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A NEW METHOD FOR DETERMINATION OF ANAEROBIC DIGESTER GASES BY TOTAL ORGANIC CARBON ANALYZER

A simple innovation is suggested as an alternative to the gas chromatographic method for analysis of anaerobic digester gases by means of a total organic carbon analyzer.

All gas injections into the instrument must be performed at constant temperature in order to obtain reproducible results. Injections on the total carbon channel refer to the amount of carbon dioxide, methane and impurity gases, whereas those into the inorganic carbon channel refer to carbon dioxide, so that the methane content could be evaluated from the difference. The results obtained are compared with gas chromatographic data. The benefits of this method compared to that of the gas chromatographic are lower analysis cost and the fact that no skilled operator is needed.

1. INTRODUCTION

The gases produced in the anaerobic decomposition of wastewaters are mainly methane and carbon dioxide with small amounts of hydrogen, hydrogen sulfide, nitrogen etc. For about twenty years now, gas chromatography has replaced the Orsat method [1], the main drawbacks of which consist in cumulative errors due to consequential volumetric analyses. At present gas chromatography is used as a matter of routine for these determinations, however, the analysis costs are claimed to be too expensive [1] mainly due to helium used as carrier gas, column packings etc.

The main aim of this brief report is to suggest a simple method for anaerobic digester gas determinations using a total carbon analyzer, which overcomes the above-mentioned drawbacks.

2. EXPERIMENTAL

2.1. INSTRUMENTS AND APPARATUS

A Beckman total organic carbon analyzer mod. 915 used, was equipped with a mod. 865 infrared analyzer and a linearizer board mod. 633756. A gas chromatograph of Carlo Erba Company Mod. Fractovap G V used was equipped with a thermoconducibility

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detector, two stainless steel columns (length 2 m, i.d. 4 mm) packed with chromosorb 102 (80–100 mesh) and conditioned at 100°C for 24 hours.

Helium was used as carrier gas at a flow rate of 40 cc/min and at a column temperature of 40°C.

Standard and anaerobic digester gases were introduced with Hamilton syringes. Gas sampling bulbs for gas storage were used in order to attain room temperature (22±0.1°C).

2.2. REAGENTS

Standard gases, methane and carbon dioxide of the purity of 99.97% were purchased by the Matheson gas product company. Oxygen and helium of the purity of 99.95% were used as carrier gases for carbon analyzer and gas chromatographic determinations, respectively.

3. PROCEDURE

Calibration curves on a total carbon analyzer were made by introducing pure gases i.e. methane and carbon dioxide on total carbon and inorganic carbon channels, respectively. Gas volumes of 10, 25, 40 and 50 μl corrected for attenuation against detector responses gave straight calibration lines, so that each gas volume could be calculated by direct proportion. Following that 50 μl of unknown gas mixture were introduced into both channels. A similar procedure was carried out with the gas chromatograph obtaining straight calibration lines for both gases of the same volume range. Peak heights were computed for gas mixture and the volume percentage of each gas was calculated in the same way.

4. RESULTS AND DISCUSSION

Introduction of the unknown gas mixture into the total carbon channel allows to calculate of first the total carbon percent, and then, impurity gases from the difference with the calibration curve value, while inorganic channel response gives the carbon dioxide amount whence the methane percentage can be evaluated.

Table

Comparison of carbon analyzer and gas chromatograph results
Porównanie wyników otrzymanych za pomocą analizatora całkowitego węgla organicznego i chromatografu

Type of instrument	Methane and carbon dioxide amounts	Carbon dioxide amounts	Impurities	Methane
	%			
Total organic carbon analyzer	96.5	34	3.5	62.5
Gas chromatograph		35.3		62.5

In order to test the reliability of the method, the same unknown mixture was simultaneously introduced into the gas chromatograph.

For comparison the values obtained with both instrumental techniques are listed in table. They represent the mean of ten repetitive determinations with a standard deviation of $\pm 1\%$.

5. CONCLUSIONS

Considering that the time of analysis for TOC and gas chromatographic methods is almost equivalent (i.e. about four minutes), the method suggested has the following advantages:

1. Costs of the analysis are lower for the TOC method. In view of the fact that helium, used for gas chromatographic determinations at flow rate of 40 cm^3/min, is almost ten times more expensive than oxygen used for TOC determinations at flow rate of 150 cm^3/min, it follows that analysis costs are for the former method twice or three times larger.

2. TOC method requires a less skilled operator, as the chromatographic method needs more control operations (i.e. injection port, oven and detector temperatures, column packing, careful control of gas flow rate, etc.).

TOC analyzer can, moreover, be used directly both for gas and liquid analyses, while gas chromatograph requires normally column and detector replacement and a new time consuming calbration of the instrument.

REFERENCES

[1] *Standard methods for the examination of water and wastewater*, 14th edition, 1975, APHA-WPCF.

NOWA METODA OZNACZANIA GAZÓW ANAEROBOWEJ KOMORY FERMENTACYJNEJ PRZEZ ANALIZATOR CAŁKOWITEGO WĘGLA ORGANICZNEGO

Sugeruje się prostą technikę (jako alternatywę metody chromatografii gazowej) analizy gazów z beztlenowej komory fermentacyjnej za pomocą analizatora całkowitego węgla organicznego.

Wprowadzenie próbek gazu do instrumentu musi być dokonywane w stałej temperaturze, tak aby można było otrzymać powtarzalne wyniki. Wprowadzenie do kolumny całkowitego węgla pozwala ustalić ilości dwutlenku węgla, metanu i gazów zanieczyszczonych, podczas gdy wprowadzenie do kolumny węgla nieorganicznego pozwala oznaczyć dwutlenek węgla, tak aby z różnicy można było oszacować zawartość metanu. Otrzymane wyniki porównano z wynikami analizy chromatografii gazowej. Korzyści zaproponowanej metody, w porównaniu z chromatografią, to niższe koszty analizy oraz fakt, że nie wymaga ona fachowego operatora.

NEUE METHODE ZUR BESTIMMUNG DER ZUSAMMENSETZUNG DES FAULGASES MIT HILFE DES TOC-ANALYSATORS

Vorgeschlagen wird eine relativ einfache Technik zur Bestimmung der Zusammensetzung des Biogases aus Faulkammern mit Hilfe eines TOC-Analysators — als Alternative zur Gaschromatografie.

Um reproduzierbare Ergebnisse zu gewährleisten, muß die Gasprobe bei einer konstanten Temperatur in den Analysator eingeführt werden. Der Probeeingabe in die TOC-Kolonne folgt die Bestimmung der CO_2- und CH_4-Mengen sowie der Begleitgase. Durch Probeeingabe in die C_{anorg}-Kolonne, wird nur die CO_2-Menge bestimmt. Die Differenz wird als Methan angenommen. Die Ergebnisse wurden mit denen der Gaschromatografie verglichen. Bei vergleichbarer Sensitivität, ist die TOC-Methode einfacher und billiger.

НОВЫЙ МЕТОД ОПРЕДЕЛЕНИЯ ГАЗОВ АНАЭРОБНОЙ БРОДИЛЬНОЙ КАМЕРЫ С ПОМОЩЬЮ АНАЛИЗАТОРА ПОЛНОГО ОРГАНИЧЕСКОГО УГЛЯ

Предлагаются простые инновации (в качестве альтернативных методов газовой хроматографии) в анализе газов в анаэробной бродильной камере с помощью анализатора полного органического угля.

Все инжекции газа в инструмент должны производиться при постоянной температуре таким образом, чтобы можно было получить повторяемые результаты. Инжекции на канал полного угля относятся к количеству углекислого газа, метана и к загрязнённым газам, в то время как инжекция на канал неорганического угля относится к углекислому газу таким образом, чтобы из разности можно было оценить содержание метана. Полученные результаты сопоставлены с данными по хроматографии. Выгоды этого метода, по сравнению с выгодами хроматографического метода, это более низкие расходы анализа, а также то, что при его применении не требуется оператор специалист.