PROTOCOL FOR THE OPERATION OF PROFICIENCY TESTING SCHEMES

1. GENERAL INFO: The Chemical Metrology Service of the General Chemical State Laboratory plans and operates Proficiency Testing schemes (PT schemes) under the trade name SCHEMA (**S**cheme for **CHE**mical **M**easurement **A**ssessment) according to the International Standard ISO/IEC 17043:2023 -Conformity assessment, General requirements for the competence of proficiency testing providers. Based on an annual program, which is available on the IAPR website, different rounds of PT schemes are offered for a variety of substrates. Moreover, PT schemes may also be conducted on specific request; in such a case, the design of the PT scheme is tailored to the special requirements of the customers.

2. BRIEF DESCRIPTION: The main purpose of PT schemes is the voluntary assessment of services provided by laboratories performing measurements and calibrations. In this context, and with respect to 17043:2023 requirements, the General Chemical State Laboratory (GCSL) undertakes the design, production and dispatch of homogeneous and stable samples according to a predefined schedule. Participating laboratories select the parameters to determine from the ones available, use an analytical method of their choice and are required to report their results within a predefined time frame. The PT scheme provider collects and evaluates the results, using a valid statistical procedure and issues the final report of the PT scheme, where laboratory performance is evaluated by comparing the submitted results to an assigned value (using z-scores or other performance criteria). The use of appropriate coding ensures the anonymity of the participating laboratories and the confidentiality of the results.

3. PARTICIPATION: The annual SCHEMA program is available on the Proficiency Testing webpage at the IAPR website. In the particular document, the rounds of PT schemes offered, the available substrates, the parameters that will be determined and the possible dates are presented. The interested parties state their preferences by completing the appropriate form and returning it to the provider. Two weeks before sample distribution, the provider verifies the registration of the participant by sending the participation form, where details and important dates for the PT scheme are indicated. Every participant receives an official notice with instructions regarding the payment of the participation fees and the dispatch cost at an account held at the Bank of Greece. A proof of payment must be sent to provider; otherwise, the General Chemical State Laboratory reserves the right to withhold the final report from the participants that have not settled their accounts.

4. CONFIDENTIALITY: The personnel of the Chemical Metrology Service of the General Chemical State Laboratory are bound to operate under strict confidentiality. All information concerning the identity of the participating laboratories is confidential and pertinent data are handled only by suitably authorized personnel. Participants can elect to waive confidentiality within the proficiency testing scheme for exceptional circumstances. The information included in SCHEMA reports should not be used for purposes other than the participants' performance assessment without the previous written consent of the provider. The data presented in the final report may be used by the provider for scientific purposes.

5. PLANNING: The planning procedure of PT schemes is an exclusive responsibility of the provider and cannot be assigned to suppliers. The PT provider may refer to external expertise concerning the intercomparison activities by means of a steering committee of acknowledged proficiency. Whenever appropriate, the PT schemes are also supported by advisory expert groups, where internal staff and experts participate to enhance access to scientific

and professional expertise. Sample preparation (production and packaging) is controlled and performed either at the GSCL premises or at the premises of a supplier. Samples are submitted to homogeneity and stability assessment according to standard requirements (e.g. ISO 13528:2022, IUPAC IHP). Homogeneity and stability measurements maybe assigned to other laboratories, under the supervision of the provider in order to ensure that ISO/IEC 17025:2017 requirements are met. The technical details of sample preparation are recorded by the PT provider and included in the final report of the scheme, together with the statistical analysis of homogeneity.

6. DISTRIBUTION: Sample delivery is contracted to a specialized distribution service and operated according to the predefined schedule. All participants are informed in time for the operation of the PT scheme, as well as for its exact schedule. On the date of sample dispatch, the following documents are sent to the participants by email: a cover letter (where a unique laboratory code is suppled for each participant), a note with instructions (where details an sample handling are presented), a form for acknowledging sample receipt, a form for submitting the results and a technical questionnaire. Participants can trace sample dispatch through a unique tracking number, and are kindly asked to inform the provider on sample receipt by completing and returning the respective form. In case sample delivery is delayed on the part of the PT provider, the participants are informed before the predefined sample dispatch date. In case of delivery failure or defective samples, the PT provider assumes responsibility for the dispatch of new items.

7. DETERMINATIONS-RESULTS: Participating laboratories determine the parameters they select using an analytical procedure of their choice (participants are strongly encouraged to apply official or/and validated analytical methods). They are required to submit their results, as well as to complete and return the accompanying technical questionnaire within the deadline, using the appropriate forms sent by the provider. Results submitted after the aforementioned date will not be accepted. In the same context, non-numeric results or zero results will not be taken into account for the PT scheme evaluation in the case of quantitative determinations. Before the issue of the final report (where the assigned values are officially presented), it is possible for the participants to modify/replace values submitted in time, as long as the PT scheme provider is officially informed. Submitted results cannot be withdrawn. The participating laboratories are asked to return to the provider the technical questionnaire along with their results. The submission of the completed technical questionnaire is mandatory. In case where the technical questionnaire is not submitted, the Chemical Metrology Service reserves the right not to use the results of the participating laboratory for the determination of the consensus assigned value.

8. STATISTICAL ANALYSIS- PERFORMANCE EVALUATION: After collecting result forms, data are submitted to statistical analysis using valid statistical procedures according to internationally accepted standards (e.g. ISO 13528:2022, IUPAC IHP). Using appropriate statistical methodology, possible outliers within the data set are identified. Application of robust statistics allows for not excluding the outliers. The results are evaluated by comparing their deviation from the assigned value to the target value of standard deviation for the PT scheme (by means of z-scores, or other appropriate performance criteria):

$$z = \frac{(x - x_{pt})}{\sigma_{pt}}$$

where x, the result reported by the participating laboratory
x_{pt}, the assigned value (estimated as a robust consensus value from the participants' results)
σ_{pt}, the target value of the standard deviation for proficiency assessment

As a next step, the uncertainty of the assigned value is estimated and compared to the target value for the standard deviation. When $\left(\frac{u_{pt}}{\sigma_{pt}}\right)^2$ is higher than 0.10, participant performance is evaluated using z′-scores.

In cases of $\left(\frac{u_{pt}}{\sigma_{pt}}\right)^2$ ratios (where u_{pt} is the uncertainty of the assigned value) higher than 0.50, nor z-scores neither z′-scores are not issued.

9. EVALUATION: Finally, the report of the proficiency testing scheme is issued and sent to every participant, according to schedule, provided that his account has been settled. The report is distributed by *e*-mail as a pdf document. A unique and confidential code is assigned to each participant in order to ensure laboratory anonymity. The final report includes the results of all participants and the evaluation of their performance for every parameter considered. Information is provided regarding the selection and the estimation of both the assigned value and the target value of the standard deviation for proficiency assessment of the PT scheme (application of robust statistics, etc.). The final report is accompanied by an assessment questionnaire, which the participants are kindly asked to complete and return to the provider. If a participating laboratory has any complaint or appeals against the evaluation of its performance, the General Chemical State Laboratory (being the PT scheme provider) has the responsibility to undertake a thorough investigation, reply officially, and, if deemed necessary, to follow specific corrective actions (e.g. to issue and distribute a new report).

10. MANAGEMENT: The General Chemical State Laboratory has installed and is operating a quality management system that fulfills ISO/IEC 17043:2023 requirements. The policy of the provider is aligned with the quality policy of the organization, which has been operating under the requirements of the International Standard 17025:2017. The organizational structure of the provider, as well as the procedures followed concerning the control and handling of records and documents, the choice and evaluation of suppliers, the conduct of thorough audits and reviews, and the implementation of the appropriate corrective, preventive and improvement actions ensure that the requirements of the International Standard 17043:2023 are fully met, the fundamental one being to provide services of high quality and to continuously improve the quality management system.