TRADE EFFLUENT SURCHARGE SCHEME
TECHNICAL MEMORANDUM ON PROCEDURES AND METHODS FOR SAMPLING AND ANALYSIS OF TRADE EFFLUENTS

1. PRELIMINARY

1.1 *Citation and commencement*

This technical memorandum is issued under Section 13 of the Sewage Services Ordinance. It may be cited as the Technical Memorandum on the Procedures and Methods for Sampling and Analysis of Trade Effluents for the Trade Effluent Surcharge Scheme.

This technical memorandum supersedes the one issued by the then Secretary for Works on 27 February 1995 under Section 13 of the Sewage Services Ordinance.

1.2 *Application and scope*

1.2.1 The Sewage Services Ordinance sets out mechanisms for the collection of charges for the provision of sewage services to consumers and separately for the reception of trade effluent produced in the course of any trade, business or manufacture. The charges relating to the latter are based on an assessment of the quality and quantity of the materials discharged, and the Ordinance allows for the provision of a Technical Memorandum to set out the procedures and methods to be adopted for sampling, analysis, approval of laboratories, presentation of results, and any other matters relating to the establishment of specific effluent characteristics. These apply in the following circumstances :—

1. formal application by a consumer for acceptance of a specific effluent characteristics;
2. sampling and analysis undertaken by the Drainage Authority for the purposes of assigning or auditing specific effluent characteristics for an individual consumer.

1.2.2 The Drainage Authority will only consider an application for reassessment of effluent characteristics if the application is accompanied by details of proposed sampling schedules etc. as specified in this memorandum. Only following acceptance of these proposals by the Drainage Authority, may sampling and analysis commence. Once satisfactory sampling and analysis have been completed a certificate will be required from the laboratory confirming that the samples have been obtained, and that the sample preparation and the analyses have been undertaken in the manner described in this Technical Memorandum.

2. INTERPRETATION

2.1 This memorandum uses standard scientific terms. Where the Ordinance or the Regulations made thereunder defines a term, that definition applies.

2.2 In this memorandum, the following definitions also apply.

"Laboratory" — a laboratory accredited within the Hong Kong Laboratory Accreditation Scheme (HOKLAS) for the analyses described in this memorandum.

"Homogenisation" refers to the process of ensuring that the sample is uniform so that identical portions may be taken. Various techniques are used (e.g. blenders or ultrasonic mixers) in the laboratory to achieve this, dependent upon the nature of the sample.

"Methodology" is a scientific term used to describe the procedures adopted.

"COD" refers to the Chemical Oxygen Demand.

"Adsorption" is the accumulation of materials on a surface.

"Composite" has the same meaning as combine.

"Particulate Fraction" is the solid part of the sample, which will settle out of the sample on standing.

"Immiscible Fraction" is the component of the sample which does not mix with water and will separate out on standing.

"Recovery" refers to the accuracy of the COD test, comparing the value of the COD measured experimentally for a standard solution to the theoretical value for its oxidation. The amount determined experimentally (recovered) indicates the effectiveness of the laboratory analysis.

"Aliquot" is a representative portion of a sample used for analysis.

3. SAMPLING PROCEDURES

3.1 *Introduction*

3.1.1 The techniques used for the collection of samples are critical to the determination of the characteristics of the effluent discharged, especially where the nature of the waste is variable, both during the course of the working day and during the week. Dischargers should develop a sampling procedure which specifies the organisations to be employed and the methods to be adopted to ensure that representative sampling has been undertaken.

3.1.2 Detailed guidance on sampling methodology is available in various published methods, [Ref 1] & [Ref 2]. These include information for the satisfactory design of appropriate sampling programmes, such as the principles of sampling, the relevant statistical analysis and the range of techniques available to ensure that a representative sample is obtained from both homogenous and non-homogenous systems. Reference to these should enable adequate sampling arrangements to be proposed by the trader or his representative.

3.2 *Sampling arrangements —authorization*

The proposed sample collection arrangements must be approved in advance by the Drainage Authority to ensure that the sampling is valid before programme commencement. In addition, whilst the sampling programme is under way the Drainage Authority may inspect the site at any time to confirm that the agreed sampling protocol is being complied with. Following completion of sampling the discharger must confirm to the Drainage Authority that the agreed methodology has been used throughout. If the sampling is found not to conform to the approved arrangements all previous samples and results from the survey will be considered to be void.

3.3 *Sample collection*

3.3.1 Discrete individual samples must be taken throughout the working hours of the establishment, in order to establish the average concentration of COD discharged in the effluent during that period. A minimum of 96 samples per 24 hour period

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Ref 1 General Principles of Sampling and Accuracy of Results 1980—DoE Standing Committee of Analysts (Methods for the Examination of Waters and Associated Materials 1980), HMSO London ISBN 011 751491 8]

Ref 2 Sampling of Oils, Fats, Waxes and Tars in Aqueous and Solid Systems 1983—DoE SCA, HMSO London ISBN 011 7519 561] would be necessary to ensure a representative composite sample can be produced. Where the effluent flow is constant, these individual samples may be taken at 15 minute intervals and then equal portions combined (see Section 5.1). However where the flow varies it will be necessary to take individual samples at discrete flow intervals indicated by a suitable meter so that at least 96 samples are taken in a 24 hour period (i.e. if the daily flow is X m^3, then a sample must be taken for every X/96 m^3 of effluent flow)—with variable flow rates the time interval may become substantially lower or greater than the 15 minute intervals specified for constant flows.

3.3.2 Where a batch process is employed the time interval may be so short as to render collection of 96 samples impossible. In these circumstances, special arrangements (e.g. sampling the bulk tank prior to discharge) must be agreed with the Drainage Authority.

3.3.3 As an alternative to manual sampling, an automatic sampler triggered by pulses from a flow meter could be used for this purpose. This has the advantage that it automatically provides a flow weighted composite sample over the relevant periods. However, auto sampling is unsuitable for certain effluents such as :—

- effluents with a high solids and/or grease content;
- discharges from industries which could cause ragging or blockages of the equipment (e.g. textiles).

For these effluents, manual samples must be taken.

3.3.4 Individual samples must be collected in glass bottles to ensure an adequate sample of the particulate fraction is obtained, adsorption minimised and that when equal portions of these samples are composited, the portions used are representative. If the samples appear to be inhomogeneous these must be homogenised (blended) prior to compositing. All samples taken must be composited and analyzed within 24 hours of sampling (see sample preparation in Section 5).

3.3.5 At least 500 mL of each discrete sample must be taken to ensure that a representative sample has been obtained, and to allow for the subsequent combining of samples.

3.3.6 In addition care must be taken to avoid contamination of the sample and to ensure that a sample representative of the effluent characteristics is taken. Specific points that require consideration include :—

- Cleanliness of sampling equipment to avoid contamination;

- Use of wide mouth glass sampling bottles, which should be thoroughly cleaned prior to use by rinsing with sulphuric acid to remove any organics;
- Except where high concentrations of grease and solids are present, the bottle should be rinsed two or three times in the discharge stream, prior to collection of the sample;
- The need to exercise care during sampling to avoid incorporation of solids that may be attached to the effluent channel or pipe.

3.4 *Sampling location*

3.4.1 It is crucial that the sampling location and equipment be selected to ensure a representative sample is obtained. It is important that the sample location is selected in such a way as to ensure that all fractions are collected, including the dissolved, particulate and immiscible fractions, as the COD that is to be measured by the subsequent analysis may be associated with any/all of these fractions.

3.4.2 If a pump is used to deliver the sample or an automatic sampler is used, these should be selected such that flow rates within sampling lines are sufficiently high to prevent deposition of suspended materials, and the collection device for the sampler or pump must be pointed upstream to minimise any effects from the flow in the channel. Samples must be taken from a location which maintains fully turbulent conditions it may be necessary to construct a weir to achieve this. Detailed information on selection of sampling location and key considerations is provided in Refs 1 & 2.

3.4.3 To avoid the possibility of unrepresentative samples leading to anomalous results, it is essential that the conditions of sampling are clearly defined by the establishment concerned. In addition water distribution and drainage layouts must be reviewed to determine the most representative sampling locations.

3.4.4 If the establishment has more than one discharge point, the sample location should be established so that all such discharges which contain trade effluent are captured, samples being collected sufficiently far downstream of the last inflow to ensure a well mixed sample. Alternatively separate samples of each discharge must be taken and aggregated into a flow weighted composite sample for the whole establishment prior to analysis.

3.4.5 The depth and volume of flow must be recorded during sampling, together with the depth at which the sampler is positioned, to demonstrate that the sample taken is representative of the flow as a whole. This is particularly important for establishments with multiple discharge points.

3.5 *Sampling documentation*

In order to confirm the suitability of the proposals the Drainage Authority must be provided with details of the proposed sample collection arrangements. The following information must be included :—

- Number of discharge points from the establishment;
- Diagram showing discharge points and sample collection points;
- Flow rate information;
- Type of sample collection device;
- Depth of flow at time of sampling and sampling collection depth;
- Statement confirming the competence of the sampler to verify that sample *will be* representative of effluent flow;
- Description of any unusual circumstances pertinent to the sample collection;
- Description of any unusual circumstances pertinent to the process or discharge.

3.6 *Sampling Frequency*

3.6.1 The number of days of sampling required for the formal review to establish the effluent characteristics inevitably depends upon the nature of the effluent concerned. Where water usage and effluent characteristics of the establishment are highly variable both on a weekly and monthly basis, the establishment must propose a representative sampling schedule to the Drainage Authority.

3.6.2 Where there is relatively little variation in both daily water usage and daily composite effluent quality on working days (no more than 25%) the number of days of sampling required is given in the tables below. For formal applications received by the Drainage Authority before 1 July 2007, the sampling frequency in Table 1 shall apply. For formal applications received by the Drainage Authority on or after 1 July 2007, the sampling frequency in Table 2 shall apply.

Table 1

Sampling Frequency

Range of Discharged COD (kg/day)	Number of Days of Sampling
0－100	3
101－300	4
301－600	5
> 601	6

Table 2

Sampling Frequency

Range of Discharged COD (kg/day)	Number of Days of Sampling
0－50	2
51－100	3
101 – 300	4
301 - 600	5
> 601	6

3.6.3 The sampling frequency should be determined by using the current trade effluent surcharge estimate of COD load discharged (i.e. using water meter readings for the latest billing period; discharge factor, if any; and COD concentrations from generic characteristics).

3.6.4 Relevant data for the latest year and associated details of any batch processes employed by the establishment that may affect effluent quality must be supplied to the Drainage Authority with the sampling proposal.

3.6.5 The COD of the flow weighted sample for each day of sampling is determined as in Section 5 and 6, and the flow weighted average COD values required for determination of the TES charge are calculated from these in accordance with the equation given in Section 6.5.

4. SAMPLE TRANSPORT AND STORAGE

Samples should be transported to the laboratory for analysis as soon as possible following collection, and must be refrigerated (at 4℃) or iced from the time of collection. To minimise the possibility of either changes in concentration or adsorption of material onto container walls affecting the results, the samples must be analyzed within 24 hours of collection. Retention of samples for periods of longer than 24 hours prior to analysis will only be permitted if stability of the sample over a longer period can be demonstrated to the satisfaction of the Drainage Authority by the laboratory concerned. Samples with a high grease/oil content may rapidly change in nature and must be analyzed as soon as possible.

5. SAMPLE PREPARATION

5.1 Preparation of composites

5.1.1 Samples must be homogenised and combined immediately on arrival at the nominated laboratory, or on site by the sampler, if this has been agreed with the Drainage Authority. The nature of the homogenisation technique selected by the laboratory will be dependent upon the nature of the sample however the method adopted must be agreed in advance with the Drainage Authority.

5.1.2 Equal portions of each sample taken are then combined to produce the composite 24 hour sample to be used for subsequent analysis. At least two 1L composite samples must be prepared, using the same method, for each 24 hour period sampled. One to provide sufficient volume for subsequent analysis and the other to be made available to the Drainage Authority for analysis, if the Authority consider this necessary to verify original results. This must be preserved for seven working days.

5.1.3 The sample for analysis must be split to provide the two separate portions necessary for the TES scheme (settled COD and total COD). Before this is undertaken, the sample must be adjusted to a temperature of 25℃ and pH 7 using the method specified in [Ref 3], the sample should be homogenised if necessary and then two separate sub samples of 500 mL taken.

5.2 Preparation of Sample for total COD measurement

One 500 mL sub sample is homogenised and a suitable aliquot taken (refer to Section 6) to enable the total COD of the original sample to be determined.

Ref 3 Suspended Matter, Settleable and Dissolved solids in Waters and Effluents 1980－DoE SCA method－HMSO London ISBN 011 751957 X]

5.3 *Preparation of Sample for settled COD measurement*

5.3.1 The remaining sub-sample is left to settle for one hour at a temperature of 25℃, during which time the settleable solids will move to the bottom and the fats, oils and greases will rise to the top. The sample for analysis must be drawn from the middle section, whilst ensuring that the settled layers are not disturbed. The detailed procedure to be adopted is that given as [Ref 3].

5.3.2 At least 500 mL of sample should be used for separation by the above technique and at least 250 mL removed for analysis of settleable COD. A smaller aliquot may be required for the actual analysis, consistent with the requirements of the methodology.

6. METHOD OF ANALYSIS

6.1 *Introduction*

6.1.1 The TES scheme makes use of the Chemical Oxygen Demand (COD) test to provide a measure of the organic matter of a sample that is susceptible to oxidation by a strong chemical oxidant. In order to provide the two parameters adopted within the Sewage Services (Trade Effluent Surcharge) Regulation, namely COD settled and COD total, two samples are prepared as described previously and they are both analyzed by a specified standard method.

6.1.2 Analysis undertaken for the above purpose must be carried out in a laboratory with HOKLAS registration for COD analysis; this will ensure a consistent quality of test for all applications for establishment of specific effluent characteristics. Laboratory reports in connection with this must include the certification information for the laboratory conducting the analysis, along with the quality control results (specified in Section 6.4), to allow the Drainage Authority to evaluate the quality of the data provided in support of the application.

6.2 *Test Method*

6.2.1 The open reflux COD method (APHA 5220 B) [Ref 4] should be used to determine the COD concentrations of the samples. This method has the advantage of using a large enough sample to ensure a representative result, but will not include the contribution of any volatile organics, which will be lost in sampling or during the reflux conditions.

Ref 4 Standard Methods for the Examination of Water and Wastewater, 18th edition: American Public Health Association, (1992)－ISBN 0 87553 207 1

6.2.2 If other COD methods are considered suitable by the analyzing laboratory, details regarding these, including comparative performance characteristics for the samples to be analyzed, should be provided to the Drainage Authority, who will determine the acceptability of the alternative proposed.

6.3 *Possible Causes of Interference*

6.3.1 The analytical method specified for COD may be subject to various interferences, the most notable in Hong Kong being due to the possible salinity of the effluent. For effluents containing high concentrations of salt, precautions are mentioned in the method where the salinity (measured as chloride) is less than 2000 mg/L. For samples with higher chloride concentrations, the procedure for measuring COD in saline waters should be used, [Ref 5]. The options for measuring COD in saline water should be assessed by the laboratory for the samples concerned to ensure that the method selected does not affect the accuracy of the result reported－the analyst should be aware that using these technique may lead to results with a high bias. As an alternative, the sample can be diluted to reduce the chloride level to less than 2000 mg/L provided that it can be demonstrated to the satisfaction to the Drainage Authority that this does not affect the accuracy of the result. COD values must *then* be multiplied by the appropriate dilution factor.

6.3.2 In addition other potential interferences, such as those from reduced inorganic substances are described in the referenced method.

6.3.3 All of these interferences will yield COD measurements with a high bias. It is the responsibility of the laboratory conducting the analysis to demonstrate to the satisfaction of the Drainage Authority that results are biased high due to one of these interferences; otherwise results will be considered to be a true representation of the COD.

6.4 *Quality Control*

Quality control procedures are described in the referenced test method [Ref 4], and must be used to verify the accuracy of the analysis. The standard solution (of known strength) involved must be analyzed daily and the results compared to a control chart held as part of the analytical quality control procedures

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Ref 5 Procedures for overcoming C1 interference are given in :-
Correction for chloride interference in the chemical oxygen demand test: Burns, E.R. & C. Marshall, 1965, J. Water Pollut. Control Fed. 37:1716.
Dichromate reflux chemical oxygen demand: A proposed method for chloride correction in highly saline water: Baumann, F.I. 1974, Anal Chem. 46:1336.

of the laboratory concerned. Results of the analysis of this standard must be within the range of the control chart used by the accredited laboratory the relative standard deviation obtained must be within the performance characteristics of the method adopted. *Recovery must be reported along with the sample results*, and the latter will only be accepted if recovery meets these limits.

6.5 *Reporting Results*

6.5.1 When reporting analytical results for this programme, the information described below must be provided. Some of this would be transmitted directly from the sampler (which may or may not be the laboratory) to the laboratory, while other data would be generated in the laboratory itself.

6.5.2 Additional requirements for reporting both proposed sample collection arrangements and their satisfactory completion are described in Section 3.5.

6.5.3 The information required will include :－

- Identification and accreditation of the laboratory performing the analysis.
- Date, time and volume collected, date received by laboratory, and date analyzed.
- Verification by the laboratory that the sample was received in the laboratory in a cold, intact condition.
- Homogenisation technique and volume of sample analyzed.
- All analytical results in mg/L.
- Results for the associated quality control standard in percent recovery.
- Sample location in relation to flow streams and drainage/sewerage layout.
- Type of sample collection (flow weighted proportional sampler, manually composited samples, etc.)
- General observations of sample conditions.
- Flow estimates and method (e.g. water meter readings, depth/velocity monitoring etc.)

6.5.4 The results of each analysis must be reported to the Drainage Authority within three working days of commencement of analysis.

6.5.5 The laboratory will then calculate the mean flow weighted COD (total) and COD (settled) for the sampling period and provide this information to the Drainage Authority in support of the application for re-assessment. The general formula to be used for this is :－

Average COD concentration =

$$\frac{[\text{COD (day 1)} \times \text{flow (day 1)}] + [\text{COD (day 2)} \times \text{flow (day 2)}] + \text{etc....}}{\text{flow (day 1)} + \text{flow (day 2)} + \text{etc....}}$$

6.5.6 The Drainage Authority may require to verify any of the above (or other relevant) data or procedures with the persons/organisations responsible for provision before acceptance of the results of the survey.