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Short communication

Gas chromatographic–mass spectrometric analysis of mercaptan odorants in liquefied petroleum gas and liquefied natural gas

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Abstract

A gas chromatographic–mass spectrometric method for the determination of mercaptan odorants (dimethyl sulfide, *tert.*-butylmercaptan, tetrahydrothiophene) in natural gas has been developed. The gas sample filled in a 5 l Tedlar bag was introduced into the 0.5 ml volume of a sampling loop, separated on a 50 m capillary column coated with 5% phenylmethylsilicone and detected by a mass spectrometer. Natural gas samples collected from 124 sites were analyzed and the concentration of added odorants was found to be between 9.7 and 66.2 ppm (w/w). The detection limit of each odorant was below 1 ppm (w/w). The advantages of the developed technique were lower detection limits, elimination of interference peaks by introducing into the sampling loop system and selected-ion monitoring mode, and reduced total analysis time. The intra-day and inter-day precision of the established method was R.S.D.<5% ($n=5$). © 1997 Elsevier Science B.V.

Keywords: Gas; Mercaptan; Odorants; Sulfur compounds; Dimethyl sulfide; Butylmercaptan; Tetrahydrothiophene

1. Introduction

Mercaptan odorants have been used for many years in the gas industry as warning agents to protect against explosions, fires and other hazards by giving a distinctive odor to the otherwise odorless natural and liquefied petroleum gas being distributed. The addition of odorants or an odorant mixture to natural and liquefied petroleum gases takes advantage of the ability of the human nose to detect and recognize low parts per billion amounts of certain mercaptans. The odorants are present at a concentration of under 50 ppm (w/w). It is difficult to analyze the mercaptan odorants because they can undergo partial oxida-

tion reactions under laboratory conditions and tend to adsorb onto surfaces with which they come in contact. This paper describes gas chromatography–mass spectrometry (GC–MS) in the selected ion monitoring (SIM) mode, installed in the gas sampling valve system for the analyses of mercaptan odorants in natural gas samples. Generally, the analysis for mercaptan odorants has been performed using a packed column and GC–flame photometric detection (FPD) [1,2] and sulfur chemiluminescence detection (SCD) [3,4]. In the International Organization for Standardization (ISO) method [5], the sulfur compounds were analyzed with packed column and sulfur-selective FPD. However, in this experiment, the SIM mode in capillary GC–MS eliminated the problem of matrix interferences while maintaining a

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low detection limit comparable to that of the GC–FPD method.

2. Experimental

A Model 5988A GC–MS system (Hewlett-Packard, Palo Alto, CA, USA) equipped with a gas sampling valve system was used for the analysis. An Ultra-2 capillary column (5% phenylmethylsilicone, 50 m×0.2 mm I.D., 0.33 μ m film thickness) was

used. Helium was selected as the carrier gas at a flow-rate of 0.5 ml/min. The injector and transfer line temperatures were 200°C and 220°C, respectively. The split ratio for the optimum separation and sensitivity was 50:1. The oven temperature was programmed from 40°C to 110°C at a rate of 9°C/min, then increased at a rate of 10°C/min to 150°C, which was maintained for 1 min. The HP 18900F gas sampling valve system (Hewlett-Packard, DE, USA) was used for pressurized gas injection into GC–MS system. The gas sampling valve is inserted

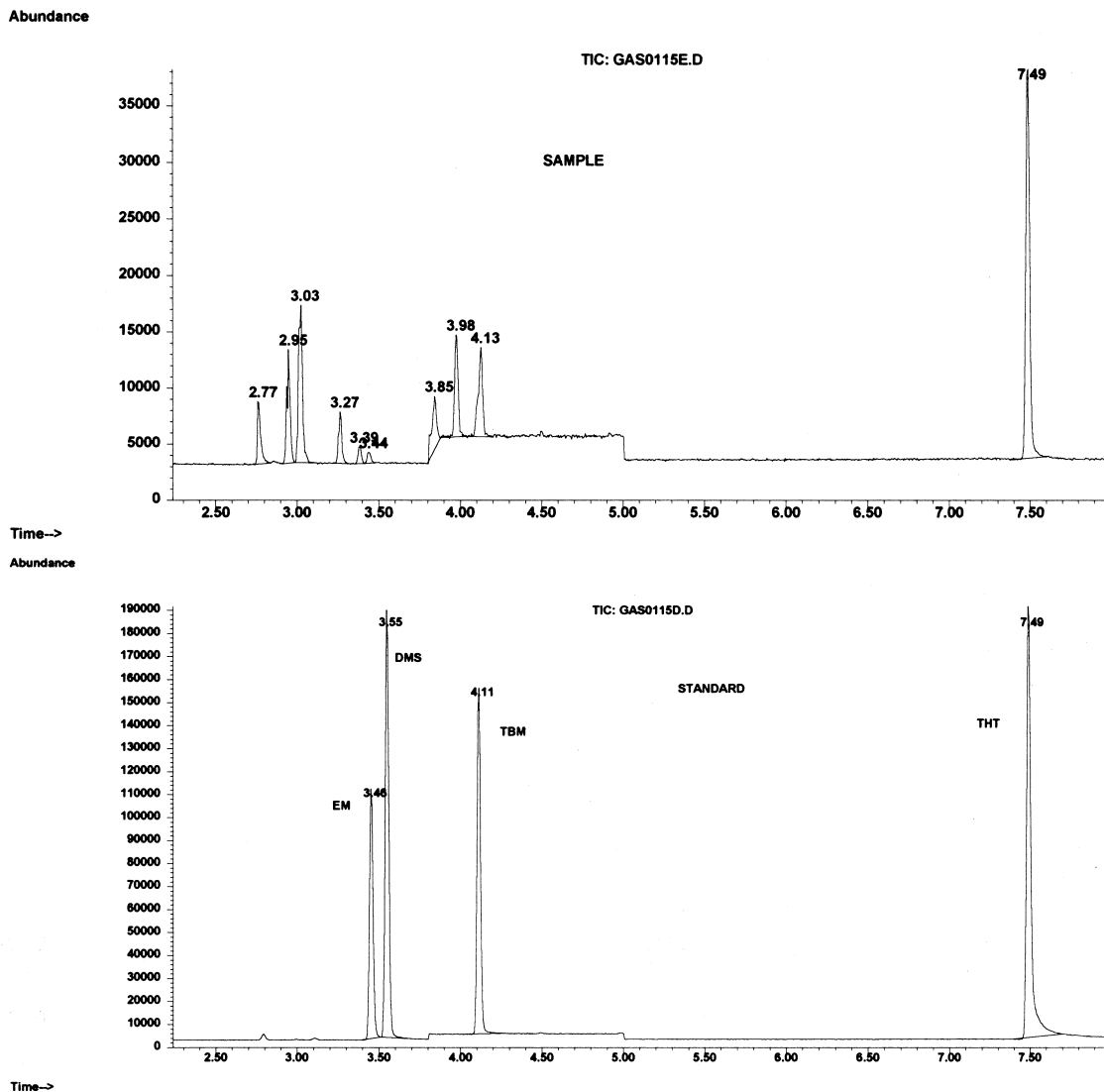


Fig. 1. Total ion chromatograms obtained from the real sample (upper) and standard (lower).

between the carrier flow controller and the capillary inlet. An aluminum jacket in the sampling valve system kept at 120°C to avoid condensation of analytes in the sampling valve is used. A 0.5 ml loop was used and sampling time was 0.3 min. The mass spectrometer was operated in the electron impact (EI) mode (70 eV) and SIM mode. The calibrations of the odorants were m/z 47, 62, 57, 90, 60 and 88, and the dwell time was 50 μ s. For calibration of the odorants, 5 l of N₂ gas was added to the Tedlar sample bag (Alltech Associates, IL, USA) and the mixture of dimethyl sulfide (DMS), *tert*-butylmercaptan (TBM) and tetrahydrothiophene (THT) was

spiked at concentrations of 1, 10, 20 and 30 ppm (w/w).

3. Results and discussion

To eliminate the adsorption of mercaptans onto metal surfaces of the loop-valve system, the loop-valve system was heated to 120°C, and the loop and connecting lines were purged twice with nitrogen gas before sample injection. Oxidation can occur in the sampling containers or the analysis system where small quantities of odorant are experimentally sub-

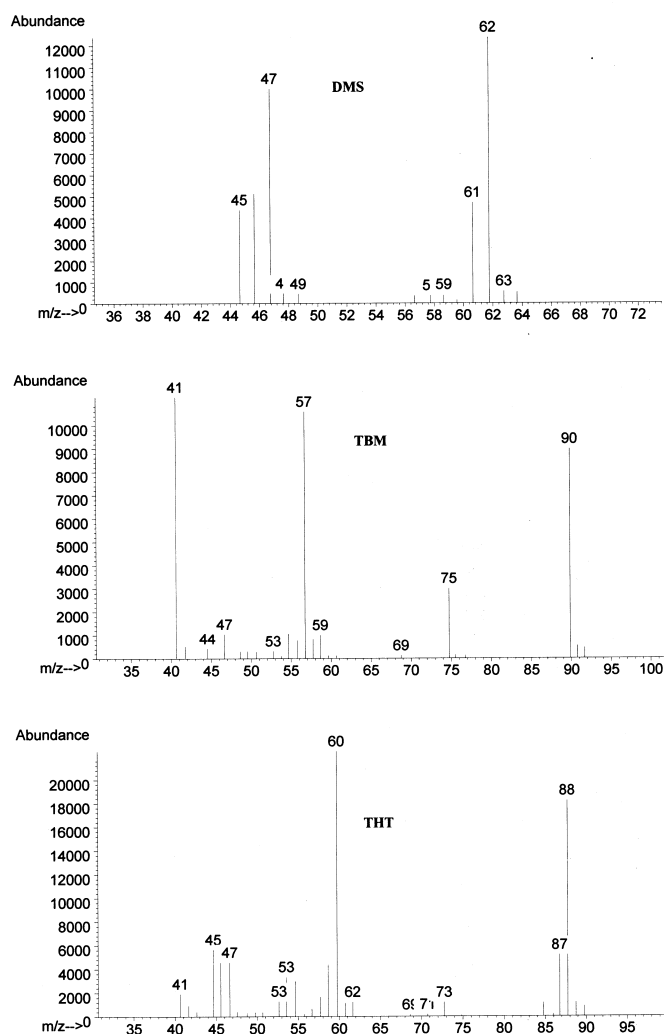


Fig. 2. EI mass spectra obtained by GC-MS at 70 eV of three odorants.

jected to heat and reactive surface. A review of the literature showed that one method to eliminate this problem was to convert all mercaptans to disulfides prior to GC analysis [6]. To prevent oxidation reactions several safeguards should be followed. Whenever possible, PTFE or PTFE-lined sample bag and connecting lines should be used. The total ion chromatograms (TICs) obtained from the real sample (upper) and standard (lower) are shown in Fig. 1. Fig. 2 shows the mass spectra for the DMS, TBM and THT standards. DMS, TBM and THT were detected at 3.55, 4.11 and 7.49 min, respectively. The chromatogram shows good resolution and peak shape and there is no overlap peak by the hydrocarbons. Calibration curves of DMS, TBM and THT were linear in the 1–30 ppm range. The lowest limits of detection were obtained by (i) increasing the injected volume (sample loop volume) to 0.5 ml, (ii) controlling the split condition (50:1) and (iii) choosing the number of selected ions. As a result, limits of detection in the SIM mode were below 1 ppm for DMS and THT and 10 ppm for TBM. The minimum quantifiable level was defined as the minimum concentration of the analyte in the Tedlar bag, giving a signal-to-noise ratio of at least 5:1 under assay conditions measured with a level of 1 ppm for DMS and THT, 10 ppm for TBM. The precision and accuracy of the method was evaluated on three consecutive days. The calibration graphs obtained showed excellent linearity and good reproducibility of the slope. The correlation coefficients for DMS, TBM and THT were $r^2=0.999$, $r^2=0.986$ and $r^2=0.998$, respectively. Run-to-run and day-to-day precision was assessed by replicating determinations of the odorants on the same day and on different days, respectively. The run-to-run precision of DMS, TBM

and THT, determined with samples containing 20 ppm of odorants were found to be 3.7, 1.9 and 4.1% (R.S.D., $n=5$), respectively. It was reported that concentrations of standards prepared using glass bulbs were found to decrease by ~30% after 24 h and by ~60% after 48 h [2]. But the standards prepared using Tedlar bags had the advantage of ease of handling and no decrease in concentration after 72 h. As evidence, the day-to-day precision was found to be 5.6% (R.S.D., $n=5$) for DMS. When using GC-FPD, it is difficult to determine the target odorants because there are several compounds containing sulfurs. But the SIM method could minimize the interference by the natural gas matrix (hydrocarbons). The concentrations of DMS, TBM and THT were in the ranges of 0.1–3.6, 9.6–23.4 and 1.1–50.7 ppm, respectively. The concentration of the sum of three odorants was 9.7–66.2 ppm. The average concentration of the odorants in the natural gases was 17.2 ppm.

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