Talanta 80 (2009) 329–337

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

An interlaboratory study as useful tool for proficiency testing of chemical oxygen demand measurements using solid substrates and liquid samples with high suspended solid content

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ARTICLE INFO

Article history:
Received 6 February 2009
Received in revised form 17 June 2009
Accepted 30 June 2009
Available online 7 July 2009

Keywords:
Interlaboratory study
Proficiency testing
Chemical oxygen demand
Anaerobic digestion
Homogeneity test
Solid substrate
Suspended solids

ABSTRACT

In 2008, the first Proficiency Testing Scheme of Chemical Oxygen Demand (*1st COD-PT^{ADG}*) was conducted to assess the results obtained for different research groups whose field work is mainly anaerobic digestion. This study was performed using four samples, two solid samples as raw materials and two solid samples to prepare high concentration suspended solid solutions. Invitations were sent to a large number of laboratories, mainly to anaerobic digestion research groups. Finally, thirty labs from sixteen countries agreed to participate, but for different reasons four participants could not send any data. In total, twenty-six results were reported to the *COD-PT* coordinator.

This study showed the importance of continuous participation in proficiency testing (PT) schemes in order to compare the results obtained. Taking into account the lack of a general standard method and high quality certified reference materials (*CRMs*), the traceability of COD determination is not currently easy to check. In addition, the spread of participants' results obtained was high and pointed to the advisability of using consensus values due to their unreliability. Therefore, the theoretical oxygen demand (ThOD) values were considered as assigned values for all the samples analysed. On the other hand, in this PT the established standard deviation (*ESD*) has been determined by the Horwitz modified function.

Participants of this *1st COD-PT^{ADG}* were asked to give a short report on the analytical method used. Although all the participants used potassium dichromate as their oxidant reagent, their experimental procedures were very different. With the purpose of comparing the results obtained, the different experimental conditions used were classified into five methods, corresponding to two main categories, open and closed reflux. The performance of laboratories was expressed by the *z*-score, whose value is considered satisfactory when *z*-score $\leq \pm 2$. The overall analytical data evaluation showed that 64% of *z*-scores obtained were outside the accepted limits.

1. Introduction

There are a large number of laboratories that can measure the chemical oxygen demand (COD). COD is an empirical determination

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doi:10.1016/j.talanta.2009.06.071

used worldwide to find out the index of pollution of any aqueous sample, although it is also used to determine the organic content of solid substrates. For COD determinations, a wide range of chemicals has been used as oxidizing agents, including dichromate, permanganate, ceric acid, iodate and persulphate. The dichromate method is preferable to other methods using different oxidants because of its superior oxidizing ability, its applicability to a wide variety of samples and its easy manipulation. In the COD reference method, samples are oxidised by potassium dichromate in an acid sulphuric medium. Silver sulphate and mercury sulphate are added to catalyse the oxidation and to suppress the interference effects of chloride, respectively. The resulting mixture is refluxed for 2 h and the residual dichromate reagent is determined by titration with standardised ferrous ammonium sulphate or spectrophotometrically. The amount of dichromate reduced is expressed as COD in the form of milligrams of oxygen consumed per litre or gram of sample.

Proficiency testing (PT) is an essential element of laboratory quality assurance. The interlaboratory comparison of an external quality control test material allows individual laboratories to compare their analytical results with those from other laboratories whilst providing them with objective standards to perform with.

The performance evaluation of anaerobic digestion processes is based on chemical analysis measurements. Accurate and precise results are essential when monitoring anaerobic reactors because only reliable analytical results can serve as a basis for drawing meaningful conclusions about the situation of the biological process and thus avoid misinterpretation. However, the COD determination of samples typically from anaerobic reactors, as solid substrates and liquid samples with a high concentration of suspended solids, is currently in the following situation:

- no companies organise COD-PT schemes.
- no appropriate certified reference materials are available for this determination.
- no references of COD analytical methods are cited in the literature.
- the frequent use of the APHA-AWWA-WPCF standard methods [1] for COD determination of solid samples and high concentration suspended solids solutions by dilution of the sample, with the consequent inaccuracy in the final results obtained.

No previous interlaboratory studies are reported in the literature about the quality of COD measurements obtained in such types of samples. For this reason, a PT was organised. The aim of this *1st COD-PT* was to take some information from the results obtained for all participants, testing the different analytical methods used and comparing the results reported in order to check their day-to-day analytical performances and improve their quality. The objective of this PT was not the evaluation of participants by a general proficiency ranking. Therefore, the ranking of participants was totally rejected and not reported.

2. Organisation of proficiency testing scheme

This study is the first attempt of a COD worldwide interlaboratory comparison using solid samples and high concentration suspended solids solutions. The scheme was organised by the Spanish National Research Council (CSIC) through the Instituto de la Grasa, specifically by the Water and Wastewater Treatment group. The PT coordinator and collaborators were responsible for designing the scheme, the preparation and validation of test materials, the production and distribution of instructions and test materials to participating laboratories, the collection and statistical analysis of the data obtained from the PT and feedback of the results to the participants.

This PT was carried out according to the International Harmonised Protocol for the PT of Analytical Chemistry Laboratories [2]. The exercise took place from September 2008, when the samples were shipped to the laboratories for analysis, to the beginning of October 2008, when the last reports of the results were received. The deadline for the reporting of results was extended upon the request of eight participants so as not to exclude their results. Although initially, thirty groups from sixteen countries agreed to participate, finally four participants could not send any data: 1 lab never received the samples, 2 labs admitted to being unable to determine the samples and 1 lab gave no explanation. Finally, twenty-six results were reported to the *COD-PT* coordinator. Firstly, the individual lab reports, including the specific results of each participant, and secondly a draft general report with the whole results were sent to participants.

The determination of COD does not require great laboratory skills or highly selective and sensitive analytical techniques and procedures with difficult validation or accreditation by recognized bodies. Therefore, no information was required to participants about their accreditation status for COD parameter according to ISO/IEC 17025 [3], or their participation in previous PTs.

3. Materials and methods

3.1. Materials

3.1.1. Description of samples

All laboratories participating in the PT to assess the COD measurement quality were required to analyse four different samples. The samples were divided into two main groups; solids samples (SS) and high concentration suspended solid samples (HC3S).

Table 1
Characterisation of solid substrates used in the *1st COD-PT*^{ADG}.

	(CRM)	(Qu)	(SuOC)
Particle size (mm)	0.2–1.0	1.4–2.0	<0.355
Moisture (%)	7.0 ± 0.3	10.1 ± 0.1	6.7 ± 0.3
Chemical composition (%dry basis)			
Carbohydrates	N.D.	67.3	20.3
Fat	N.D.	5.0 ± 0.1	0.8 ± 0.1
Protein	N.D.	18.0 ± 0.5	36 ± 1
Fibre	N.D.	7 ± 1	34.4 ± 0.5
Elemental analysis (%dry basis)			
Organic content	60.5 ± 0.2	97.3 ± 0.2	91.5 ± 0.3
C	33.3 ± 0.2	44.9 ± 0.2	45.9 ± 0.1
H	4.6 ± 0.1	6.2 ± 0.2	5.7 ± 0.2
N	4.7 ± 0.2	2.8 ± 0.1	6.6 ± 0.1
S	1.27 ± 0.04	0.009 ± 0.001	0.36 ± 0.04
Theoretical oxygen demand (mg O_2 g^{-1} TS)	988	1210	1239