immediately before instrumental measurement, and are used to compensate

for errors regarding injection quantity of samples and fluctuation of instrument. Further, the surrogate materials are added to samples at the moment of taking samples or the stage of pretreatment, and are effective for the compensation of errors during the period from addition of surrogate materials to finishing of analysis. The selection of standard materials, as well as their stage of addition and quantities, should depend on each analytical method. The minimum requirements for the selection of standard materials are as follows: (i) distinguishable with target substances; (ii) nonexistent in the sample matrix; (iii) stable during the analytical process; (iv) same behavior as target substances; (v) high detection sensitivity, etc. In case of GC/MS, radical radioisotopes like 2H and 13C are frequently used; however, it is necessary to use high-grade standard materials wherever possible to avoid problems regarding the existent quantity of non-radical substances, to adequately report the name of supplier, lot, source, conditioning method and date of manufacture of these standard materials, and to clarify the expiration date of conditioned standard solution.

4.3 Preparation of Calibration Curve and Confirmation of Linearity

The standard solution for calibration curve should be prepared as follows: (i) minimum concentration should be almost twice as IDL; (ii) preparation of five (5) different standard solutions within the linear range; and (iii) addition of surrogate material to each standard solution. These are adopted as the standard solution sequence, and it is necessary to repeatedly analyze at least three (3) times, and to calculate RRF (Relative Response Factor) inherent to each instrument used. RRF can be obtained based on the relation between the concentration ratio of target substances/correspondent internal standard materials (surrogate materials) and the response ratio (peak area ratio) using the following equation:

$$RRF = (Cis/Cs) \times (as/Ais)$$

Where,

Cis: Concentration of internal standard material in the standard solution.
Cs: Concentration of target substance in the standard solution.
As: Response value of target substance in the standard solution.
Ais: Response value of internal standard material.

If the relative standard deviation of each RRF obtained by repeated analysis of standard solution sequence is within 5%, its average value is equal to the value of RRF in the inherent instrument used. Further, this could be adopted as criteria for the judgement on calibration curve available for the quantitative analysis. When the fluctuation exceeds 5%, readjustment of instrument and re-measurement should be done. On the other hand, when there is a transition of operative condition or conditioning of new standard solution, RRF should be newly calculated by repeated analysis of standard solution in the same sequence.

At the start of analysis of actual samples, it is necessary to confirm that the new RRF value obtained by the analysis using the standard sequence consisting of 2 to 3 kinds of concentration is less than 20% compared to the criteria value of RRF. After starting the analysis of actual samples, periodical analysis of the standard solution with the same concentration as envisaged for actual samples is required, and its RRF value should be confirmed to be less than 20% of fluctuation range. Further, it is necessary to confirm that the fluctuation range of relative retention with the standard solution is less than ±5%.

If the criteria values of RRF are not calculated, every time analysis of actual samples is conducted, it is necessary to prepare the calibration curve made by the relation between ratio of concentration and response obtained through the procedure of analyzing the standard solution consisting of more than five (5) scales of concentration. It is recommendable to

prepare the calibration curve at the stage of commencement of analysis, at mid-term and at final-term. After confirmation that the fluctuation regarding gradient of primary regression line is less than 20%, the newly prepared calibration curve can be used for the quantitative analysis.

In case of analysis without use of internal standard materials or surrogate materials, every time analysis of actual samples is conducted, it is necessary to analyze the standard solution sequence under the same way as the aforementioned method, and to prepare the calibration curve based on the relation between the concentration of samples and response ratio. Frequency of preparation of calibration curve should be more than three (3) times for a sequence of sample analysis, and it is indispensable to confirm that the fluctuation range of the primary regression line is less than 20%.

4.4 Operational Blank Test

Operational blank test is also called "Blank Test", and it is conducted to confirm any contamination caused by the sample preparation or sample injection procedure to the analytical instrument, to set up the analytical condition without problems, and to maintain the reliability of analytical data. Analytical procedure is as prescribed in each analytical method, and it is necessary to confirm whether or not target parameters can be detected using conditioned samples prepared only without sample matrix. If target parameters are detected, it is needed to grasp the concentration as well as with or without other obstruction contents, and to record their values for reference as occasion arises.

If the values of operational blank tests are large, the reliability of analysis value becomes deteriorated due to not only the increase of the detection limit but also the high possibility of emergence of abnormal values caused by human error. Accordingly, values of the operational blank test should be maintained at less than the target detection limit in order not to affect the analysis data. Frequency of the operational blank test is recommended to be once per 10 samples, or once a day (Number of Samples: <10).

4.5 Method Detection Limit (MDL)

Using the samples of which concentration is near the detection limit, analysis should be done through the prescribed method, and the given analysis results should be converted into concentration. This analytical procedure should be repeated more than seven (7) times. MDL can be obtained using values calculated by the aforementioned procedures, as follows:

$$MDL = s \times t^*(n-1, 0.01)$$

Where,

$t^*(n-1, 0.01)$ is the value of the degree of freedom ($n-1$) of which the t value or risk ratio is 1% (one-sided). Further, in case the testing number is $n = 6$, the $t^*(n-1, 0.01)$ value should be 3.14.

Table-2 Student's t-variant

Number of Repetitions	Degree of Freedom (n-1)	t(n-1, 0.01), One-Sided
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821

The MDL value obtained here should be confirmed as to whether or not it satisfies the target detection limit of each analytical method. If unsatisfied, it is necessary to re-adjust the analytical instrument. Further, it is possible to adjust by increasing the sample size or further concentrating the final fill-up quantity of samples injected into the instrument; however, the procedure should be documented.

MDL varies depending on the instrument used and the procedures adopted; therefore, when such conditions have changed, the MDL should be calculated to confirm the target detection limit as circumstances demand.

On the other hand, when the contents of the target substances are excessively high or low, adequate calculation of MDL cannot be done; hence, selection and conditioning of samples should be according to the following procedures:

(1) Selection of Samples used for Calculation of MDL

Samples used for the calculation of MDL should be selected among the ones where target/interfering substances are contained as small as possible. When their concentrations are unknown, it is necessary to prepare the samples with the same quantity as actual samples, and to analyze them using GC/MS and other equipment after prescribed pre-treatment and conditioning of sample solution. If their concentrations are less than five (5) times as target detection limit including operational blank test value, and interfering substances are also non-detected, it can be used as samples for MDL calculation.

(2) Conditioning of Samples

In accordance with the analysis results of the travel blank test (see Section 4.10) and the samples used for the MDL calculation, samples should be conditioned by the following procedures:

(a) In case Target Substances are Non-Detected (less than the target detection limit)

The target substances should be added to the selected samples in order to be five (5) times the target detection limit. At the same time, the prescribed quantity of surrogate materials should be added and well mixed or homogenized. After that, the conditioned samples should be analyzed through the prescribed procedure. The homogeneity of conditioned samples always becomes a subject of discussion, because MDL calculation should be on the grounds of more than seven (7) times of the repetition analysis results. Hence, it is desirable to prepare a sufficient quantity of MDL calculation samples for the series of repetition analysis at once.

(b) In case Target Substances are Detected, but their Values are less than five (5) times the Target Detection Limit

The target substance are added to the selected samples; however, it is required that the analyzed value of added samples is equal to almost five (5) times of the target detection limit by adjusting the addition quantity. After addition, the procedure is the same as the aforementioned manner. However, when the probability of human-induced bias is judged to be high by the addition of target substances, it is possible to directly use the selected samples for the repetition analysis without addition of target substances.

In addition, when target substances are detected through the operational blank test and their concentrations exceed (5) times of the target detection limit, calculation of MDL

should not be done, and it is necessary to remove the causes by reviewing the solvents, chemical reagents and equipment used.

(3) Analysis of Conditioned Samples

Conditioned samples should be analyzed according to the prescribed method throughout all of the procedures, including extraction, pre-treatment, conditioning of the solution and measurement. Analytical sample quantity should be the same as the actual samples and repetition should be at least seven (7) times. The results can be used as the basic data for the calculation of MDL.

4.6 Method Qualification Limit (MQL)

The method quantification limit (MQL) can be calculated, as follows:

$$MQL = MDL \times 3$$

Values of less than MDL are qualitative, more than MDL and less than MQL are semi-quantitative, and more than MQL is quantitative for the evaluation of magnitude relation of concentration. However, it is necessary to consider that even qualitative and semi-quantitative analysis results obtained under a well-managed accuracy control system can be used as the effective information.

4.7 Testing for Addition & Recovery Rate

Basically, the addition & recovery rate is obtained by the relation between addition quantity and analyzed value through the following procedures: (i) the standard solution prepared for the target substances and surrogate materials should be added to the samples in order to adjust the concentration of them in the samples at about ten times as the detection limit; (ii) the same pre-treatment, conditioning of sample solution and measurements as the analytical method should be conducted. If the value obtained from the operational blank test is large and target substances are contained, trial tests should again be conducted with increased additional quantities of standard materials so that the testing for additional recovery rate is not affected. The rough standard of permissible level of additional recovery rate is from 70% to 120%. In case of the dilution method of radioisotope, the permissible level of recovery rate of surrogate materials is within the range of 50% to 120%.

If the recovery rate widely deviates from the permissible level, it is required to try taking samples again, following the extraction procedures, after investigation of the causes.

The testing for additional recovery rate should be conducted prior to the analysis of actual samples. Further, when the recovery rate has the possibility to vary due to the change of supplier or the lot of equipment and chemical reagents used, it is necessary to conduct the testing for additional recovery rate.

4.8 Stability of Instrument

It is essential to periodically analyze the stability of the instrument at the middle of standard solution sequence, and to confirm whether or not the sensitivity of each target substance or internal standard material (surrogate material) widely varies compared to the time when calibration curve was made. When relative sensitivity corresponding to intensity ratio of target substances and the internal standard materials fluctuates by more than $\pm$ 20%, re-measurement is necessary after removal of the causes.

4.9 Duplicates Samples

To keep the comprehensive reliability for sampling, pre-treatment procedures and analysis using instrument, more than two (2) samples prepared under the same condition should be

analyzed. Such analysis is called "Double Analysis". Recommendable frequency of double analysis is once per 10 samples. It is necessary to confirm that the difference between the values of more than two (2) samples analyzed is less than 30% compared to the average value of analysis results. In case of appearance of large values, re-measurement should be done after removal of the causes.

4.10 Travel Blank Test

Travel blank test is carried out to confirm whether contamination is present or not throughout the analytical process from preparation of sampling to measurement. Except for the sampling procedure, analytes should be prepared under completely the same condition and analyzed under the same procedures as the actual samples, and their analyzed values are dealt as "Travel Blank Values".

Travel blank test should not be done every time; however, to keep the reliability of sampling, the data of travel blank test should be well examined in advance and managed to enable indication as occasion arises.

5. MANAGEMENT AND EVALUATION OF ANALYTICAL DATA

5.1 Management of Abnormal/Missing Values

When unsatisfactory cases are found like large values of operational blank test, large difference between the double analysis values and abnormal values of the travel blank tests, re-measurement should be done because analysis data are considered to be unreliable and missing values. Re-measurement not only involves manpower, a long time and cost, but also hinders analysis and affects the evaluation of the entire investigation due to the different sampling periods. Therefore, it is essential to check in advance, and to pay attention to the emergence of abnormal and missing values. Further, if abnormal and missing values are obtained, it is necessary to sufficiently examine the process of their emergence, and to keep them on record in order to avoid their re-occurrence.

5.2 Recording of Operation

(1) Method of Taking Samples, Storage and Transportation

- Identification, adjustment and operation of instrument and glassware.
- Condition of target samples (sampling method, sampling locations, sampling date, etc.)
- Climatic conditions
- Condition of handling and storage of sampling vessels, etc.
- Method of transportation

(2) Information Related to Samples

- Water Quality: pH, concentration of organic pollutants, SS, etc.
- Sediment: External view, odor, water contents, ignition loss, etc.
- Biological Samples: Species, growth condition, lipid contents, etc.

(3) Method and Condition regarding Conditioning of Samples

- Water Quality: With or without filtration and its method, etc.
- Sediment: With or without removal of pore water and its method, etc.

- Biological Samples: Sampling position and its method, etc.

(4) Method of Pre-Treatment

- Modification, change for the better, improvement factor and so on
- Other remarkable items

(5) Records regarding Operational Condition and Calibration of Instrument

- Suppliers of equipment, product number, performance condition, etc.
- Record of operation and maintenance

(6) Various Kinds of Values Obtained in the Course of Analysis

- Sample size for the analytical procedures, extract quantity, condensation ratio, etc.
- Setting condition of each instrument, etc.

6. REPORTING WITH REGARD TO ACCURACY CONTROL

All records and information regarding accuracy control must be documented during the sample analysis. These records include:

(1) Sample identification including taking samples, transportation and storage.

(2) Analytical procedures such as date of analysis, method number for the analytical method used, condition of pre-treatment, generated raw data, calculation process, analytical calibration/standardization/frequency, corrected/reported data, and name of the analysis staff.

(3) Determination of IDL (Instrument Detection Limit).

(4) Determination of MDL (Method Detection Limit).

(5) Determination of Detection Limit at the sample analysis.

(6) QC check samples preparation, QC requirements, QC routine checks related to the analysis such as operation blank test, double analysis, travel blank test, testing for additional recovery rate, data validation/reduction and so on.

(7) Others (preparation of reagents, standards, electronic data documentation).

References cited:

1) Monitoring and Survey Manual, Part II Analysis Method, Chapter 2 Accuracy Control of Measurement, Japanese Ministry of Environment.
2) Environmental Sampling and Analysis for Technicians, MARIA CSUROS.
3) Accuracy Control System on Instruments, Shimadzu
4) Results of profociency tests, Japanese Ministry of Environment.
5) Description Method for Analysis Data, Japanese Ministry of Environment.

ANNEX

(1) SAMPLE AND PARAMETER OF JAPANESE PROFICIENCY TEST CONDUCTED DURING RECENT YEARS

(2) OUTLINE OF JAPANESE PROFICIENCY TEST CONDUCTED BY MINISTRY OF ENVIRONMENT

(3) DESCRIPTION METHOD FOR ANALYSIS DATA REGARDING REPORTABLE LOWER LIMIT

(4) CALUCULATION METHOD OF S/N RATIO

(5) MAINTENANCE OF LABORATORY INSTRUMENTS

(6) STORAGE AND PREPARATION FREQUENCY OF SELECTED STOCK AND STANDARD SOLUTIONS

Annex(1) Sample and Parameter of Japanese Proficiency Test Conducted During Recent Years

Year	Samples	Parameters	Remarks
1998	Adjusted Water Samples-1	Fluorine, Boron, Nitrate/Nitrite, Lead and Selenium	
	Adjusted Water Samples-2	Pesticides	
	Dust and Sediment	Dioxin	
1999	Adjusted Wastewater Samples	Nitorgen Compounds (Nitrate, Nitrite, Ammonia and T-N)	
	Adjusted Water Samples	Uranium, Endocrine Disrupters and Pesicides	Sample No.1, 2, 3
	Soil Samples	Dioxin and Coplerner PCB	
2000	Adjusted Water Samples-1	Antimony, Nikel, Mercury and Cadmium	
	Adjusted Water Samples-2	Stylene dimer, Stylene Trimer and Estradiol	
	Adjusted Water Samples-3	Dioxin and Coplerner PCB	
	Sediment Samples	Dioxin and Coplerner PCB	Taken sample in the lake
2001	Adjusted Water Samples	COD, T-N and T-P	
	Endocrine Disrupters	Phthalic acid-di-n-butyl and Nonyl-pehnol	
	Dioxin Compounds	Dioxin and Coplerner PCB	
2002	Adjusted Soil Samples	COD, T-N and T-P	
	Endocrine Disrupters	Phthalic acid-di-n-butyl and Nonyl-pehnol	
	Adjusted Air Samples	Benzen, Trichloro-ehylene, Tetrachloro-ehylene, Dichloro-methane	
	Dust Samples	Dioxin and Coplerner PCB	

Annex(2) Outline of Japanese Proficiency Test Conducted by Ministry of Environment

Item	Correspondence	Supplementary Explanation	Remarks
Execution Body	Ministry of Environment	Actual working is proceeded by JEHC	
Objective of Proficiency Test	1. To confirm the variation among the environmental Laboratories in the whole country.		
	2. To improve the analytical technology in the laboratory staff with recognition of own analytical techniques.		
	3. To improve the analytical technology and accuracy after examine of merits and demerits of each analytical method, and to secure the credibility of the environmental monitoring data.		
Entry Laboratories	1998: Totally 492 Laboratories (Public: 79, Private: 413) ,Collect Rate: 94.3%	Water Samples	Dioxin: 75
	1999: Totally 514 Laboratories (Public: 90, Private: 424), Collect Rate: 92.3%	Water Samples	Dioxin: 98
	2000: Totally 476 Laboratories (Public: 78, Private: 390), Collect Rate: 93.23%	Water Samples	Dioxin: 127
	2001: Totally 522 Laboratories (Public: 99, Private: 423), Collect Rate: 95.8%	Water Samples	Others: 153 -180
	2002: Totally 477 Laboratories (Public: 94, Private: 383), Collect Rate: 96.2%	Water Samples	Dioxin: 157
Examination of Submitted Documents	Some entry laboratories did not attatch calibration curve and chromatogram.		
Interview Survey	To confirm the reason why unsatisfactory analysis results has been obtained, the interview survey is conducted for each laboratory.	Survey items: adopted method, analytical process, standard solution used, analytical equipment used, ratio between blank test and detected value,	
Site Visit Survey	To confirm the further reason why unsatisfactory analysis results has been obtained, site visit survey is conducted at the laboratory that submitted unsatisfactory analysis results which has not been identified the reason through the interview survey.	Totally five (5) laboratories were investigated in 2002 by site survey.	
Statistical Arrangement	Various statistical arrangement has been conducted in the analytical results.		

Annex(3)-1 Description Method for Analysis Data regarding Reportable Lower Limit

Classification	Parameters	Unit	Reportable Lower Limit	Description Method			Environmental Standards etc.
				Effective Digit	Under Decimal Point	Under Reportable Limit	
General Parameters	pH	-	-	-	1	-	6.0～8.5
	Dissolved Oxigen (DO)	mg/l	0.5	2	1	<0.5	2.0～7.5
	BOD	mg/l	0.5	2	1	<0.5	1.0～10
	COD (Acidic method)	mg/l	0.5	2	1	<0.5	1.0～8.0
	Suspended Substance (SS)	mg/l	1	2	Integral Number	<1	1.0～100
	Total Coliform	MPN/100 ml	-	2	Exponent	-	50～5,000
	Greese & Oil (N-hexzne Extract)	mg/l	0.5	2	1	ND	ND (1)
	Total Nitrogen (T-N)	mg/l	0.05	2	2	<0.05	0.1～1.0
	Total Phosphorus (T-P)	mg/l	0.003	2	3	<0.003	0.005～0.1
Hazardous Substances	Cadminium (Cd)	mg/l	0.001	2	3	<0.001	≦0.01
	Total Cyanide (T- CN)	mg/l	0.1	2	1	ND	ND (0.1)
	Lead (Pb)	mg/l	0.005	2	3	<0.005	≦0.01
	Chromium Hexavalent (Cr^{6+})	mg/l	0.01	2	2	<0.01	≦0.05
	Arsenic (As)	mg/l	0.005	2	3	<0.005	≦0.01
	Total Mercury (T-Hg)	mg/l	0.0005	2	4	<0.0005	≦0.005
	Alkyl-Mercury	mg/l	0.0005	2	4	ND	ND(0.0005)
	PCB	mg/l	0.0005	2	4	ND	ND(0.0005)
	Di-chloro-methan	mg/l	0.002	2	3	<0.002	≦0.02
	Tetra-chloro-methan	mg/l	0.0002	2	4	<0.0002	≦0.002
	1,2-di-chloro-ethan	mg/l	0.0004	2	4	<0.0004	≦0.004
	1,1-di-chloro-ethylene	mg/l	0.002	2	3	<0.002	≦0.02
	Cis-1,2-di-chloro-ethylene	mg/l	0.004	2	3	<0.004	≦0.04
	1,1,1-tri-chloroethane	mg/l	0.1	2	1	<0.1	≦1
	1,1,2-tri-chloroethane	mg/l	0.0006	2	4	<0.0006	≦0.006
	Tri-chloroethylene	mg/l	0.002	2	3	<0.002	≦0.03
	Tetra-chloro-ethane	mg/l	0.0005	2	4	<0.0005	≦0.01
	1,3-di-chloropropane	mg/l	0.0002	2	4	<0.0002	≦0.002
	Tiuram	mg/l	0.0006	2	4	<0.0006	≦0.006
	Simazine (CAT)	mg/l	0.0003	2	4	<0.0003	≦0.003
	Thiobencarb	mg/l	0.002	2	3	<0.002	≦0.02
	Benzene	mg/l	0.001	2	3	<0.001	≦0.01
	Celennium (Se)	mg/l	0.002	2	3	<0.002	≦0.01
	Nitrite & Nitrate	mg/l	0.02	2	2	<0.02	≦10
	Fluoride	mg/l	0.01	2	2	<0.01	≦0.8
	Boron	mg/l	0.02	2	2	<0.02	≦1
Specific Substances	Phenol	mg/l	0.01	2	2	<0.01	-
	Copper (Cu)	mg/l	0.01	2	2	<0.01	-
	Zinc (Zn)	mg/l	0.01	2	2	<0.01	-
	Iron (Soluble Fe)	mg/l	0.01	2	2	<0.01	-
	Manganese (Soluble Mn)	mg/l	0.01	2	2	<0.01	-
	T-Cromium (T-Cr)	mg/l	0.01	2	2	<0.01	-
Other Parameters	Ammonium-N (NH_3-N)	mg/l	0.01	2	2	<0.01	-
	Nitite (NO_2-N)	mg/l	0.01	2	2	<0.01	-
	Nitite (NO_3-N)	mg/l	0.01	2	2	<0.01	-
	Organic Nitrate (Org-N)	mg/l	0.01	2	2	<0.01	-
	Kjelder-N	mg/l	0.01	2	2	<0.01	-
	Particulate Nitrogen (P-N)	mg/l	0.05	2	2	<0.05	-
	Ortho-Phosphorous (Or-P)	mg/l	0.01	2	3	<0.05	-
	Soluble Phosphorius (D-P)	mg/l	0.003	2	3	<0.003	-
	Electroconductivity (EC)	mS/m	-	2	1	-	-
	Chloride	mg/l	1	2	Integral Number	<1	-
	Salinity	%	-	-	2	-	-
	Detergent (ABS)	mg/l	0.01	2	2	<0.01	-
	Chlorophil-a	μg/l	0.1	2	1	<0.1	-
	Pheophichin	mg/l	0.1	2	1	<0.1	-
	Tri-halomethan-generation-potential	mg/l	0.001	2	3	-	-

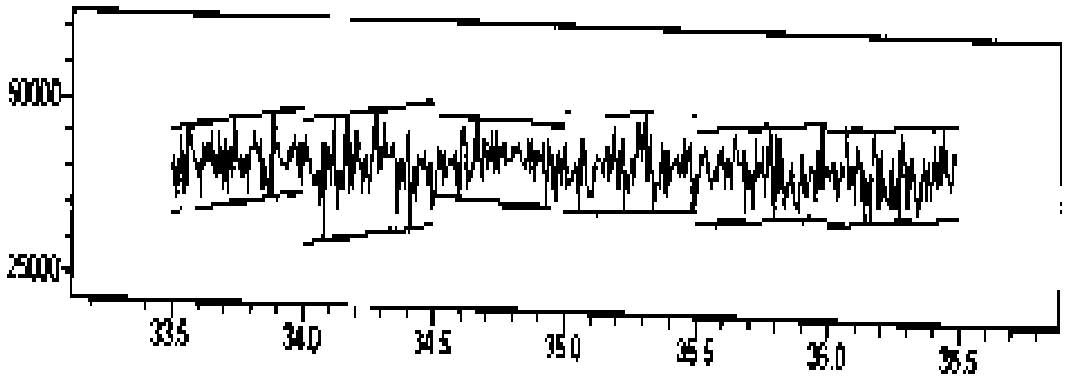
Annex(3)-2 Description Method for Analysis Data regarding Reportable Lower Limit

Classification	Parameters	Unit	Japanese Cases					Uruguayan Cases			
			Reportable Lower Limit	Description Method			Environmental Standards etc.	Reportable Lower Limit	Description Method		Environmental Standards etc.
				Effective Digit	Under Decimal Point	Under Reportable Limit			Effective Digit	Under Decimal Point	
General Parameters	pH	-	-	-	1	-	6.0～8.5	-	2～3	1～2	2～3
	Dissolved Oxigen (DO)	mg/l	0.5	2	1	<0.5	2.0～7.5	5	2～3	1～2	2～3
	BOD	mg/l	0.5	2	1	<0.5	1.0～10	5	-	-	5～15
	COD (Acidic method)	mg/l	0.5	2	1	<0.5	1.0～8.0	30～50	-	-	-
	Suspended Substance (SS)	mg/l	1	2	Integral Number	<1	1.0～100	10	2	-	700
	Total Coliform	MPN/100 ml	-	2	Exponent	-	50～5,000	10	2	-	500～1000
	Greese & Oil (N-hexzne Extract)	mg/l	0.5	2	1	ND	ND (1)	10	2	-	ND～10
	Total Nitrogen (T-N)	mg/l	0.05	2	2	<0.05	0.1～1.0	-	-	-	-
	Total Phosphorus (T-P)	mg/l	0.003	2	3	<0.003	0.005～0.1	-	2	1～3	0.025
Specific Substances	Lead (Pb)	mg/l	0.005	2	3	<0.005	≦0.01	0.02	2	1～3	0.03～0.05
	Chromium Hexavalent (Cr^{6+})	mg/l	0.01	2	2	<0.01	≦0.05	0.005～10	1～2	2～4	-
	T-Cromium (T-Cr)	mg/l	0.01	2	2	<0.01	-	0.01～0.005	2	3	0.05～0.5
Other Parameters	Ammonium-N (NH_3-N)	mg/l	0.01	2	2	<0.01	-	0.02～0.05	2	1～3	0.02
	Nitite (NO_2-N)	mg/l	0.01	2	2	<0.01	-	-	2	3	-
	Nitite (NO_3-N)	mg/l	0.01	2	2	<0.01	-	0.05	2	2	10
	Electroconductivity (EC)	mS/m	-	2	1	-	-	-	3	1	-

Annex (4)

CALUCULATION METHOD OF S/N RATIO

The S/N ratio is the ratio of the signal to the noise level cannot directly found by a numeric equation. The answer is sought by repeatedly calculating two (2) parallel line lines that fulfill the condition.



The above figure is an image of the circumstances when finding the noise level from 33.5 minutes to 36.5 minutes in 0.5-minute steps. First, the range is divided into 0.5 minute intervals and parallel lines are found in each section that fulfill the following conditions. The line in the upper position shall be above all of the points of the chromatogram. The line in the lower position below all of the points of the chromatogram. The distance between the two (2) lines in the intensity direction shall be minimized. The average distance between the various parallel lines in the noise level shall be calculated.

Annex(5) Maintenance of Laboratory Instruments (1/2)

Instruments	Maintenance Activities	Frequency
pH meter	Clean electrodes	D
	Refill electrodes	W or AN
	Change battery	AN
Conductivity meter	Clean electrodes	D
	Change battery	AN
DO meter	Clean electrodes	D
	Change membrane	AN
	Change battery	AN
Ion selective electrodes	Clean electrodes	D
	Store electrodesas described	Short term
Reference elctrodes	Clean electrodes	D
	Use proper filling spolution and storage	D
Balances	Clean pan	D
	Replace light bulb	A (I) (C)
	Adjust scale deflection	A (I) (C)
Spectrophotometer VIS/UV	Check lamp alignment	W
	Replace lamp	AN
	Clean windows	Q (I) (C)
	Change desiccant	D
	Check gas leakage	D
Spectrophotometer IR	Clean sample cell	D
	Clean windows	M
	Change desiccant	Q
	Check gas leakage	D
AAS (Frame)	Clean nebulizer	D
	Clean burner head	D
	Check tubing, pump and lamps	D
	Clean quartz windows	D
	Check electronics	SA (I) (C)
	Check optics	A (I) (C)
AAS (Graphite)	Check graphite tube	D
	Flush autosampler tubing	D
	Clean furnance housing and injecttip	W
	Check electronics	SA (I) (C)
ICP	Clean lealing torch	W
	Clean neblizer and spray chamber	W
	Check tubing and vacuum pump oil	W
	Check water lines, gases torch compartment	D
	Check electronics	SA (I) (C)
	Check wavelength calibration, adjust as needed	SA (I) (C)

Annex(5) Maintenance of Laboratory Instruments (2/2)

Instruments	Maintenance Activities	Frequency
TOC analyzer	Check interelement interference standard	SA
	Clean injection port	M
	Change catalyst	M
	Inspect combustion tube	SA
Gas chromatographs	Check sept, gas flow	D
	Clean GC syringes	D
	Check for leaks	D
	Replace column	Q
	Clean injection port	M
	Check electronics	Q (I) (C)
	Check tempCheck temperature cal	Q (I) (C)
Purge and trap	Check for leaks	M
	Clean starger	W
	Change trap	A
	Check purge flow	M
Autoanalyzer	Check for leaks, flush system	D
	Clean spill after use	D
	Clean sample probe	M
	Check tubing	M
	Clean optics	Q (I) (C)
	Clean pump rollers, platens, colorimeter filter	M
	Clean flow cells, check oil, lubricate gears	SA (I) (C)
Refrigerators, ovens, incubator	Clean interior	M
	Check temperature against certified thermometer	A
Autoclaves	Check gaskets	W
	Clean interior	M
	Sterilization indicator tape	D
	Timing mechanism check	SA (I) (C)
Turbidimeter	Clean instrument housing	M
	Clean cells	D
Thermometers	Check for cracks and gaps in the mercury	D
Autosampler	Check needles and tubing	D
	Clean up	M

Note*: D=Daily, W=Weekly, M=Monthly, A=Annualy, SA*Semiannualy, I=Instrumentation,specialyst, C=on contract, AN= as needed, Q=Quarterly.

Annex(6) Storage and Preparation Frequency of Selected Stock and Standard Solutions

Test	Calibration stocks and standards	Storage	Preparation frequency
pH	pH 4.00, 7.00, 10.00 buffers	Room temperature	Expiration date indicates
Conductivities	0.01 M KCl	Room temperature, Glass stop bottel	6 Months
Turbidity	400 NTU stock, Dil. Standard	Refrigerate	1 Month
Bromide Br	500 ppm stock	Room temperature	1 Week
Cyanide CN	1000 ppm stock	Refrigerate	1 Month, check weekly
Fluoride F	100 ppm stock	Room temperature	3 Months
Ammonia-Nitrogen NH^3-N	1000 ppm stock	Refrigerate	3 Months
Nitrate-Notrogen NO_3-N	1000 ppm stock	Refrigerate, preserve with chloro	6 Months
Nitirite-Nitroge NO_2-N	250 ppm	Refrigerate, preserve with chloro	3 Months
Phosphorus PO_4-P	50 ppm	Refrigerate	3 Months
Silica SiO_2	10 ppm	Refrigerate in tightly stoppered plastic bottle	1 Month
Sulfate SO_4^{2-}	100 ppm	Room temperature	6 Months
Metals	1000 ppm	Room temperature	Exiration datw indicates
	10 to 100 ppm standards	Room temperature preserve with 0.5% HNO_3	1 Month
COD	500 ppm	N/A	Prepare fresh for each
TOC	1000 ppm and 10 to 100 ppm standards	Refrigerate in brown bottles	3 Months
Oil and grease	"Reference oil" calibrate each time used 1000 ppm	Freezed in sealed container	3 Months
Total phenols	1000 ppm	Refrigerate in brown bottles	3 Months
Trace organics	Concentration depends on mehtods and analytes	Fleeze in individually	Expiration date indicates

ANNEX (13)

Guideline for Laboratory Waste Management

– Treatment of Laboratory Wastewater –

September 2006

CTI Engineering International Co., Ltd

GUIDELINE FOR LABORATORY WASTE MANAGEMENT –TREATMENT OF LABORATORY WASTEWATER

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ANNEX

List of Tables

CHAPTER I INTRODUCTION

1.1 Background

In the framework of managing the environment, the laboratory becomes very important, because laboratory can generate authentic data that will be the basis upon which appropriate policies concerning the management is made.

The environmental laboratory is the laboratory that conducts test parameters of physics, chemistry and biology, in accordance to the prevailing laws in the framework of managing the environment. In performing these activities, the environmental laboratories will produce waste, in the form of liquid, solid, and gaseous wastes. These wastes could come from left over chemicals no longer able to be used (expired); disposed material after the sampler analysis had been conducted, and from left over samples already analyzed.

Laboratory wastes are characterized by their toxicity and variety, even though their quantities are small and their disposal not continuous, requiring specific handling.

What become a problem with environmental laboratories and the wastes they produce is the absence of a guide specially made for their management. For this reason, the writers attempt, through this writing, to present a guide to manage wastes from environmental laboratories, as an alternative guide.

1.2 Purpose and Objectives

This guideline contains guidance on performing management of laboratory wastes with the objective to:

(1) To become an alternative guide for environmental laboratories to manage wastes they produce;

(2) To enable environmental laboratories to self-manage waste they produce using the appropriate methods, taking into consideration related regulations implemented by the government; and

(3) To enable environmental laboratories to dispose their wastes safely into the environment.

1.3 Scope of Guideline

The scope of guideline is as follows:

(1) To give the knowledge on the temporary storage of generated laboratory wastes;

(2) To explain the treatment method for wasted such as selection of method, basic style of device, necessary chemicals and apparatus, how to treat heavy metals, cyanide, fluoride, how to recover used silver nitrate and how to recycle used organic solvents;

(3) To give the information on discharging the treated laboratory wastes; and

(4) To explain the minimization of wastes.

CHAPTER II GENERAL ASPECTS

2.1 Organization of Laboratory Waste Management

To continuously prevent the environmental pollution, management system for laboratory waste treatment should be functioning, and responsible personnel should be designated and proceeding each process for as shown in Fig. 2.1.

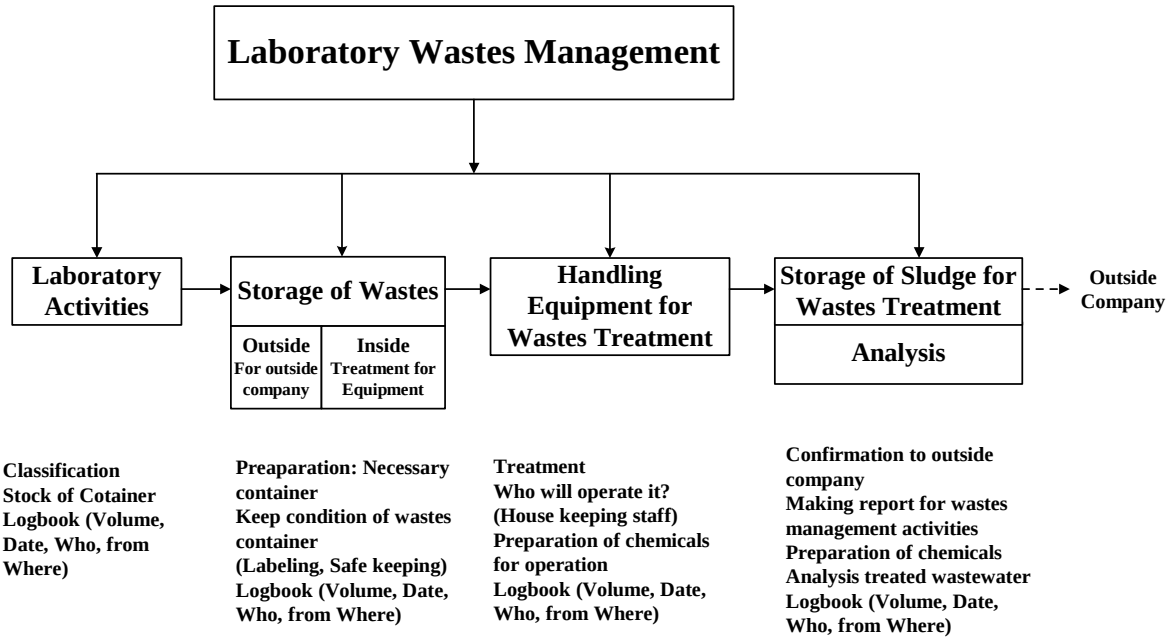


Fig.2.1 Whole System for Laboratory Wastes Management

2.2 Procedure for the Collection of Wastes from Environmental Laboratories

Wastewater from laboratories has the following features.

- Various substances exist together including extremely harmful and dangerous ones.
- The coexistence ratio of substances in the wastewater is different.
- The amount of wastewater is different depending on time.

Therefore, the following attention is necessary for treatment.

- It is necessary that the person who puts out the wastewater must classify with the sense of responsibility for safety and surely treatment.
- It is effective to use the method that is able to treat several kinds of substances all together, because it is difficult to classify it completely.

- It is effective/necessary to use adsorption method together, because toxic substance that is difficult to treat by oxidation and coagulation method often exists together.

Laboratory wastes come in the forms of liquid solid as well as gaseous wastes.

Collection of liquid wastes is illustrated through the following diagram as well as categorization of liquid wastes produced by environmental laboratories.

In practice, the collection of waste is conducted in container with following requirements:

(1) Plastic container that is corrosive resistant

(2) Volume of the container should be conformed with the category of the waste.

(3) Container must ensure safety

(4) Labeled in accordance to the category of waste

(5) Should include instructions for storage or each category or waste, for example: “store at a pH less than 7”, etc.

The following is an example of a label for waste container:

Aa-1-EMC **Aa-1-EMC-0001**

Aa= Aa category

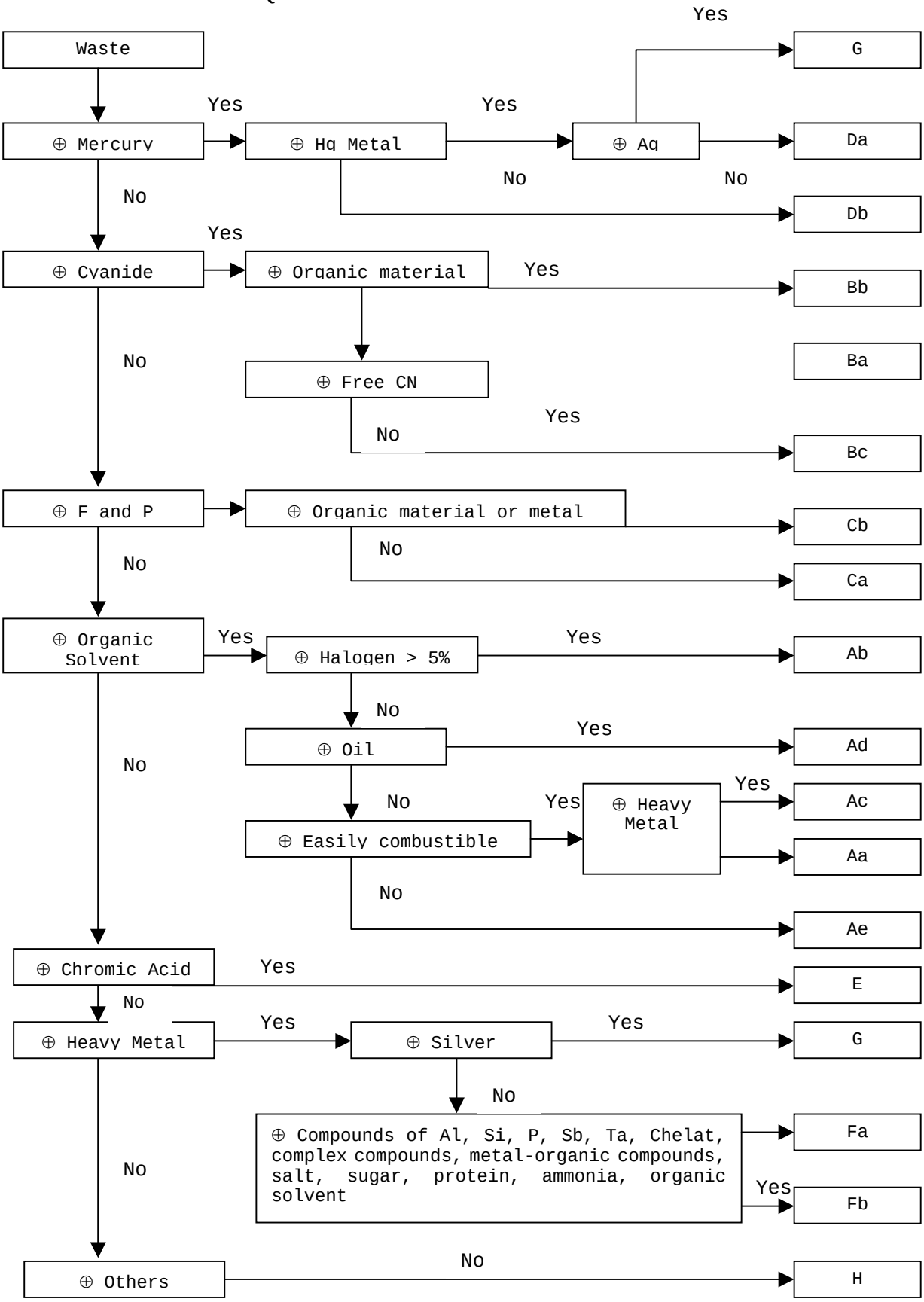
1- EMC= Water laboratory – EMC

01= queue number of container.

In addition to the above, waste collection must be controlled in a “Control Sheet” that must be filled by the personnel disposing the waste based on the instructions from the waste management organizer. This is important because the contents of the Control Sheet must be acknowledged by the waste management organizer as data of waste characteristic used to determine the type of processing required.

The control sheet must be filled by the personnel disposing the waste each time he disposes waste, and this sheet must be made available in any laboratory. The sheet must then be submitted to the head of the waste management when the waste in the container is full and stored in the stored in the storage room.

FLOW DIAGRAM OF LIQUID WASTE COLLECTION



After identifying the source of the waste and identifying its category, a number of steps to collect laboratory waste must be carried out as follows:

(1) Waste from Remnants of Analysis

(a) After the analysis is performed, dispose of this analyzed material into the containers according to tables 2,3, and 4 already available in the laboratory.

(b) Rinse the glassware with clean water using a spray bottle to cleanse the remnants of chemicals in the glassware, making the glassware free from chemicals as it enters the wash area. This rinse water is also disposed into containers according to table 2, 3 and 4 as mentioned in step number 1.

(c) Fill in “waste control sheet”

(d) Place glassware into the wash area

(e) If the container is full, immediately report this to the heal of the waste management organizer who is appointed in each laboratory, in order to exchange it with an empty container labeled accordingly.

(f) The waste management organizer will exchange the full container with an empty container with the same label and provided with a numbering accordingly.

(g) Personnel shall bring the full container to the waste storage area, applying identification and numbering.

(2) Used Vessels for Chemicals

(a) Bottle use for chemicals must be rinsed by clean water, and the rinse water is poured into waste containers in accordance to the flow diagram, under the supervision of the waste management organizers.

(b) The bottle is cleaned in the cleaning area.

(3) Glassware Fragments

Glassware fragments must be separated between those fragments that are contaminated with chemical substances and those that are clean.

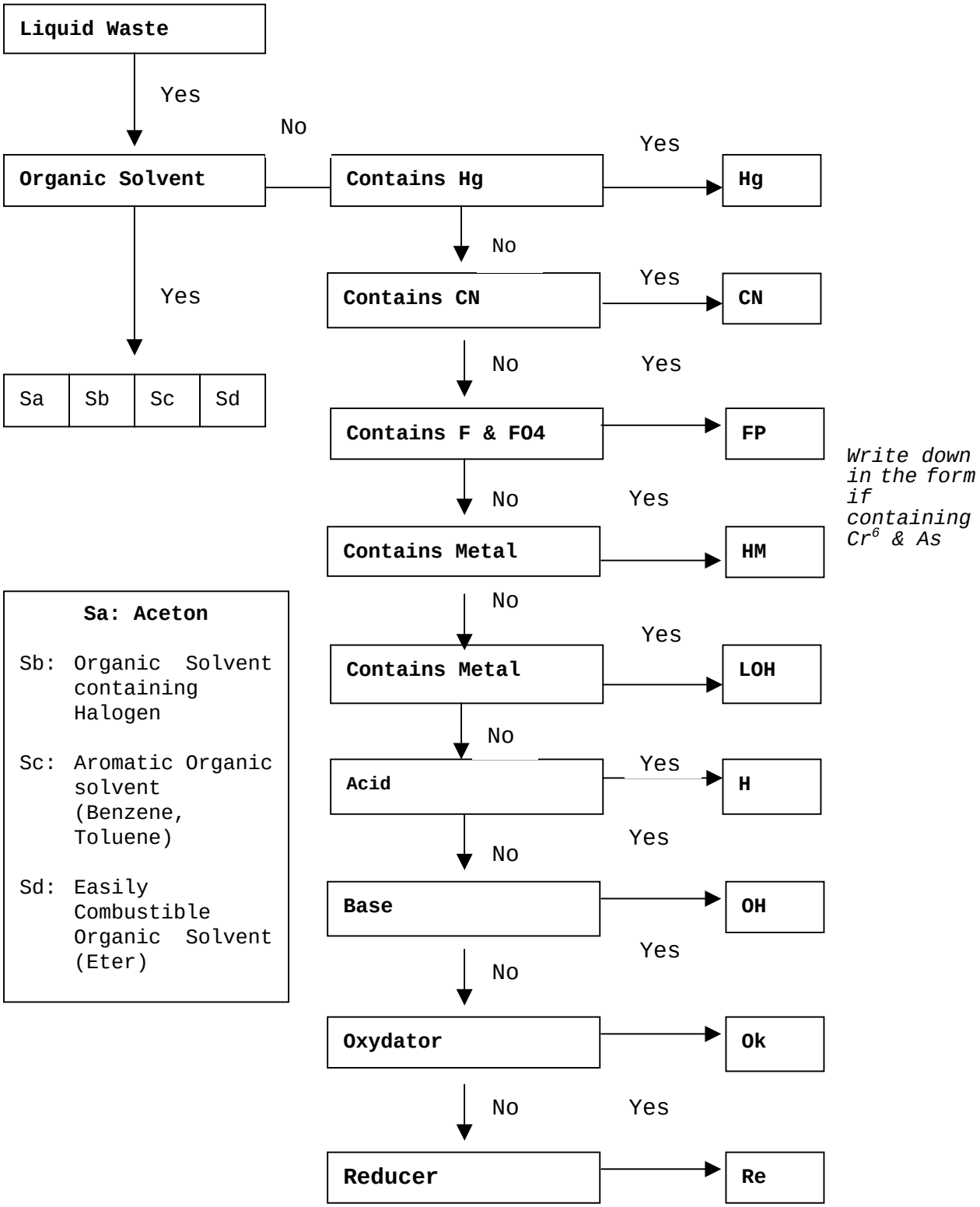
(4) Tissue and Filter paper

Tissues and filter paper that are contaminated by chemicals must be stored in a separate container.

(5) Unused Chemicals

Collection of chemical substances that are not used because it does not meet the specifications or its effective use has expired must follow “Flow Diagram for the Collection of Unused Chemicals” illustrated bellow. The collection should be made in its original package, requiring only to be categorized.

FLOW DIAGRAM OF UNUSED CHEMICALS DISPOSAL



CHAPTER III LABORATORY WASTES TREATMENT

3.1 Selection of Treatment Methods

Treatment methods can be selected from performance, difficulty of purchase and operation of device as shown in Fig 3.1 It is recommendable to use the methods that painted gray color in Table-1 attached in Annex.

3.2 Basic Style of the Device

Basic process for the dissemination of the technology for the laboratory wastes treatment is to set of the device for the general-purpose type and the adsorption type as shown in Fig.3.2. It is possible to introduce the device step by step according to the necessity for installation of treatment system.

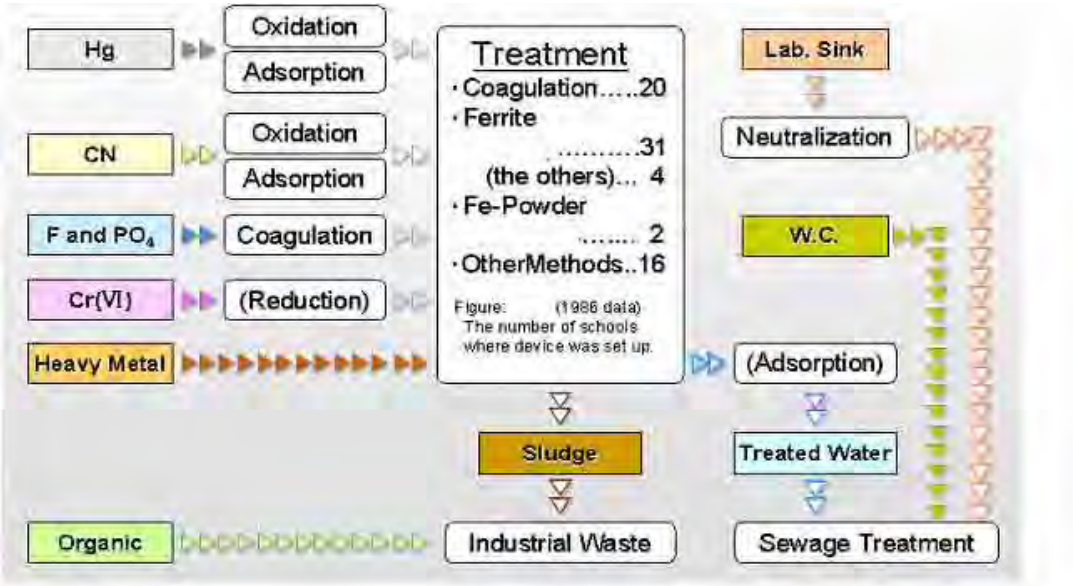
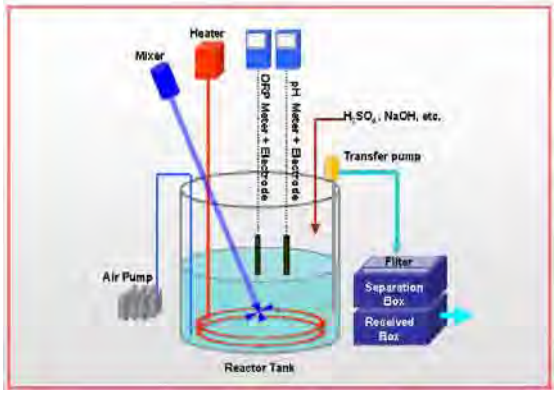
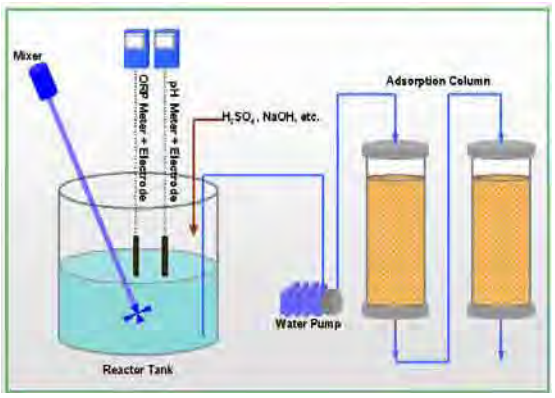


Fig.3.1 Selection of Treatment Methods



General-purpose type



Adsorption type

Fig.3.2 Basic Style of the Device

3.3 General Information

(1) Necessary Chemicals

To start the wastes treatment, it is necessary to store following chemicals:

Chemical Reagent	Necessity for 1 Treatment	For 24 Treatment in a month	Necessity for a year
$NaOH/Ca(OH)_2$	100 gram	2,400 gram	28.8 kg
H_2SO_4	50 ml	1,200 lt	14.4 L
$Al_2(SO4)_3$	100 gram	2,400 ml	28.8 kg
$KMnO_4$	10 gram	240 gram	2.88 kg
$SnCl_2$	20 gram	480 gram	5.76 L
HNO_3	20 ml	480 ml	5.76 L
Filter	5 sheet	120 sheet	15 box
Iron powder	450 gram	10,800 gram	129.6 kg
Gas Acetylene			2 tube

(2) Necessary Apparatus for Storage of Wastes

Following material and apparatus are necessary to store the wastes generated from laboratory activities: (i) Container 50 L, (ii) Big size plastic bag and (iii) Big size bucket 50 L.

CHAPER IV DISCHARGE OF TREATED WASTES

4.1 General

All laboratory wastewater discharged to the water body should comply with national and local standards as shown in Table-6 attached in ANNEX. These are designated to protect surface wasters and to maintain the quality of wastewater from wastewater treatment system.

4.2 Discharging Point

The treated water has been generally discharged to drainage in Japan. Similarly, the treated water by the device can be discharged to this system.

4.3 Checking Wastewater Quality

It is necessary to check the water quality of the treated water and the final discharge water at points as shown in Fig.4.1, and confirm the regulation.

Fig.4.1 Sampling points for Checking Wastewater Quality

These monitoring data should be recorded and reported to the responsible persons. If the treated wastewater quality exceeds the criteria for discharging, emergent survey for confirming the function of treatment system and certain countermeasures for recovering of system should be taken.

CHAPTER V WASTE MINIMIZATION

5.1 General

Waste minimization means a reduction in both the volume and the physical hazards or toxicity of the material. The Laboratory, as a generator of hazardous waste, must do its best to integrate pollution prevention into laboratory management.

Waste minimization has many advantages. Smaller quantities of waste mean less impact on the environment at the time of disposal. Waste minimization leads to safer conditions in the lab and in handling and transporting the waste. It also lessens disposal costs, benefiting everyone in the Laboratory community. Waste minimization activities can be grouped into four broad categories:

(1) Consideration on Sample Volume

(2) Treatment to reduce hazards

(3) Substitutions of less hazardous materials

(4) Procedural changes to minimize generation

(5) Improved laboratory management practices

5.2 Consideration on Sample Volume

The volume of sample brought to the laboratory by the consumer must be limited in its quantity, sufficient enough to conduct the analysis. Therefore, the laboratory must have a list pf sample volumes required for each parameter in a particular batch of analysis (duplo, recovery, etc.) and must be informed to the consumer.

An agreement must be made with the consumer stipulating that the excess samples, after analysis is performed, shall be returned to the consumer at the same tome that the consumer obtains the certificate of test results or it shall be returned to the consumer at any time it is no longer required.

5.3 Treatment to reduce hazards

The last step of an experimental procedure should include treatment methods to reduce or eliminate the hazardous of experimental byproducts. It is recommendable to eliminate corrosives from wastes through neutralization. Small quantities of inorganic acids - hydrochloric, sulfuric, phosphoric, nitric - can be neutralized and flushed down the drain. Never release chromic acid to the drain, however, even if neutralized. Bases such as sodium, ammonium, and potassium hydroxide can also be neutralized and flushed down the drain. Laboratory quantities of oxidizers can be treated in the laboratory as can small quantities of water-reactive or pyrophoric materials.

The toxicity of some compounds can be reduced. Sodium cyanide can be treated to yield sodium cyanate; ethidium bromide can be reacted to a non-mutagenic waste; waste epoxy monomers can be polymerized to a safe solid.

Other techniques include treating organo-sulfur wastes with bleach to reduce odors, deactivating organo-metallic compounds, and reclaiming metals, especially silver from photographic solutions.

5.4 Substitutions and Elimination

It is necessary to minimize hazardous wastes by substituting less hazardous materials in your experiment. This has the collateral advantage of improving worker safety. The following substitutions are recommended: To use biodegradable detergents or other nonchromium-containing cleaners for glassware, and to use biodegradable detergents such as Alconox in place of ethanol-base baths. Use non-mercury based preservatives. Use red liquid (alcohol), metal, or digital thermometers. Substitute sodium hypochlorite for sodium dichromate Substitute alcohols for benzene. Substitute cyclohexane for carbon tetrachloride. Substitute ethanol for formaldehyde in biological specimen preservation. Use water-based paints instead of oil-based paints. Eliminate the use of pigments containing heavy metals in art practices. In photography labs, eliminate silver from waste streams through recovery. In teaching labs, eliminate experiments using heavy metals. Replace with iron, cobalt, copper, etc. Substitute biodegradable liquid scintillation cocktails for xylene- or toluene-based cocktails. Try to substitute nonchlorinated solvents for chlorinated solvents.

5.5 Procedural Changes

Wastes can be minimized by implementing procedural changes such as: 1. To use micro-scale procedures or simply scale down the magnitude of experiments. 2. To distill spent solvents for reuse. 3. To segregate halogenated waste from non-halogenated wastes. 4. To segregate organic liquids from inorganic wastes. 5. To segregate very toxic wastes (potassium cyanide, acrolein, etc.) from less toxic wastes. 6. Not to do mix chemical waste with normal office trash or food waste (All waste contaminated with hazardous materials is considered a hazardous waste). 7. To avoid reagents or paints containing heavy metals. 8. To use spent solvent for the initial glassware rinse and fresh solvent for the final rinse only. 9. To purchase lecture bottles only from companies who will accept their return when empty. 10. To reuse developers in photography labs. 11. To recover metals for recycling or reuse by precipitation.

5.6 Management Practices

Good laboratory management can go a long way towards avoiding unnecessary waste generation. Order only the quantity of material which you anticipate using. Many chemicals have a limited shelf-life. For example, diethyl ether may begin to form peroxides within several months after opening. This is especially important for peroxide-formers and

reactive material. It is much safer and less expensive to dispose of a flammable liquid than it is to dispose of a flammable liquid that contains peroxides.

One person should order chemicals for one group, thereby minimizing duplicate orders. It is necessary to keep an updated inventory of all the chemicals that are in the lab so that unnecessary orders are not placed. This is a highly recommended practice and a legal requirement for some groups. It is important to share excess and unexpired chemicals with other groups. Keep containers labeled so they do not later become unknowns which require costly analysis.

Finally, it is essential to remember that waste minimization begins when planning an experiment and to consider the kind and quantity of waste which will be generated and adjust the experimental design to minimize it.

REFERENCES

1) Final Report “Laboratory Waste Managemnet Guide” Local Hazardous Waste Management Program in King County USA, July 2005.
2) Law & Regulation, Ministry of Environment (KLH) second edition.

ANNEX

Table I. Categories of Waste from Environmental Laboratories

Category	Component	Notes
Aa: Organic solvent and flammable	1. Alifatis Hydrocarbon: Petroleum Ether, Hexane, Heptane, Octane, and its type 2. Alifatis compounds containing oxygen, Acetyl, alcohol, acetone, Methyl Ethyl Keton, Acetic, Ester, etc. 3. Alifatis compounds containing Nitrogen: Acetonitril and its type. 4. Aromatic Hydrocarbon: benzene, toluene, xylene, styrene, and its type. 5. Aromatic compound that contain Nitrogen: pyridine and its type. 6. Others: Organic solvent that contains Sulfur, Crude, and its type.	▪ Write down pH and all components in the form. ▪ Write "Flammable: on the label. ▪ Avoid contact with sunshine.
Ab: Organic solvent that contain Halogen.	1. Alifatis compounds containing Halogen: Chloroform, methyl chloride, dichloromethane, carbon tetra-chloride, methyl bromide, methyl-iodide, and its type. 2. Aromatic compounds that contain Halogen: Chloro-benzene, Benzyl Chloride, and its type.	▪ Halogen concentration > 5% ▪ Write down pH and all components in the form.
Ac: Organic solvent containing heavy metal	1. Containing heavy metal and organic solvent > 5% 2. Organic solvent from chelate heavy metal compound: MIBK + DDTC + heavy metal, Chloroform + dithizone + heavy metal, Butyl Acetate + DDTC + heavy metal.	▪ Write down pH and all components in the form.
Ad: Oil	Kerosene, mineral oil, lamp oil, creosote oil, spindle oil, turbine, transformer oil, gear oil, motor oil, and its type oil form plants and animal.	▪ Write down pH and all components in the form. ▪ Write "Flammable on the table. ▪ Avoid contact with sunshine. ▪ Keep always away from PCB
Ae: Non-combustible Organic water	1. Waste water that contains small amounts of hydrocarbon. 2. Waste water that contain small mounts of halogen (<5%)	Waste water that contains small mount of hydrocarbon. Wastewater that contain a small amount of halogen (<5%) Other organic compounds.

Category B (Cyanide)

Category	Component	Notes
Ba: Inorganic Cyanide	1. Fee Cyanide: Sodium Cyanide, Potassium Cyanide, and its type. (If containing inorganic material, put into Bb container)	▪ Write down pH and all components in the form. ▪ Store in pH > 10.5
Bb: Cyanide compound containing organic material	1. Cyanide containing organic material	▪ Write down pH and all components in the form. ▪ Store in pH > 10.5

Category C (Fluoride and Phosphor)

Category	Component	Notes
Ca: Inorganic Fluoride or Phosphor	1. Inorganic fluoride and its compounds: Hydrofluoric acid, Boro-fluoride compound, Silicone-fluoride compound and its type. 2. Inorganic Phosphor compound: Buffer phosphate, and its type.	▪ Write down pH and all components in the form.
Cb: Fluoride or phosphor containing organic material or heavy metal	1. Organic fluoride compound: Trifluoro acetic acid, and its type. 2. Organic-phosphorous compound 3. Fluoride or phosphate containing organic material 4. Fluoride or phosphor containing heavy metal.	▪ Write down pH and all components in the form

Category D (Mercury)

Category	Component	Notes
Da: Mercury metal	1. Metal Mercury, Amalgam Mercury, Thermometer, Manometer, and its type. 2. Inorganic Mercury compound: Mercury Chloride, Nessler Reagent, and its type.	▪ Store in container that can be covered and fill with water (for metal Hg)
Db: Organic Mercury	Organic mercury and its type	▪ Write down pH and all components in the form. ▪ Organic mercury, in particular alkyl mercury, must be stored separately and converted into inorganic mercury using Acid-permanganate.

Category E (Chromic Acid)

Category	Component	Notes
E: Chromic acid	Waste water containing Chromic acid (Chrome phosphate must be stored in a Cb container)	■ Write down pH and all components in the form

Category F (Heavy Metal)

Category	Component	Notes
Fa: Inorganic heavy metal	1. Compound from metal: Mg, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, In, Sn, Ba, Pb, Bi, Ce, Gd. 2. Containing a small amount of metal compounds of Ge, As, Se, Sr, Y, Zr, La, Sm	■ Write down pH and all components in the form
Fb: Heavy Metal containing organic material	1. Compounds from metal: Al, Si, P, Sb, Ta, and chelate compound, complex compounds. 2. Heavy metal compounds containing organic compounds, sugar, protein, fat, ammonia, and organic solvent. 3. If containing Arsenic compound such as Cacodyl Acid, write in form.	■ Write down pH and all components in the form

Category G (Acid and Base)

Category	Component	Notes
G: Silver	Silver and or its type	■ Write down pH and all components in the form

Category H (Others)

Category	Component	Notes
H: Others	1. Those not included in the above categories	■ Write down pH and all components in the form

The following is an example of a control sheet:

Waste Disposal Control Sheet

Name of Laboratory: … Water……

Category: … G-1-EMC-0001

Volume: … 20 litters

Source of waste	Work Method (Flowchart Analysis)	Composition of Reagent used (Concentration)	pH of Waste	Date of Disposal	Vol. (ml)	Personnel
1. COD Sample Analysis	Sample + H_2SO_4 + $HgSO_4$ + $AgSO_4$ + $K_2Cr_2O_7$ ↓ Destruction ↓ Spectro-photometer	H2SO4 (M), $AgSO_4$ (M), $HgSO_4$ (M), $K_2Cr_2O_7$ (M)				

Table 2. Categories of waste from Water Quality Laboratories

No.	SOURCE OF WASTE	METHOD OF ANALYSIS	CATEGORY OF WASTE
1.	Chloride Analysis	Mohr Argentometry	
	a. Chloride standardization		G
	b. Test sample analysis, Chloride < Quality standard		G
	c. Test sample analysis Chloride > Quality standard		G
2.	Sulfide Analysis	Sulfuric Acid Amine	
	a. Sulfide standard		Cb
	b. Test sample analysis, Sulfide < Quality standard		Cb
3.	Silica Standard	Millibdosilicate	
	a. Silica standard		Fb
	b. Test sample analysis, Silica < Quality standard		H
	c. Test sample analysis, Silica > Quality standard		Fb
4.	Total Phosphate Analysis	Ammonium Molibdat	
	a. Phosphate standard		Cb
	b. Test sample analysis, Phosphate < Quality standard		Fb
	c. Test sample analysis, Phosphate > Quality standard		Cb
5.	Detergent Analysis	Methylene Blue	
	a. Detergent standard		Ad
	b. Test sample analysis, Detergent < Quality standard		Ad
	c. Test sample analysis, Detergent > Quality standard		Ad
6.	Total Hardness Analysis	Titrimetric EDTA	
	a. Test sample analysis, Hardness < Quality Standard		H
	b. Test sample analysis, Hardness > Quality Standard		Fb
7.	P-Alkalinity Analysis	Titrimetric	
	a. P-Alkalinity Standard		Fa
	b. Test sample analysis, P-Alkalinity < Quality Standard		H
	c. Test sample analysis, P-Alkalinity > Quality Standard		H
8.	m-Alkalinity Analysis	Titrimetric	
	a. m-Alkalinity Standard		Fa
	b. Test sample analysis, m-Alkalinity < Quality Standard		H
	c. Test sample analysis, m-Alkalinity > Quality Standard		H
9.	Heavy Metal Analysis	AAS	
	a. Heavy Metal Standard		Fa

	b. Test sample analysis, Heavy Metal < Quality Standard		H
	c. Test sample analysis, Heavy Metal > Quality Standard		H
10.	Mercury Analysis	Cold Vapor	
	a. Mercury Standard		Da
	b. Test sample analysis, Mercury < Quality Standard		Fb
	c. Test sample analysis, Mercury > Quality Standard		Da
11.	Cr^{6+} Analysis	Difenil Karbazid	
	a. Cr^{6+} Standard		Fa
	b. Test sample analysis, Cr^{6+} < Quality Standard		H
	c. Test sample analysis, Cr^{6+} > Quality Standard		Fb
12.	Fluoride analysis	Alizarin Red	
	a. Fluoride Standard		Cb
	b. Test sample analysis, Fluoride < Quality Standard		H
	c. Test sample analysis, Fluoride > Quality Standard		Cb
13.	Ammoniac Analysis	Indo Phenol Blue	
	a. Ammoniac Standard		Fb
	b. Residue from the distillation process		Fa
	c. Test sample analysis, Ammoniac < Quality Standard		Fb
	d. Test sample analysis, Ammoniac > Quality Standard		Fb
14.	COD Analysis	K-Bichromate	
	a. COD Standard		G
	b. Test sample analysis, COD < Quality standard		G
	c. Test sample analysis, COD > Quality standard		G
15.	BOD Analysis	Winker	
	a. Test sample Analysis, BOD < Quality standard		Fb
	b. Test sample analysis, BOD < Quality standard		Fb
16.	Color Analysis	Pt-Co (Colorimetry)	
	a. Color Standard		Fa
17.	Nitrite Analysis		
	a. Nitrite Standard		Ab
	b. Test sample analysis, Nitrite < Quality standard		Ab
	c. Test sample analysis, Nitrite > Quality standard		Ab
18.	Phenol Analysis	Amino Antipirin	
	a. Phenol Standard		Bb
	b. Residue from the distillation process		Cb
	c. Test sample analysis, Phenol < Quality		Bb

	standard		
	d. Test sample analysis, Phenol > Quality standard		Bb
19.	Sulfate Analysis	Turbidimetry	
	a. Sulfate Standard		Ab
	b. Test sample analysis, Sulfate < Quality standard		Ab
	c. Test sample analysis, Sulfate > Quality standard		Ab
20.	Cyanide Analysis	Pyridin Pirazolon	
	a. Cyanide Standard		Bb
	b. Residue from the distillation process		Cb
	c. Test sample analysis, Cyanide < Quality standard		Cb
	d. Test sample analysis, Cyanide > Quality standard		Bb
21.	Nitrate Analysis	Brusin Sulfate	
	a. Nitrate Standard		Fb
	b. Test sample analysis, Nitrate < Quality standard		H
	c. Test sample analysis, Nitrate > Quality standard		H
22.	Oil and Fat Analysis	Gravimetry (n-Hexane)	
	a. Test sample analysis, remains from extraction		H
23.	Total Nitrogen Analysis		
	a. Total Nitrogen Standard		Fa
	b. Test sample analysis, Total Nitrogen < Quality standard		Fa
	c. Test sample analysis, Total Nitrogen > Quality standard		Fa
24.	TOC Analysis	Conductivity	
	a. TOC Standard		H
	b. Test sample analysis, TOC < Quality standard		Fa
	c. Test sample analysis, TOC > Quality standard		H
25.	Arsenic Analysis	AAS-Flameless	
	a. Arsenic Standard		Fb
	b. Test sample analysis, Arsenic < Quality standard		H
	c. Test sample analysis, Arsenic > Quality standard		Fb