Halogenated hydrocarbons in land fill gas

Application Note

Energy & Fuels

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Introduction

The Centraal Overijsselse Nutsbedrijven NV exploits a gas well on a land fill in Delden, The Netherlands. The gas is dried and supplied to a chemical company for the generation of energy in steam boilers. The energy needed by the plant is supplied by a gas engine-generator set, fueled with land fill gas.

It consists mainly of methane, carbon dioxide, nitrogen and air. Additionally, the gas also contains pollutants like volatile halogenated hydrocarbons and hydrogen sulfide. These compounds could cause problems with end use of the gas.

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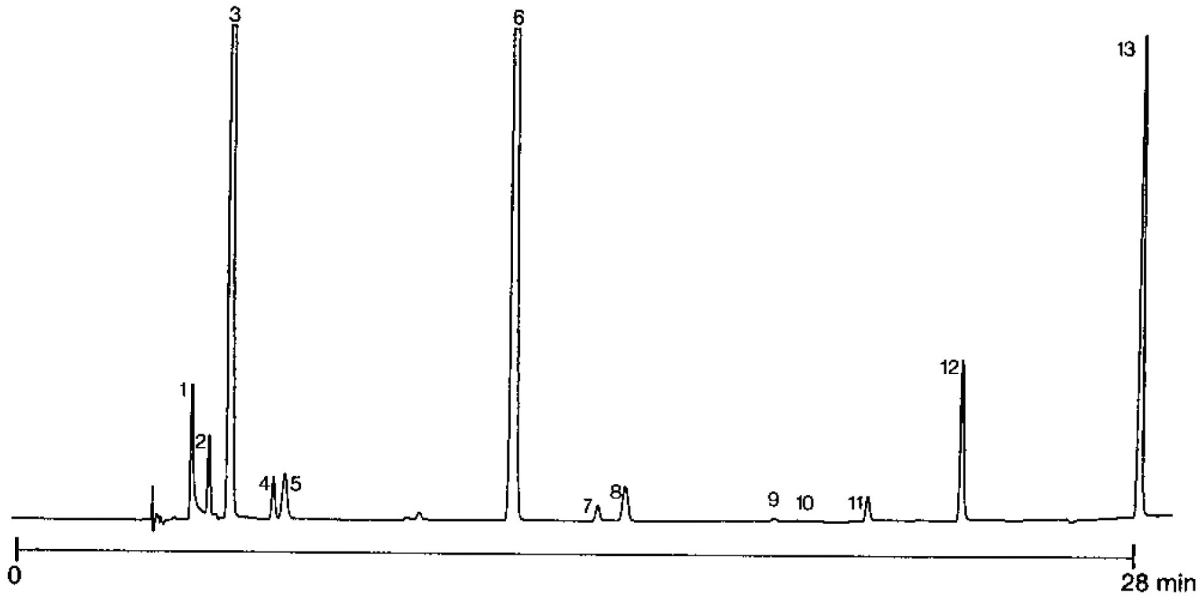
Conditions

Technique	: GC-capillary
Column	: Agilent CP-Sil 5 CB, 0.32 mm x 25 m fused silica WCOT CP-Sil 5 CB (5.0 µm) (Part no. CP7680)
Temperature	: 30 °C (5 min) ⟶ 105 °C, 5° C/min ⟶ 200 °C, 10 °C/min
Carrier Gas	: N_2, 20 kPa (0.2 bar, 3 psi)
Injector	: Splitter, 30 mL/min T = 250 °C
Detector	: ECD, range 3, att. 2^4 T = 280 °C
Sample Size	: 1000 µL

Peak identification

	methane	58%
	carbon dioxide	38%
	nitrogen	3%
	oxygen	0.5%
1.	hydrogen sulfide	50 ppm
2.	Freon 22	
3.	Freon 12	1.9 ppm
4.	chloroethene	1.7 ppm
5.	Freon 114	0.2 ppm
6.	Freon 11	0.1 ppm
7.	dichloromethane	0.2 ppm
8.	Freon 113	< 0.005 ppm
9.	1,2-dichloroethene	
10.	trichloromethane	< 0.05 ppm
11.	1,1,1-trichloroethane	0.5 ppm
12.	trichloroethene	0.1 ppm
13.	tetrachloroethane	< 0.1 ppm



ppm range analysis

For the determination of the volatile halogenated hydrocarbons in land fill gas we use a CP-Sil 5 CB column (0.32 mm x 25 m, df = 5.0 µm). This column gives a good separation of all the compounds of interest in the gas. Using an ECD, it proved possible to detect hydrogen sulfide, oxygen, Freons and other halogenated hydrocarbons.

Reference gas

(100 µL reference gas + 900 µL air)

Peak identification

	concentation:
1. oxygen	18.8%
2. Freon 12	1 ppm
3. chloromethane	0.9 ppm
4. neon 114	0.9 ppm
5. Freon 11	1 ppm
6. trichloromethane	1 ppm
7. 1,2-dichloroethane	1.3 ppm
8. tetrachloromethane	1.1 ppm
9. trichloroethene	1.5 ppm
10. tetrachloroethene	

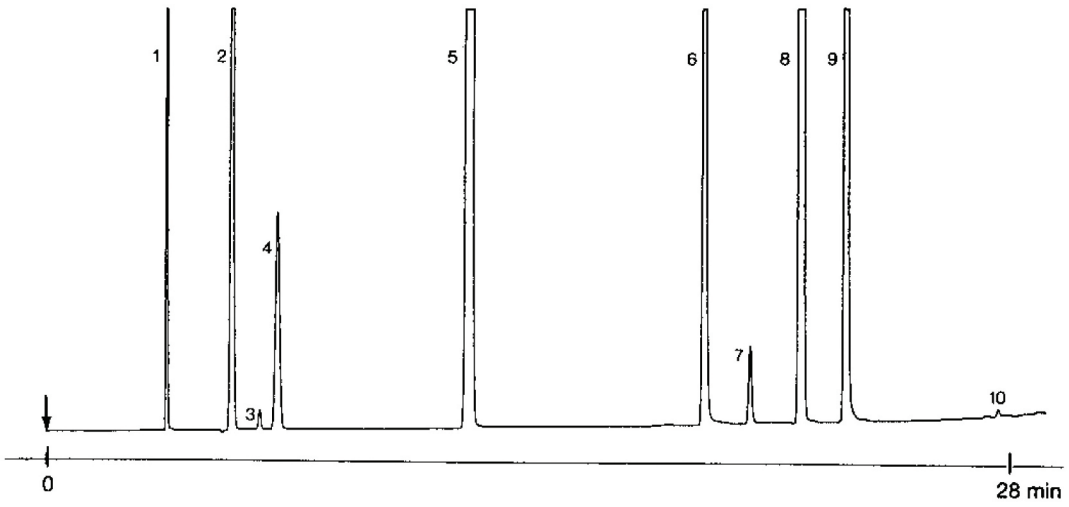
Analysis procedure

The injection volume is adapted to the sensitivity of the detector. Samples are taken in 1000 mL glass bottles, and the gas is injected with a syringe (up to 1000 µL). The results of an analysis are compared with calibration curves. For each compound a calibration curve is made from 0 to 10 ppm with steps of 1 ppm by means of dilution of the calibration gas. For hydrogen sulfide a separate calibration curve is made up to 60 ppm. The curves are compared with a calibration gas and are corrected if necessary. In 1985 the results of the analysis of land fill gas were compared with those of the Battelle Institute, Frankfurt (BRD) where the same type of analysis is performed.

Conclusions

Using the above mentioned column, the halogenated hydrocarbons present in land fill gas can be separated very well. It proves possible to detect compounds like hydrogen sulfide, oxygen, Freons and halogenated hydrocarbons. Retention times are reproducible.

The injection volume has to be adapted to the sensitivity of the detector for hydrocarbons with only one halogen atom. An injection volume of 1 000 µL proves to give no problems.



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Printed in the USA
31 October, 2011
First published prior to 11 May, 2010
A00300

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