Control of VFAs in anaerobic reactors: Is it an easy task? What do we know about off-line analytical performance?

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Abstract

Anaerobic digestion (AD) is sensitive to many environmental factors and, therefore, a robust control of the process is essential to avoid possible instability due to metabolic disturbances. One of the analytical measurements considered as a "crucial key parameter" are the volatile fatty acids (VFAs). They are very important intermediates metabolites that in stable AD systems are produced by hydrolytic-acidogenic bacteria and utilized by methanogenic microorganisms to produce methane. Thus, the VFAs imbalance and following accumulation is interpreted as a process inhibition. Total amount of organic acids (TVFA) to control the relative changes over time has been suggested as useful tool, and a variety of techniques (titrimetric, chromatography, infrared) for online monitoring has been assayed. However, TVFA are not sufficient information to reveal the overall reactor status and individual components have been put forward as being of particular interest. Although some tentatives have been described as on-line measurements, normally the different individuals VFAs are determined by off-line chromatographic techniques such as GC and HPLC. Considering that no standard method is available, the majority of research groups on this field use different analytical procedures characterized by diverse factors such as instrument, column, injector, experimental conditions, preparation of sample and calibration. No previous information was reported on the literature about the harmonization of analytical results relating to individual VFAs. Therefore an interlaboratory comparison was organised using a diluted standard sample. The general performance of data proportioned in this interlaboratory comparison was assessed using the z-score value. The overall performance at starting target error (7.5% of CV) was 45.6% of satisfactory results. In addition, a linear model was obtained to relate the general performance against the fit for purpose criterion to analyze the data. To achieve an overall 75% of satisfactory results the target error should be almost three times higher, from the initial 7.5% to 20.9%. Further evaluation of the experimental results will include an in-depths analysis of the laboratories´ individual methods.

Keywords

Control, Monitoring, Volatile fatty acids, Interlaboratory, Proficiency Test

INTRODUCTION

It is well known that volatile fatty acids (VFAs) concentration in anaerobic reactors provides a

suitable parameter for controlling the balance of the "liquefaction" and "gasification" phases of a digester. A sudden increase in the VFAs concentration is considered as an indicator of imbalance between these two phases. Therefore, a strict control of the digester balance including the concentration of individual VFAs is most essential. There are on the literature different chromatographic methods (GC/HPLC) to determine the VFAs, each of them with specific characteristics such as: instrument, column, injector, experimental conditions, preparation of sample and calibration. Considering the lack of information about the analytical performance on VFAs determination, an interlaboratory comparison (ILC) study was organised to obtain further information. Specifically, a proficiency testing scheme (PTS) was organised. A PTS can be defined as a set of analyses conducted by a number of laboratories on identical portions of the same material by any method for the purpose of demonstrating the performance of the laboratory or analyst (Horwitz, 1994). The main purposes of PTS are: i) to test the ability of a laboratory to obtain measurement results similar to those of peer laboratories; ii) to document participant's measurement performance; iii) and for education and training.

The main objective of this research work was to evaluate the general performance of this determination among participants that routinely determine the individuals VFAs. Firstly, the reported results of VFAs analyses have been evaluated from the analytical quality point of view. Secondly, the results were assessed in relation to fitness for purpose target error.

MATERIAL AND METHODS

Liquid Sample (Reference Material)

It was a solution prepared by dilution of a standard mixture of nine VFAs at 10 mM commercially available (Supelco brand; reference: 4750U). Participating laboratories were free to select the individual VFAs to be measured.

Analytical Methods

The participating laboratories were free in the choice of the analytical method that they consider appropriate to perform the analyses, but they should be consistent with their normal routine practice. Additionally, to further study the results reported, the participants were requested to provide detailed information about their analytical methodologies.

PTS assessment

The performance of each individual laboratory participant was assessed by the z-score. A participant's result is converted into a z-score according to the following equation:

$$\boldsymbol{z\text{-}score = (X_{EV} - X_{AV}) / \sigma_{PT}}$$

where X_{EV} is the laboratory experimental value. X_{AV} is the assigned value (estimation of the true value of the measurand that is used for the purpose of calculating scores), and σ_{PT} is the fitness for purpose based "standard deviation for proficiency assessment", defined as a target value for the acceptable deviation from the assigned value. To carry out the analytical performance in this PTS, X_{AV} was assigned from the certified value and $\boldsymbol{\sigma_{PT}}$ of individual VFAs was calculated from overall coefficient of variation (CV) value using the Horwitz modified functions which consider the concentration level of analyte (Thompson, 2000)

Each result from a laboratory can be categorised as satisfactory/acceptable (z-score$\leq\pm2$), questionable/doubtful ($\pm2<$z-score$\leq\pm3$) or unsatisfactory/unacceptable (z-score$>\pm3$). On the other hand, it is interesting to know the overall PTS performance considering the results of each individual VFAs reported by all the participating laboratories. Garner and Dobbs (2004) proposed a classification about overall PTS performance using four categories relating to z-scores considered as acceptable: i) Good (90-100 %), ii) Satisfactory (75-90 %), iii) Moderate (50-75 %) and iv) Poor (<50 %). It is unrealistic to expect a 100 % overall acceptable z-score, only based on statistical considerations, but they propose 75% overall acceptable z-score to be achievable routinely.

RESULTS AND DISCUSSION

The experimental values reported by participating laboratories are shown in Table 1. As can be seen the assigned values can be considered as low-medium concentration, they ranged from 60 to 129 mg/L. The performance of each participating laboratory was assessed by the internationally accepted z-score. On the other hand, Table 2 shows the z-score assessment using the theoretical fitness for purpose criterion. Although all the individual VFAs were not analyzed by the same number of participants, the overall analytical performance was obtained without considering this variable. It is important to note that short chain VFAs (C2 and C3) were reported with less trueness that longer chain ones. This fact could negatively influence the usefulness of C3/C2 ratio as sensitive indicator of reactor "stress" or failure (Nordstedt and Thomas, 1985; Hill et al., 1987).

Table 1. Assigned and experimental values of VFAs reported by different participating laboratories

VFA	C2	C3	iC4	C4	iC5	C5	iC6	C6	C7
X_{AV} (mg/L)	**60**	**67**	**92**	**87**	**101**	**101**	**115**	**115**	**129**
Laboratory	**EXPERIMENTAL VALUES- X_{EV} (mg/L)**								
A	47	142	164	168	206	204			
B	40	51	58	57	67	70	78	77	85
C	53	68		88	96	86	127	91	117
D	35	62		72	94	99			
E	55	63	67	72	75	75			
F	67	83	90	91	107	107			
G	52	81	77	80	113	102			
H	93	76	76	71	96	109	107	107	
I	91	68	90	84	116	108			
J	77	97	100	96	107	125		131	142
K	55	70	80	83	93	94		100	109
L	65	80	87	98	105	107		132	
M	25	112	93	96	123	101	133	124	147
N	50	67	77	75	87	83			
O	114	121				125			
P	93	130	151	140					
Q	297	380	417	401	500	500			
R	106	104	97	32	54	63			
S	56	73		90	52	53		58	65
T	61	83	106	102	129	128		146	166
U	57	73	84	83		101		120	133
V	80	6	92	94	117	112			
W	29	38	52	44	51	52	59	60	
X	90	106	116	120	134	136			

Table 2. Results of the overall z-score assessment (CV = 7.5%)

VFAs	n	/z-score/≤2		2</z-score/≤3		/z-score/>3	
		n	%	n	%	n	%
C2	24	9	37.5	2	8.3	13	54.2
C3	25	9	36.0	2	8.0	14	56.0
iC4	20	10	50.0	3	15.0	7	35.0
C4	23	12	52.2	4	17.4	7	30.4
iC5	21	10	47.6	2	9.5	9	42.9
C5	23	11	47.8	1	4.3	11	47.8
iC6	5	2	40.0	1	20.0	2	40.0
C6	11	6	54.5	1	9.1	4	36.4
C7	8	4	50.0	1	12.5	3	37.5
Total	**160**	**73**	**45.6**	**17**	**10.6**	**70**	**43.8**

Figure 1 shows the overall general performance reported by participating laboratories. For the theoretical or Horwitz target error (7.5% CV) the general performance was low, with only 45.6% of z-scores considered as acceptable. It can be noted that the increase in the target error correlates to a better analytical performance. The relation was found to be almost linear. It can be calculated that to achieve an overall analytical performance considered as satisfactory (75 % of z-scores reported as acceptable), a considerable increase in the tolerated target error would be necessary from 7.5% to 20.9% of CV.

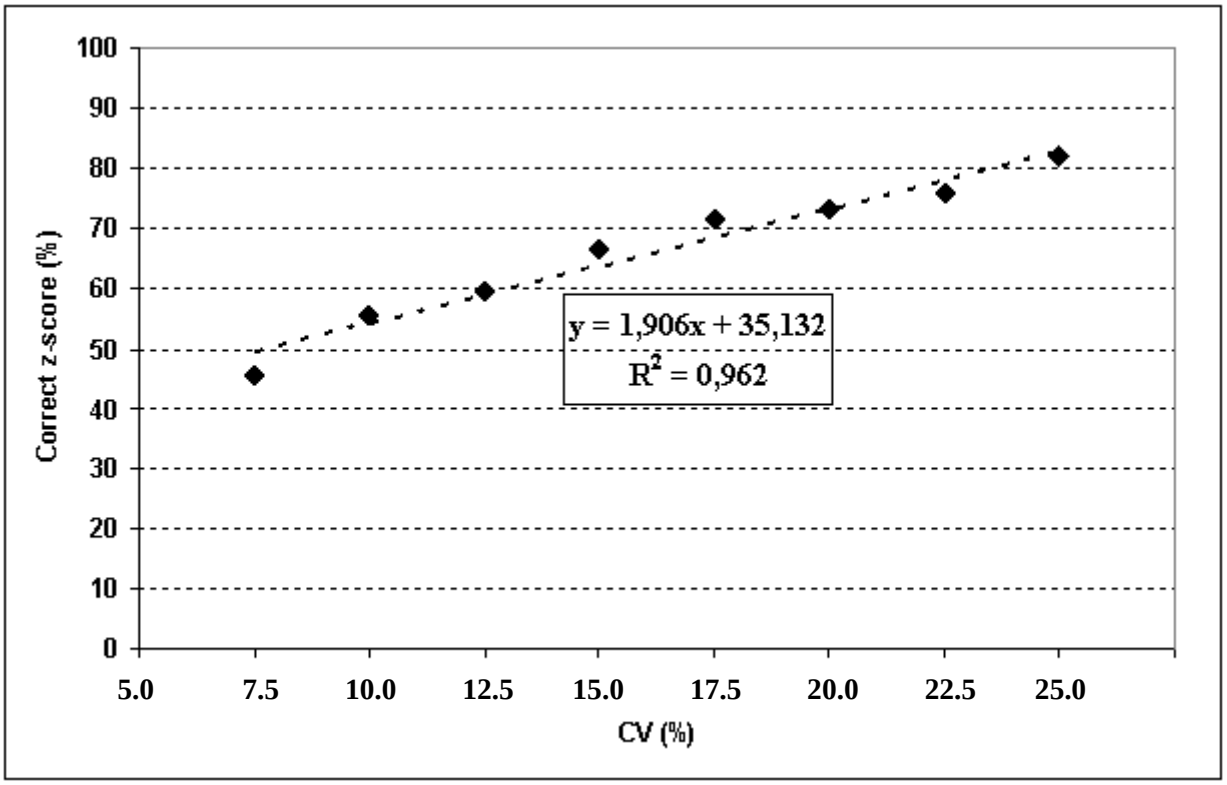

Figure 1. Evaluation of overall z-score (%) versus fitness for purpose target error (CV%)

As a conclusion, the participation in a PTS can be considered as useful tool to determine the analytical performance of a measurement. In this case, a first step to improve the reliability of individual VFAs analyses is to further evaluate the different experimental procedures utilized by the participating laboratories. This includes all the factors defining the analytical methods such as instrument, column, injector, experimental conditions, preparation of sample and calibration.

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