The Determination of Tertiary Dodecyl Mercaptan by Low Thermal Mass Gas Chromatography–Dual Plasma Sulfur Chemiluminescence Detection

Ronda Gras[1], Jim Luong[1],*, **Patric Eckerle[2],** and **Randy Shearer[3]**

[1]Dow Chemical Canada, PO BAG 16, Highway 15, Fort Saskatchewan, Alberta, Canada T8L 2P4; [2]Dow Chemical Germany, Werk Rheinmuenster, Industriestrasse 1, Dow Deutschland GMBH & Co., Germany; [3]Rentech Inc, 12401 E. 37th Avenue, Denver, CO 80239

Abstract

Tertiary dodecyl mercaptan (TDM) is commonly used as a chain transfer agent in the manufacturing process of styrene/butadiene latex for use in carpet and paper industries. A gas chromatographic technique has been successfully developed for the measurement of TDM based on its sulfur content for material identification, trend analysis, or for the monitoring of un-reacted residual material in final products. The method employs low thermal mass gas chromatography (LTM-GC) and a dual-plasma sulfur chemiluminescence detector (DP-SCD) to attain a high degree of sensitivity and selectivity. Using the technique described, a detection limit in the range of 0.5 ppm (v/v) TDM and less than 1 min analysis time can be achieved. Response is linear over four orders of magnitude with high degree of repeatability of less than 5% RSD.

Introduction

In the process of manufacturing latex such as styrene-butadiene, a chain transfer agent is required. The chain transfer agent assists in the polymerization to make products of the desired molecular distribution. Previously, chlorinated compounds such as carbon tetrachloride and chloroform have been used for this application, but because of their toxicity and negative environmental effects, it is no longer a practice to employ said compounds for the manufacturing of latex used for the carpet and paper industries. Instead, use of tertiary dodecyl mercaptan (TDM) is preferred for the applications described. As a result of the world demand for latex and the magnitude of the associated industries, TDM has become a chemical of industrial significance.

From a manufacturing standpoint, TDM is a mixture of isomeric thiols produced from oligomers of propylene tetramer or sometimes, isobutylene trimer. Propylene tetramer is produced by oligomerization of propylene in the presence of a Friedel-Crafts type catalyst such as sulfuric acid. TDM is produced by passing hydrogen sulfide and either propylene tetramer or isobutylene trimer over a catalyst such as boron trifluoride (1,2). Because of the fact that there are many permutations of the

tetramer structure, and hence the location of the –C=C– bond, the thiol group can be located in many different positions, resulting in a product mixture of isomers with an average boiling point range around 230°C.

Recently, there has also been some increased concerns regarding to the accumulation of TDM in the environment (3,4). The open literature contains little to no information on the analysis of TDM. This is partly due to the fact that the matrix can be quite complex. An example would be water soluble emulsion polymer, comprizing hundreds of components which can cause chromatographic interference. Also, alkyl mercaptans such as TDM are difficult to analyze due to reasons such as the alkyl
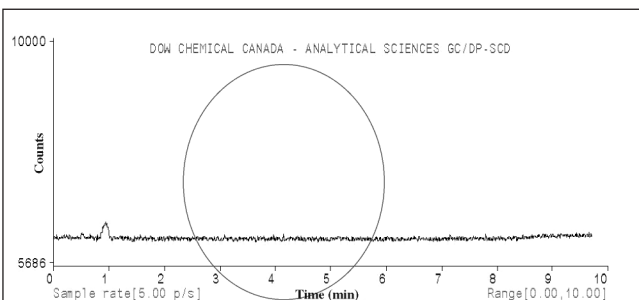

Figure 1. An injection of 1 μL of iso-octane (solvent) on the analytical system. Note the high degree of selectivity (lack of response to hydrocarbons) towards sulfur compounds.
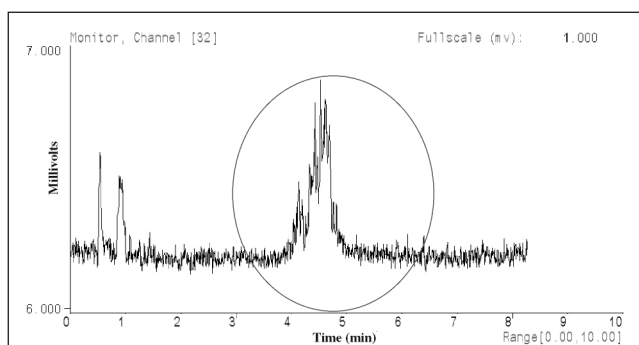

Figure 2. A chromatogram of 10 ppm (v/v) TDM in iso-octane. Chromatographic conditions: 50°C held for 1 min, increased 30°C/min to 280°C and held for 2 min.

* Author to whom correspondence should be addressed.

chains are C_8 to C_{15} in size and cover a wide range of boiling points, the polarity of the individual components in TDM varies with the degree of thiolation, the location of the R-SH moiety. In addition to the differences in polarity and boiling points of the TDM components, the product can also contain a fraction of relatively non-polar, non-thiolated tetramer. For the measurement of TDM, an internal method involves the use of headspace gas chromatography in combination with flame photometric detection (FPD) had been developed (5). The method, however, has its constraints, including competing vapour–liquid equilibrium of solutes in the sample and the lack of linear dynamic range of the FPD.

As a result, a new chromatographic method is required for raw material identification of TDM, for trend analysis, and for the monitoring of residual material in the final products.
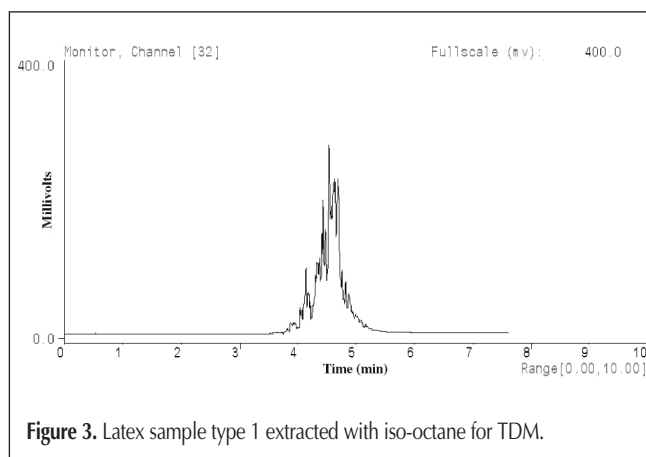
The new chromatographic method was developed with three enablers: (*i*) Liquid–liquid extraction to remove TDM isomers from their respective matrices; (*ii*) Low thermal mass gas chromatography to deliver the flexibility of either speciation of individual sulfur compounds, or peak compression to combine individual sulfur compounds into one discreet peak with high temperature programming capability and to improves overall sample to sample throughput; (*iii*) Dual plasma sulfur chemiluminescence detector (DP-SCD) to offer the highest degree of selectivity for TDM isomers, equi-molar response and a respectable linear dynamic range.

This report summarizes the method development and analytical results obtained.

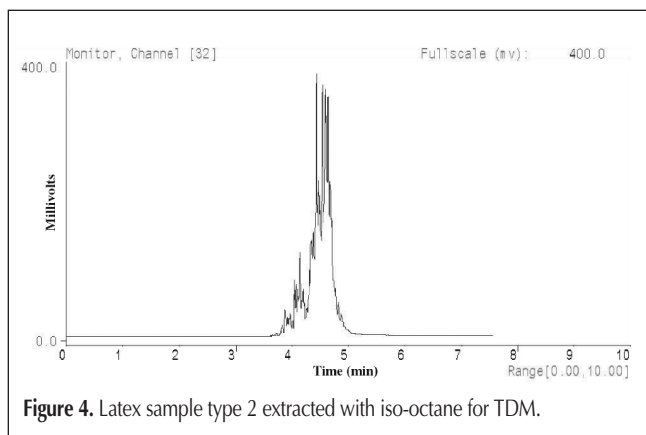**Figure 3.** Latex sample type 1 extracted with iso-octane for TDM.

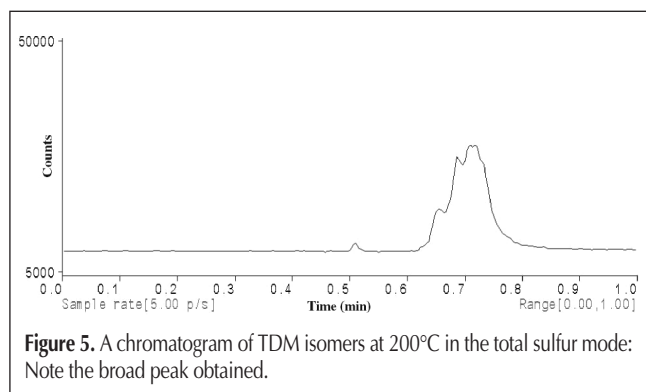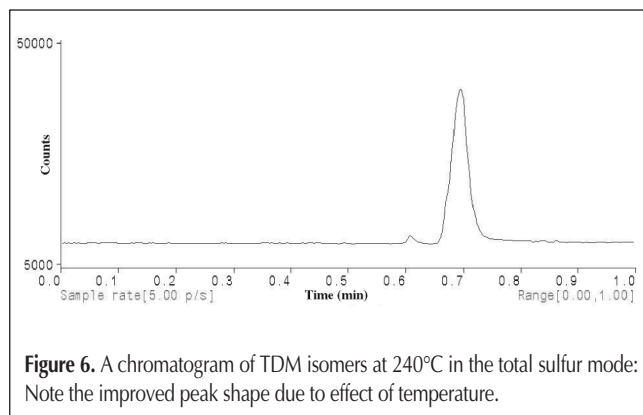**Figure 4.** Latex sample type 2 extracted with iso-octane for TDM.

Figure 5. A chromatogram of TDM isomers at 200°C in the total sulfur mode: Note the broad peak obtained.

Figure 6. A chromatogram of TDM isomers at 240°C in the total sulfur mode: Note the improved peak shape due to effect of temperature.
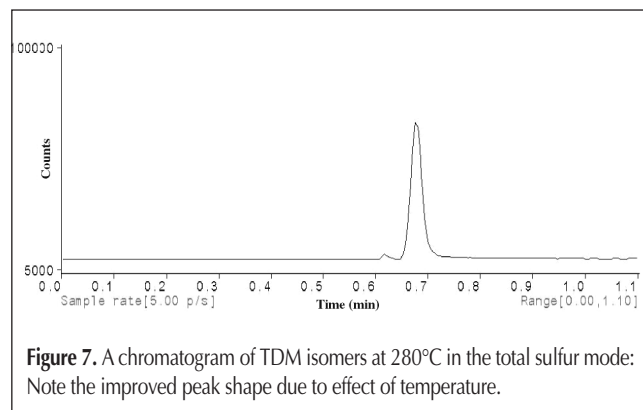

Figure 7. A chromatogram of TDM isomers at 280°C in the total sulfur mode: Note the improved peak shape due to effect of temperature.
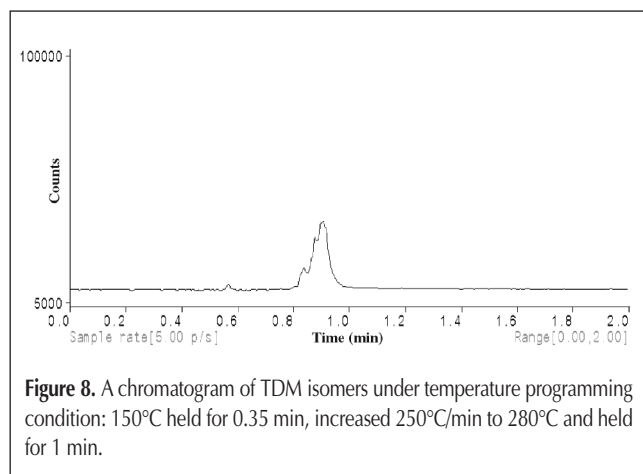

Figure 8. A chromatogram of TDM isomers under temperature programming condition: 150°C held for 0.35 min, increased 250°C/min to 280°C and held for 1 min.

Experimental

An Agilent HP-6890N gas chromatograph (Wilmington, DE) equipped with two split/splitless injectors, a flame ionization detector, a DP-SCD (Agilent Technologies, Boulder, CO) and an Agilent 7673C autosampler were used for the application development. The gas chromatographic conditions used were as follows: split/splitless injector in split mode, at 250°C, Focus™ liner, with split ratio of 10:1 for trace analysis or 100:1 where the level of TDM exceeds the maximum calibration range of 1000 ppm. The oven was held at 275°C isothermally. The DP-SCD was operated at 802°C, with hydrogen at 47 mL/min, air at 62 mL/min, and pressure at 357 torr. 1 µL was injected for each analysis.

A RVM LTM-68A LTMGC module was also used. The column module was connected directly to the injector and the detector of the Agilent HP-6890N GC using standard column ferrules and nuts. A 18 metre × 0.25 mm i.d. × 0.25 micron Varian VF-1ms column was used in the module for separation. Helium was used as carrier gas, with average linear velocity of 50 cm/s at 20 psig inlet pressure. For speciation, the following temperature programming was employed: 50°C, held for 1 min; increased at 30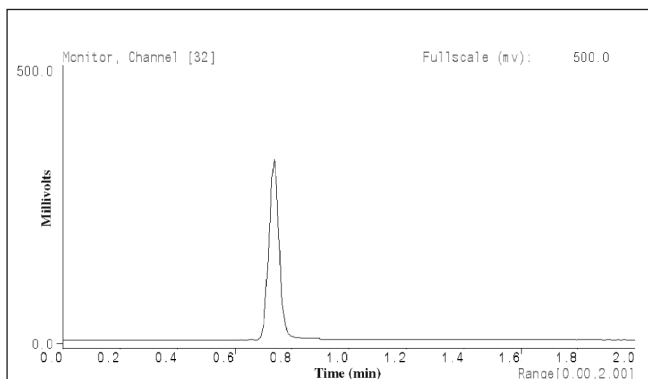°C/min to 280°C and held for 2 min. For total sulfur measurement, the following temperature programming was selected: 200°C, held for 0.15 min, increased at 500°C/min to 250°C and held for 2 min.

In 2001, Mustacich et al. was granted two patents for the invention of low thermal mass gas chromatography (LTM-GC) (6,7,8). This led to the recent commercialization of a radically new disruptive technology to achieve ultra fast temperature programming and unprecedented cool down time, with a power consumption of only about 1% of conventional GC. Based on resistive heating, the low thermal mass design, coupled with the high surface area offers a theoretical rapid temperature programming rate of up to 30°C per second, or 1800°C/min, in addition to an unprecedented cooling down time. Power consumption is approximately 1% that of conventional GC, primarily due to the effective heating of interstitial air with the random positioning of the heating wire in the toroid, and the low

Figure 9. A chromatogram of TDM isomers under temperature programming condition: 200°C held for 0.15 min, increased 500°C/min to 250°C and held for 1 min.
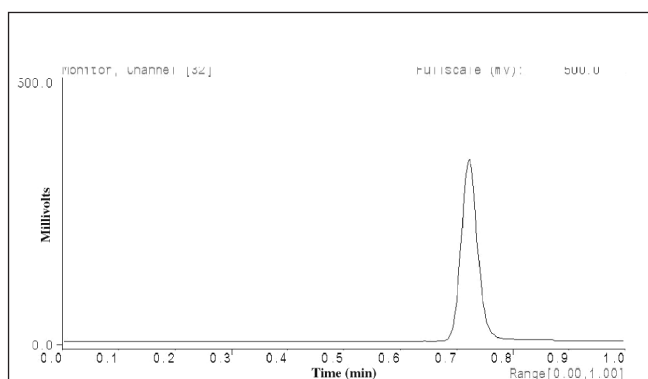

Figure 10. A chromatogram of TDM isomers under temperature programming condition: 220°C held for 0.15 min, increased 500°C/min to 250°C and held for 1 min.
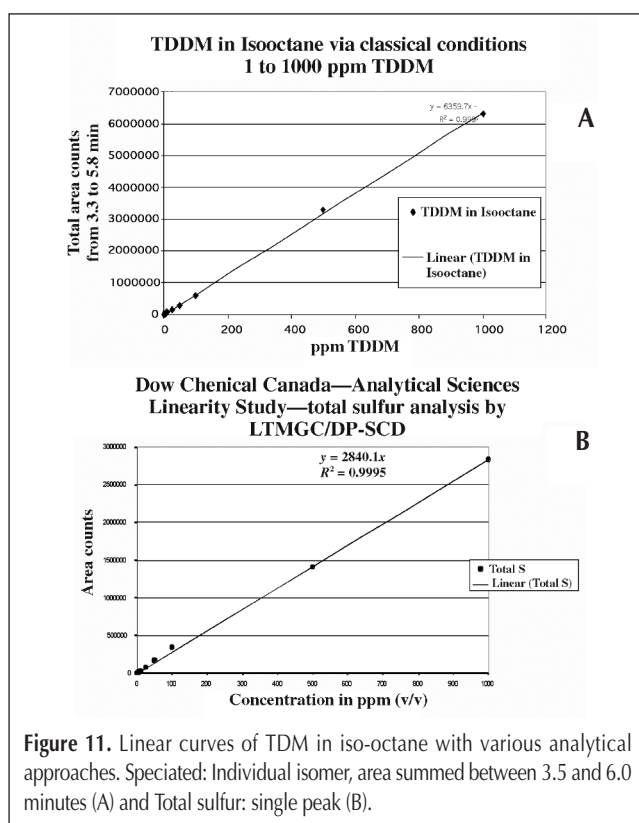

Figure 11. Linear curves of TDM in iso-octane with various analytical approaches. Speciated: Individual isomer, area summed between 3.5 and 6.0 minutes (A) and Total sulfur: single peak (B).
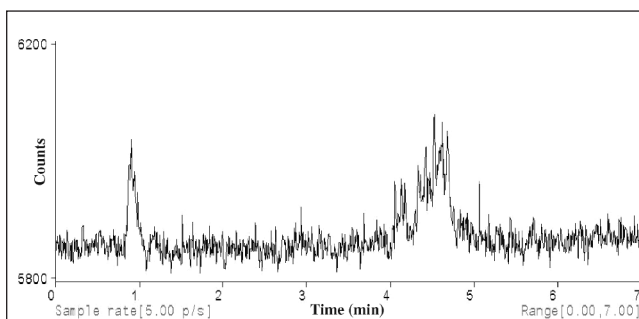

Figure 12. A chromatogram of 1 ppm (v/v) of TDM in iso-octane in the speciated mode. Concentration approaching actual detection limit of the system.

667

thermal mass of the assembly (8).

The described features, such as rapid heating which lead to rapid remobilization of trapped solutes, rapid cooling, low power consumption in addition to independent oven control of up to four modules per GC make LTMGC ideal for use with the application described herein.

TDM standard was obtained from Aldrich Chemicals (Oakville, Ontario, Canada), while iso-octane was used to extract residual TDM from various commercially available latex products. The extraction procedure involved adding 5 mL of iso-octane to 2.5 gram of sample and mechanically agitating for 120 min. The resulting extract analyzed by the procedures described herein.

Discussions

The GC technique involved offers dual-analytical capability of either speciation or rapid measurement for total sulfur compounds using the same hardware (9). Because TDM is a mixture of isomeric thiols with a range of boiling points, both the classical separation and the total sulfur approach were considered and performance data summarized below:

The classical separation approach
With the employment of the highly selective and sensitive DP-

SCD, under optimized conditions, the possibility of false positives from interfering hydrocarbons such as residual propylene tetramer or isobutylene trimer can be mimized, if not eliminated (9). If sulfur-containing bactericide is used and its boiling point is outside the range of TDM such as in the case of KATHON, it can be chromatographically separated from the distribution of TDM isomers. For quantitative analysis, the areas of the distribution of TDM isomers were summed together.

Method optimization includes mainly sample size so that the selectivity of the detector towards sulfur containing compounds is not compromised and oven temperature profile.

Figure 1 shows a chromatogram of a 1 μL injection of iso-octane. Note the lack of response of the detector against the matrix used in the retention time of interest, specifically in the region between 3.5 and 6.0 min. Figure 2 shows a chromatogram of 10 ppm (v/v) of TDM. Note the respectable sensitivity obtained. Figures 3 and 4 show chromatograms of typical iso-octane extracts of residual TDM in two different type of styrene-butadiene latex.

The GC conditions used were as follows: Split/splitless injection system, 1.0 μL injection; SR: 100:1 or 10:1. The LTMGC and temperature profile were: VF-1ms (18 m × 0.25 mm i.d. × 0.25-μm); 50 cm/s helium (20 psig inlet pressure); Temperature: 50°C held for 1 min, increased at 30°C/min to 280°C and held for 2 min; Host oven, 275°C; DP-SCD; Burner, 802°C; Vacuum, 357 Torr; H_2: 47mL/min; Air 62 mL/min.

The total sulfur approach
In the total sulfur approach, the separation power of the column is compressed by operating the column at an elevated temperature. The rationale of this approach is that because all the isomers of TDM are compressed into one discreet, Gaussian peak, in theory, the sensitivity of the method can be improved and since chromatographic separation is not required, shorter analytical time can be attained. The downside, however, is if there is any sulfur containing compounds in the sample retainable by the chromatographic column, it will also be measured as TDM.

Method optimization involved selecting the appropriate operating temperature for the analytical column to obtain a symmetric peak for reliable quantitative work. Peak symmetry quality was compared between maintaining the column temperature isothermally versus a slight temperature program. Figure

Table I. A Comparison of Precision Between Two Approaches

| Speciated Individual isomers		Single peak Total sulfur	
Run	Counts	Run	Counts
1	2,734,206	1	188,565
2	2,831,196	2	198,393
3	2,877,138	3	198,552
4	3,021,790	4	201,533
5	2,876,081	5	203,116
6	2,779,599	6	192,999
7	3,026,342	7	191,584
8	3,062,429	8	198,297
9	2,857,473	9	187,647
10	2,809,881	10	194,463
Average	2,887,614	11	191,737
SD*	112,243	12	188,257
%RSD	3.9	13	201,053
		14	195,142
		15	196,791
		16	191,908
		17	186,948
		18	193,095
		19	192,697
		20	200,286
		Average	194,653
		SD	4920
		%RSD	2.5

*SD = standard deviation.
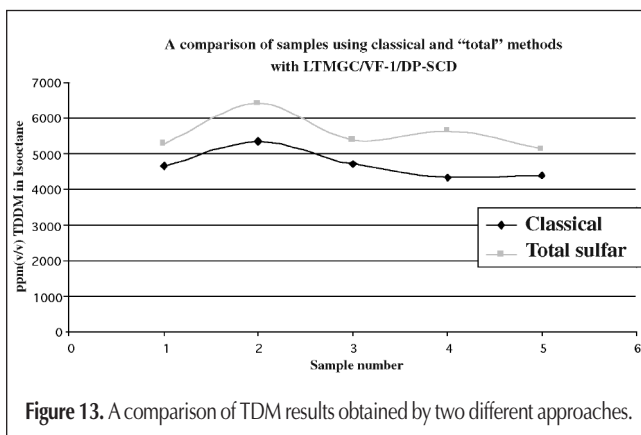
Figure 13. A comparison of TDM results obtained by two different approaches.

5, 6, and 7 show chromatogram of TDM isomers at 200°C, 240°C, and 280°C while Figures 8, 9, and 10 show chromatogram of TDM isomer under various temperature programming conditions with initial temperature at 150°C, 200°C, and 220°C.

The gas chromatographic conditions used were as follows: 1.0 µL injection; SR, 100:1 or 10:1. LTMGC and temperature profile were as follows: VF-1ms (18 m × 0.25 mm i.d. × 0.25 µm); 50 cm/sec Helium (20 psig inlet pressure); temperature, 200°C held for 0.15 min, increased at 500°C/min to 250°C; Host oven, 275°C. DP-SCD: Burner, 802°C; Vacuum, 357 Torr; H_2, 47 mL/min; Air, 62mL/min

Comparison of performance between the two approaches

In terms of precision, as stated earlier for the speciated method, the distribution of individual isomers of TDM between 3.5 and 6.0 min was integrated, whereas for the total method, the discreet peak representing TDM was integrated. Standards containing 1000 ppm (v/v) of TDM in iso-octane were used for the evaluation. A relative standard deviation of 2.5% ($n = 20$) was obtained for the speciated method while a relative standard deviation of 3.9% ($n = 10$) was obtained for the total sulfur method. The results obtained were tabulated in Table I.

In terms of linearity, over the range from 1 ppm to 1000 ppm (v/v) TDM, correlation coefficients R^2 of 0.9994 and of 0.9995 were obtained for the speciated and the total sulfur method, respectively. The detection limit for TDM by the total sulfur method was found to be 0.5 ppm (v/v) TDM whereas 1.0 ppm (v/v) for the speciated method as shown in Figures 11 and 12.

Table II shows a comparison of five iso-octane extract samples containing TDM. It was found the results obtained were comparable amongst the two methods; despite there is a trend that the TDM results obtained by the total sulfur method is consistently elevated as shown in Figure 13. Some plausible explanations for this bias include the samples might have a different distribution of isomers than TDM used for calibration, or more of the TDM is detected in the samples as isomers are thermally band compressed into a much shorter peak width than classical method. Nevertheless, the results obtained show that the concept of tracking for the presence of TDM by measuring its sulfur content and associated retention time range in the speciated method or by measuring its sulfur content alone can be employed for the material identification, trend monitoring, or the measurement of residual TDM in various matrices. If a high degree of accuracy is required, the results obtained by using said techniques must be compared to other assaying techniques.

Conclusions

A gas chromatographic technique has been successfully developed for the measurement of TDM based on its sulfur content for raw material identification, trend analysis, or for the measurement of un-reacted material in the final products.

The method employs LTM-GC offering the flexibility either for speciation of individual sulfur compounds or delivering peak compression to combine individual sulfur compounds into one discreet peak without changing of hardware, and a DP-SCD to attain a high degree of sensitivity and selectivity. Using the technique described, a detection limit in the range of 0.5 ppm (v/v) TDM with less than 1 min analysis can be achieved. Response is linear over four orders of magnitude with a high degree of repeatability of less than 5%.

Acknowledgements

Table II. A Comparison of Five Iso-Octane Extract of TDM From Latex Samples Under Two Operating Conditions: Speciate and Total

Speciate: Individual isomers		
Sample #	Area counts	ppm TDDM
1	2,943,432	4638
2	3,387,471	5338
3	2,991,420	4714
4	2,742,534	4321
5	2,734,206	4308
5 (control duplicate)	2,831,196	4461
Single peak: Total sulfur		
Sample	Area Counts	ppm TDDM
1	1,275,009	5190
1 (control duplicate)	1,313,176	5345
2	1,573,582	6405
3	1,323,256	5386
4	1,381,066	5621
5	1,256,298	5113

References

1. W. Schulze, J. Lyon, and G. Short. Synthesis of tertiary alkyl mercaptans. *Ind. Eng. Chem.* **40(12):** 2308–13 (1948).
2. J. Frantz and K. Glass. A new process for dodecyl mercaptan. *Chem. Eng. Prog.* **59(7):** 68–73 (1963).

3. DEFRA, "UK Co-coordinated Chemical Risk Management Program – Environmental Chemicals", Department of Environment, Food and Rural Affair, 2008. http://www.defra.gov.uk/ENVIRONMENT/chemicals/ukrisk.htm, accessed date: January 13, 2008

4. A. Girling, L. McLauchlin, and R. Wildey. Environmental Risk Assessment Report: Tert-dodecanethiol (CAS 25103-58-6). Environmental Agency, Rio House, Waterside Drive, Aztec West, Bristol BS324UD, 2004.

5. P. Eckerle and B. Fouchet. Residual TDM in emulsion polymers by headspace capillary chromatography, using flame photometric detection. Dow Internal Report DOC 7443, Rheimunster, Germany, February 28, 2005.

6. R. Mustacich and J. Everson. Reduced power consumption gas chromatograph system. US Patent 6,217,829, April 17, 2001.

7. R. Mustacich and J. Richards. Electrically insulated gas chromatograph assembly and method of fabricating same. US Patent 6,209,386, April 3, 2001.

8. J. Luong, R. Gras, R. Mustacich, and H. Cortes. Low thermal mass gas chromatography: principles and applications. *J. Chromatogr. Sci.* **44(4):** 253–61 (2006).

9. R. Gras, J. Luong, and R. Shearer. A unified approach for the measurement of individual or total volatile organic sulfur compounds in hydrocarbon matrices by dual-plasma chemiluminescence detector and low thermal mass gas chromatography. *J. Chromatogr. Sci.* **45(10):** 671–76 (2007).

10. R. Benner and D. Stedman. "Universal Sulfur Detection by Chemiluminescence", Analytical Chemistry, 61 (1989), 1268–71.

11. R. Shearer. Development of Flameless Sulfur Chemiluminescence Detetion: A pplications to Gas Chromatography. *Journal of High Resolution Chromatography* 421–26 (1990).

12. C. Poole. *The Essence of Chromatography*. Elsevier Science B.V., Amsterdam, the Netherlands, 2003.

13. W. Jennings. *Analytical Gas Chromatography*, Second Edition, Academic Press, New York, 1997.

14. R. Nadkami and A. Kishore. Determination of sulfur in petroleum products and lubricants: a critical review of test performance. American Laboratory **32:** 16–29 (2000).