APLAC Proficiency Testing Program
(APLAC T078)
Polycyclic Aromatic Hydrocarbons in Sediment

1. OBJECTIVE

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic pollutants that are known to exhibit carcinogenic and mutagenic properties. These compounds are produced anthropogenically under high temperature combustion of fossil fuels in automobile engines, cooking stoves, power plants, refineries and various industrial activities. PAHs are widely distributed and accumulated in the environments such as atmospheric air, water, sediment, etc. Phenanthrene (PHE), fluoranthene (FLT), benzo(a)anthrancene (BAA), benzo(a)pyrene (BAP) and benzo(ghi)perylene (BGP) in sediment sample are chosen as representative PAHs, in terms of their high mass emission or high toxicity equivalence, for the present program. This is the second round APLAC PT for PAH in sediment and the first round was completed in May 2009 with a participation of 58 laboratories.

The aim of the program is to evaluate the performance of laboratories for analysing the above five PAHs in sediment on the basis of reference assigned values provided by the organizers.

2. ORGANIZERS

Government Laboratory (GLHK) is the proficiency testing provider and Hong Kong Accreditation Service (HKAS) is the proposer. This program is organised under the auspices of APLAC.

3. RESPONSIBILITIES

GLHK is responsible for preparing, packaging and dispatching samples, performing homogeneity and stability tests, collecting test results from participating laboratories, conducting statistical analysis of data, handling participants' queries and issuing interim and final reports.

HKAS is responsible for proposing this program for approval by the APLAC Proficiency Testing Committee, inviting participants, circulating the draft report and final report to participants and acting as a contact point between APLAC, participating accreditation bodies / participants and GLHK.

4. APPLICATION FEE

Free of charge.

5. SELECTION OF PARTICIPANTS

APLAC members as well as other non-APLAC members will be invited to participate in the programme. Invitations will be sent to all APLAC members and other accreditation bodies. Participating accreditation bodies will be asked to nominate laboratories to participate and indicate the accreditation status of the nominated laboratories for the test. The number of

laboratories shall be preferably **limited to 100**. Therefore, a restriction on the number of participating laboratories from each accreditation body may need to be imposed. When the number of enrolments exceeds the limit, participants will be selected on a first come first served basis and the organisers will, as far as possible, allow at least one laboratory to participate in this program from each accreditation body.

6. TEST MATERIAL

Preparation of test material was performed in accordance with ISO/IEC 17043:2010 [1]. In brief, About 5 kg of contaminated sediment samples were collected from a coastal site in Hong Kong. The samples were immersed in about 10L of acetone for removing trapped moisture and killing microbes. The mixture was continuously stirred for thirty minutes and then placed inside a fume hood in the Clean Room (Class 1000) for air-drying at room temperature. The dried samples were confirmed by an accredited GC-MS method to be free of analytes under study. About 15L of acetone containing appropriate quantities of PHE, FLT, BAA, BAP and BGP standards were added into the dried sample. The slurry mixture was thoroughly stirred for 2 days and then air dried in the Clean Room. The dried samples were filtered through 1.7 mm sieves in order to get rid of larger brick and stone fragments, shell debris and other foreign substances. The collected sediment particulates were grounded to fine powder with high speed blenders and then thoroughly mixed. Homogenized powder was then packed into cleaned and nitrogen-flush amber glass bottles, each in 30 g portion. More than 150 bottles of sediment samples were finally prepared and stored at room temperature before shipment.

Approximate ranges of the five PAHs are as follows:

PAH	Approximate Conc. Range (mg/kg)
Phenanthrene (PHE)	1 to 10
Fluoranthene (FLT)	1 to 10
Benzo(a)anthrancene (BAA)	1 to 10
Benzo(a)pyrene (BAP)	1 to 10
Benzo(ghi)perylene (BGP)	1 to 10

7. HOMOGENEITY & STABILITY TESTS

Not less than ten samples were taken randomly from the prepared bottles of samples and analyzed in duplicate for determining the sample inhomogeneity in accordance with the recommendation stipulated in ISO13528:2005 [2]. A random sample will be analyzed in triplicate at room temperature (about 25 °C) and at an elevated temperature (about 37 °C) for monitoring the stability of analytes between sample dispatch and after submission of results.

8. DETERMINATION OF ASSIGNED VALUES

Assigned reference values of the five PAHs were determined by isotope dilution gas chromatography mass spectrometry (ID-GCMS) technique. Isotope dilution mass

spectrometry is considered by the Comité Consultatif pour la Quantité de Matière (CCQM) as one of the preferable analytical methods for the provision of accurate and precise results. The ID-GCMS method used in provision of assigned values in this program had been employed for the analysis of PAHs in sediment in the CCQM inter-laboratory comparison programs (CCQM-P69 in 2005 and CCQM-K50 in 2007). The results showed high degree of equivalence with those of other participating national measurement institutes in both programs. This demonstrated that the ID-GCMS method used for the determination of reference value assignment is of high reliability.

9. REPORTING RESULTS

Participants will be provided with ONE sample bottle each containing about 20 g of dried sediment powder. They are requested to determine the concentrations (in mg/kg), on received basis, of the five PAHs, namely phenanthrene, fluoranthene, benzo(a)anthrancene, benzo(a)pyrene and benzo(ghi)perylene in the given sample with a method of their choice, which should be consistent with their routine procedures. Test results, expanded measurement uncertainties* and other technical details shall also be reported in the given result sheets to the organizers. If the determination has been carried out in duplicate or triplicate, laboratories can, if they wish, report all the results obtained. In such case, the mean result will be used for performance assessment.

**Measurement uncertainty is best estimated within the individual laboratory environment. An estimate of uncertainty of measurement is normally based on the combination of a number of influencing parameters (components of uncertainty) such as errors in reference values, instrument errors, repeatability, thermal effects, weighing errors, inhomogeneity etc. As stipulated in ISO Guide to the Expression of Uncertainty in Measurement [3], the influence of each component of uncertainty on the measurement result should be quantified and expressed numerically as a standard deviation. These values are then combined according to the rules of the propagation of uncertainty to produce a combined standard deviation (combined standard uncertainty) and the combined standard uncertainty is multiplied by a coverage factor to produce an expanded uncertainty at the required level of confidence*.

Participants should be aware that any submitted result is considered final and accordingly such data and units should be thoroughly checked before submission.

10. PERFORMANCE ASSESSMENT

Performance of the participating laboratories is assessed using z-score which is calculated as:

$$z = \frac{x_i - x}{\sigma}$$

where x_i = reported result of individual participant
x = assigned values provided by the organizers
σ = standard deviation estimated from the Horwitz Equation

z-Score is commonly interpreted as:

(i)	$\lvert z \rvert \leq 2$	Satisfactory
(ii)	$2 < \lvert z \rvert < 3$	Questionable
(iii)	$\lvert z \rvert \geq 3$	Unsatisfactory

Laboratories having a |z| score equal to or larger than 3 shall thoroughly investigate their results for the discrepancy and those having a z-score in the range $2 < |z| < 3$ are also encouraged to review their results.

11. SUBMISSION OF RESULTS

Participants should submit their results electronically to GLHK on or before the deadline. Results submitted after the deadline will not be accepted. Under no circumstances, correction or adjustment of analytical data will be accepted after the issuance of the interim report.

12. ISSUANCE OF REPORTS

Upon completion of data analysis, the organizers will issue an interim report to participants and their respective accreditation bodies for checking the correctness of analytical data. The draft final report will then be prepared and submitted to APLAC PT Committee for comment and approval. Upon approval by the APLAC PT Committee, an electronic copy of the Final Report will be distributed to participants and their respective accreditation bodies.

Final report, part of the final report or its summary will be posted onto the websites of APLAC, GLHK and HKAS for public interests.

13. PROGRAM SCHEDULE

Event	Period
Preparation of sample	Mar – Apr 2010
Homogeneity testing	May 2010
Submission of proposal to APLAC PT Committee for approval	June 2010
Stability testing	Jul – Oct 2010
Invitation of participants	Jul – Aug 2010
Dispatch of samples	Sept 2010
Submission of results	Oct 2010
Statistical analysis of results	Nov 2010
Interim report	Nov 2010
Submission of draft report to APLAC PT Committee	Jan 2011
Approval of draft report by APLAC Proficiency Committee	Feb 2011
Distribution of final report	Feb 2011

14. CONFIDENTIALITY

The organizers (APLAC, HKAS and GLHK) strive to maintain strict confidentiality with respect to composition of the test sample distributed and the performance of all participating laboratories. To preserve this confidentiality, participants receive reports giving all results for that assessment but without identifying individual laboratories. The code number assigned to a participant in this program is only made known to the contact person or authorized person of his laboratory, the respective nominating accreditation bodies and the organizers.

This program is conducted in the belief that participants will perform the analysis and report results with scientific rigour. Collusion and falsification of results are clearly against the spirit of this program.

15. CONTACT PERSONS

Dr. Yiu-chung Wong, GLHK
10/F, Homantin Government Offices,
88 Chung Hau Street, Homantin, Hong Kong
Fax: +852 2194 1147
Tel.: +852 2762 3853
Email: ycwwong@govtlab.gov.hk

Mr. Wang-wah Wong, HKAS
36/F, Immigration Tower,
7 Gloucester Road, Wanchai, Hong Kong
Fax: +852 2824 1302
Tel.: +852 2829 4813
Email: wwwong@itc.gov.hk

16. REFERENCES

1. International Standards Organization. ISO/IEC 17043:2010, Conformity assessment - General requirements for proficiency testing, ISO, Geneva, Switzerland.

2. International Standards Organization. ISO 13528:2005, Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO, Geneva, Switzerland.

3. International Standards Organization. ISO/IEC G98:2008, Guide to the Expression of Uncertainty in Measurement (GUM), ISO, Geneva, Switzerland.