Journal of Chromatography A, 1216 (2009) 2776–2782

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Practical method for the measurement of Alkyl mercaptans in natural gas by multi-dimensional gas chromatography, capillary flow technology, and flame ionization detection

R. Gras[a], J. Luong[a,*], V. Carter[a], L. Sieben[a], H. Cortes[b]

[a] Dow Chemical Canada, P.O. Bag 16, Highway 15, Fort Saskatchewan, Alberta T8L 2P4, Canada
[b] Dow Chemical USA, 1897B Building, Midland, MI 48667, USA

ARTICLE INFO

Article history:
Available online 13 September 2008

Keywords:
Multi-dimensional gas chromatography
Capillary flow technology
Deans switch
Methylmercaptans analysis
Impurities in natural gas
Sulfur containing compounds

ABSTRACT

Volatile sulfur compounds such as alkylmercaptans are undesired impurities in natural gas streams. As a result, natural gas treatment and purification services are essential in many industries that utilize natural gas either as a fuel or in a chemical process. While there are many analytical methods that can be employed for the measurement of mercaptans, a simple, practical, and easy-to-implement method is required for remote field deployment. An analytical method, based on multi-dimensional gas chromatography (MDGC), *capillary flow technology* and flame ionization has been successfully developed for the application described. Results based on the technique showed alkylmercaptans can be accurately measured with a minimum detection limit of 200 ppb (v/v) or better, a linear range of up to 100 ppm (v/v), and a relative standard deviation ($n = 10$) of 1.2% or less were obtained by manual injection with a total sample-to-sample analysis time of less than 15 min.

1. Introduction

Sulfur containing compounds such as mercaptans are often found in natural gas streams and viewed as undesirable impurities [1–3]. The presence of these compounds can cause plant corrosion, catalyst poisoning, or odor to products produced. Amine sweetening processes remove these contaminants so that the gas is marketable and suitable for transportation. Amine gas treatment is a proven technology that removes mercaptans as well as hydrogen sulfide and carbon dioxide from natural gas and liquid hydrocarbon streams through absorption and chemical reaction [4–6]. There are many analytical methods that can be used for the measurement of mercaptans in order to determine the effectiveness and long term performance of the treatment process [7–13]. Unfortunately cost-of-ownership and skills required to perform these methods have been some key limiting factors. As a result, a reliable, but practical and simple to operate analytical method was needed for remote field deployment for the application described.

A gas chromatographic technique, based on conventional multi-dimensional gas chromatography, *capillary flow technology*, flame ionization detection was successfully developed and implemented. This paper summarized the results obtained.

2. Experimental

An Agilent 6890N gas chromatograph equipped with two split/splitless injectors, two flame ionization detectors, and capillary flow plate used as a Deans Switch, PN No. 2855B, Rev C, and a 3-way, 24 V dc, 5 W fluid automation switching valve (FAS PN No. 6-311-003-46) was used for flow switching.

Gas chromatographic conditions used are as follows—gas chromatograph: Agilent 6890N; injector: split/splitless in split mode with split ratio of 5:1, temperature: 250 °C; column set employed: first dimension: 15 m × 0.32 mm ID, 1 μm VF-WAXms, second dimension: 6.5 m × 0.32 mm ID, CP-PoraBOND Q, restrictor: 1 m × 0.18 mm ID, deactivated but uncoated fused silica. Inlet pressure: 9.6 psig; aux pressure: 7.4 psig, (a) flow rate flame ionization detection (FID) system 1 (FID1) (VF-WAX ms + restrictor): 3.6 mL/min, (b) flow rate FID system 2 (PoraBOND Q): 4.0 mL/min. Oven profile: (a) 40 °C (2 min), 20 °C/min to 250 °C (2 min). FID systems: hydrogen: 35 mL/min, air: 400 mL/min, auxiliary: nitrogen at 25 mL/min, temperature: 250 °C.

* Corresponding author at: Dow Chemical Canada, Analytical Sciences, P.O. Bag 16, Highway 15, Building 158, Fort Saskatchewan, Alberta T8L 2P4, Canada.
Tel.: +1 780 998 8668; fax: +1 780 998 6709.
E-mail address: luong@dow.com (J. Luong).

0021-9673/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2008.09.029

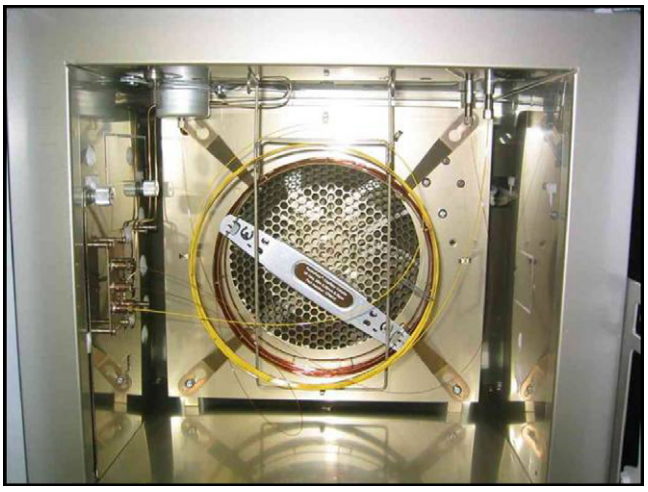

Fig. 1. Setup of multi-dimensional gas chromatography with capillary flow technology for mercaptans in natural gas on an Agilent 6890N GC. Note the compactness of the in-column switching device on the left side of the oven wall.

Other column sets tested for the application include:

Column set 1: first dimension: 30 m x 0.25 mm ID, 1 μm VF-1 ms; second dimension: 30 m × 0.25 mm ID, 1 μm VF-WAXms.
Column set 2: first dimension: 30 m × 0.25 mm ID, 1 μm VF-1701 ms; second dimension: 30 m × 0.25 mm ID, 1 μm VF-WAXms.

Alkyl mercaptan standards were obtained from Scott Specialty while natural gas was supplied by ATCO Gas, Edmonton, Alberta, Canada.

3. Results and discussion

3.1. Analytical techniques for measuring alkylmercaptans

Volatile Alkyl mercaptans in a hydrocarbon matrix such as natural gas are typically measured by the use of either a dedicated gas chromatographic analyzer which employs multi-valves and multi-columns [7,8], or by highly selective and sensitive detection methods such as flame photometric detection (FPD), Pulsed-flame photometric detection (P-FPD), Dual-plasma chemiluminescence detection (DP-SCD), DMD, Amperometric sulfur detection (ASD), or mass spectrometry (MS) to name a few [7–13]. While these analytical solutions are adequate, there are constraints associated with each of the techniques described, such as higher cost of ownership, longer time to setup or to reach operational status, more analytical skills to operate, more logistic needs such as the requirement of a vacuum pump, or the need for an radioactive source license. These constraints made the techniques difficult for field deployment especially where limited analytical resources and lab infrastructures are available.

Conventional multi-dimensional gas chromatography, also known as heart-cutting two-dimensional (2D) GC is a viable alternative to improve the separation resolution, selectivity and peak capacity [14–25]. Heart-cutting 2D, either by valves or by flow modulation, also referred as Deans switching, is a relatively simple but efficient way for target analysis. In heart-cutting methods, only effluents of interest, typically co-elution pairs from the first dimension are transferred into the second dimension. One of the key challenges in implementing heart-cutting 2D-GC; however, lies on the interface which requires low-dead-volume, high degree of inertness, leak-free, and efficient sample transfer. The advent of commercially available, highly accurate electronic pressure control systems of up to the third decimal place such as those offered by contemporary gas chromatographs, combined with innovations like capillary flow technology aided in eliminating many deficiencies encountered with heart-cut 2D-GC and make practicing heart-cutting 2D-GC simple and highly reliable [26]. Capillary flow technology plate, employed as a microfluidic Deans switch is a new generation of improved flow switching device. It affords non-contact switching, no moving parts, highly deactivated, low thermal mass, and the capability of being heated up to 400 °C making it an ideal for use as an in-oven switching device [27].

In this application, with the substantial gain in peak capacity, synergized by two highly selective columns with two different separation mechanisms, a traditionally difficult application can be attained by an ubiquitous, non-selective detection method such as FID with minimal possibility of having false positive for alkyl mercaptans measurements. Fig. 1 shows the set up of multi-dimensional chromatography with capillary flow technology. Note the compactness of the in-column switching device. A sample is injected onto the VF-WAXms column (first dimension) where rough separation between mercaptans and hydrocarbons takes place. The effluent from the VF-WAXms column flows towards the first detector (FID1) via a deactivated, but uncoated 0.18 mm ID fused silica restrictor. When a transfer is required, the effluent from the VF-WAXms column is diverted onto the PoraBOND Q column (second dimension) where the separation of mercaptans from potential chromatographic interferences takes place. The mercaptans are then detected by the second FID system (FID2). Fig. 2 shows a configuration of the analytical system.

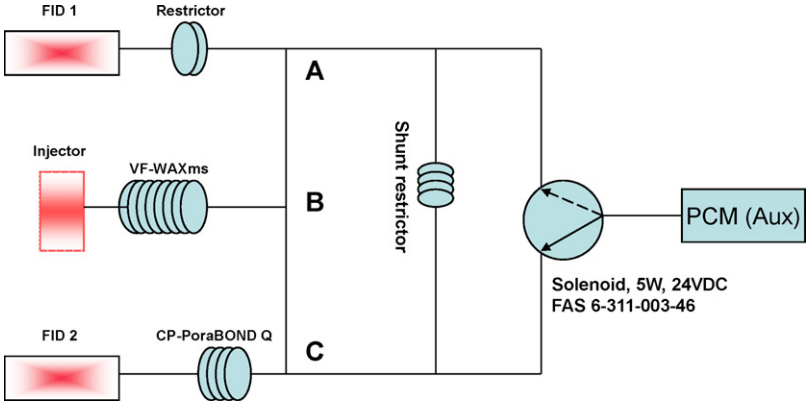

Fig. 2. Analytical system configuration.