Analysis of part-per-billion level of arsine and phosphine in light hydrocarbons by capillary flow technology and dielectric barrier discharge detector☆

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ABSTRACT

A practical gas chromatographic procedure has been developed and implemented for the measurement of arsine and phosphine in hydrocarbons such as propylene at the part-per-billion level. The successful measurement of arsine and phosphine at the level mentioned was attained by incorporating a large volume injection technique to increase the mass of solutes delivered for sensitivity improvement, capillary flow technology to keep the matrix from entering the detector by either back-flushing through the inlet vent, or by heart-cutting if required, and dielectric barrier discharge detector operating in argon mode for sensitivity enhancement, as well as offering improved selectivity towards the solutes cited. Using the technique described a complete analysis can be conducted in less than 4 min. A relative standard precision of less than 1.7% was achieved with repeated injections at the concentration level of 25 and 125 ppb (v/v) each of arsine and phosphine in nitrogen with a practical detection limit at the 5 ppb (v/v) level. Correlation coefficients of greater than 0.9999 were obtained for arsine and phosphine over a range from 10 to 2500 ppb (v/v). The analytical methodology was proven to be reliable in continuous operation during the first 6 months of deployment.

1. Introduction

Arsine and phosphine are undesirable contaminants in natural gas. Arsine gas is naturally produced in geothermal steam. As the oil and gas industry extracts gas from deeper, hotter geological formations, arsine may even become a bigger issue in the future. Phosphine is formed from putrefaction of organic matter. The presence of arsine or phosphine in light hydrocarbons such as propylene can lead to poisoning of catalyst in subsequent gas processing systems, or pass into downstream final products.

Arsine and phosphine can be analyzed by gas chromatography. Depending on the hydrocarbon involved, the separation of arsine and phosphine from the matrix can be conducted by either wall-coated open tubular or porous layer open tubular column technologies [1–3]. Detection of arsine and phosphine can be carried out by mass spectrometry, GC detectors such as photo-ionization, thermionic, flame photometric detection or other detection means [2–10]. While these techniques were found adequate, there are constraints involved with the techniques mentioned such as the lack of ultra-trace sensitivity, higher cost of ownership, the analytical skills required to operate the analytical system particularly in remote laboratories, and long term analytical system stability/reliability.

In order to address some of the limitations cited earlier, a practical gas chromatographic approach has been developed and implemented for the measurement of ppb levels of arsine and phosphine in hydrocarbons such as propylene. This technique also has the potential of being used in the analysis of analytes mentioned with different matrices. To achieve the low detection limit, large volume injection in combination with the use of a dielectric barrier discharge detector operating in argon mode was employed. Capillary flow technology was also use to facilitate the back-flushing of the matrix from the detector as well as heart-cutting should this become necessary.

2. Experimental

An Agilent 6890N Plus gas chromatograph (Agilent Technologies, Wilmington, DE, USA) equipped with two split/splitless inlets operating in split mode, one flame ionization detector and one dielectric barrier discharge detector operating in argon mode (AIC Corporation, Albuquerque, NM, USA) was used in the method development.

A large volume gas injection system (LVGIS) was used for sample introduction [11,12,13]. A 2000 μL injection loop was installed

Table 1
Gas chromatographic conditions.

Gas chromatograph	Agilent 6890N
Inlet	Split/splitless in split mode at a rate of 1:2
Liner	FocusLiner™
LVGIS injector system	
Transfer pressure	35 psig
Injection volume	2000 μL
Interface	Polymeric seal with removable needle
Column	25 m, 0.32 mm i.d., 7 μm Varian CP-PoraBOND Q™
Carrier gas	Helium
Carrier gas average velocity	60 cm/s with inlet head pressure at 27.2 psig
Oven conditions	40 °C (4 min)–15 °C/min–150 °C (5 min)
Detector	Argon-mode dielectric barrier discharge detector
Detector gas flow	8 mL/min argon
Detector temperature	250 °C
Back-flush conditions	
Inlet pressure	5 psig for 1.5 min, then 1 psig from 1.5 to 4 min
Auxiliary pressure	19.6 psig for 1.5 min, then up to 25 psig from 1.5 to 4 min
2D-GC heart-cut conditions (as described in Fig. 1)	
Fraction cut time	0.8–1.2 min
Restrictor	1.6 m, 150 μm of uncoated but deactivated fused silica

with the LVGIS. Separation of solute from the matrix was carried out with a 25 m, 0.32 mm i.d., 7 μm CP-PoraBOND Q™ (Varian Inc., Middelburg, The Netherlands). Further improvement in separation power for the solutes mentioned was achieved by the incorporation of a heart-cutting technique with capillary flow technology. In this case, an additional 25 m, 0.32 mm i.d., 7 μm CP-PoraBOND Q™ was employed in the second dimension.

Standards used for testing were obtained from Scott Specialties Gases (Longmont, CO, USA) while commercial grade propylene was obtained either locally at the Dow Chemical Canada LHC-1 hydrocarbon production facility in Fort Saskatchewan, Alberta, Canada or from Linde Canada Ltd. (Edmonton, Alberta, Canada).

Table 1 lists the gas chromatographic conditions used.

3. Results and discussions

3.1. Column selection for phosphine and arsine analysis

Phosphine (CAS 7803-51-2) and arsine (CAS 7784-42-1) as well as the hydrocarbon matrix they are in can be considered as light, fast moving molecules. Typical columns used in this type of application include low phase ratio non-polar wall-coated open tubular columns (WCOT) or porous layer open tubular columns (PLOT) which offer a higher degree of retention and selectivity for the solutes mentioned. A variety of columns were evaluated for said application [14]. Amongst the PLOT columns, the CP-Lowox™, an ionic sorbent column technology, was found to be unsuitable for said application. Silica based columns such as Agilent GasPRO™ or Varian SilicaPLOT™ were found to deliver respectable performance albeit with lower retention capacity for the matrix. Another class of PLOT column that was found to offer reliable separation for the solutes of interest is based on divinyl benzene. As a result, a CP-PoraBOND Q™ was selected for the application described, offering a balance of inertness and selectivity against the matrix of interest, in this case, propylene.

One of the concerns involves the use of PLOT column technology is adsorbent particle shedding. The shedding of adsorbent particles has the potential of plugging the flow channel of the capillary flow Deans switch device. This in turn can cause retention time shift. No pluggage issue has been encountered during the first 6 months

of operation with the use of the PLOT columns cited, neither in the first nor second dimension. Prior to connecting the columns to the capillary flow Deans switch device, we highly recommend the columns be purged with carrier gas at a flow of 50 mL/min for 15 min to remove any particles that might have been dislodged during shipment of the columns from the manufacturers.

3.2. Enabling technologies for method performance improvement

In order to attain ultra-trace ppb level detection for arsine and phosphine, the gas chromatographic analytical system was optimized for maximum sensitivity by using:

(1) *Large volume gas injection system*: This injection system, with its original concept for liquid injection reported by Zou and Firor [11], and for gas injection by Luong et al. [12,13] affords the injection of a large volume of gas of up to 5000 μL without compromising the peak symmetry of the solute. In this specific application, a sample loop of 2000 μL was employed.
(2) *Capillary flow technology*: The incorporation of a capillary flow plate in Deans switch mode has a synergistic effect in that the flow plate can be used to effectively prevent the sample matrix from entering the detector either by back-flushing, or heart-cutting the solutes onto the second dimension should extra peak capacity be required [15–19]. Fig. 1 shows the configuration of the analytical system and the two-dimensional chromatography flow conditions.
(3) *Dielectric barrier detector* (DBD): The employment of a DBD operating in argon mode offers a high degree of sensitivity for the solutes of interest. The DBD operating in argon mode is highly selective against molecules such as O_2, N_2, H_2O, CO, CO_2, and CH_4. This high degree of selectivity is achieved due to the high-ionization potentials these molecules possess over that of the reaction gas used; argon which has an ionization potential of 11.4 eV. The DBD in argon mode is a low-maintenance GC detector, requiring only one single reaction gas in the range of 5–10 mL/min [20,21]. While there are other GC detectors that can provide similar performance for the solutes involved such as P(FPD), PID, MSD, the DBD offers lower long term cost-of-ownership with ease-of-use, thereby, can be effectively deployed in plant laboratory or remote site environments for practical and routine analysis.

3.3. Method performance

Using the technique described, with repeated injections, a relative standard precision of less than 1.7% was achieved at the concentration of 25 and 125 ppb (v/v) each of phosphine and arsine in nitrogen. Correlation coefficients of greater than 0.9999 were obtained for phosphine and arsine over a range from 10 to 2500 ppb (v/v) as illustrated in Fig. 2. Fig. 3 shows chromatogram of 25 ppb (v/v) each of phosphine and arsine in nitrogen respectively. Note the excellent separation between the two components. Based on the data collected, under optimized analytical conditions, a limit of detection of 5 ppb (v/v) for arsine and phosphine can be attained.

Fig. 4 illustrates using conventional gas chromatographic technique: phosphine and arsine are well separated from their matrix, propylene in less than 1.5 min. But, it will take about 30 min for the detector baseline to return back to a normal level if propylene is allowed to pass through the detector. The slow recovery of baseline is due to the counter-current flow geometry of the detector and the low detector gas flow employed to minimize dilution and improved sensitivity performance [20,21]. Approaches that can be employed to resolve the issue mentioned include venting, or back-flushing the propylene matrix after the phosphine and arsine have eluted. With
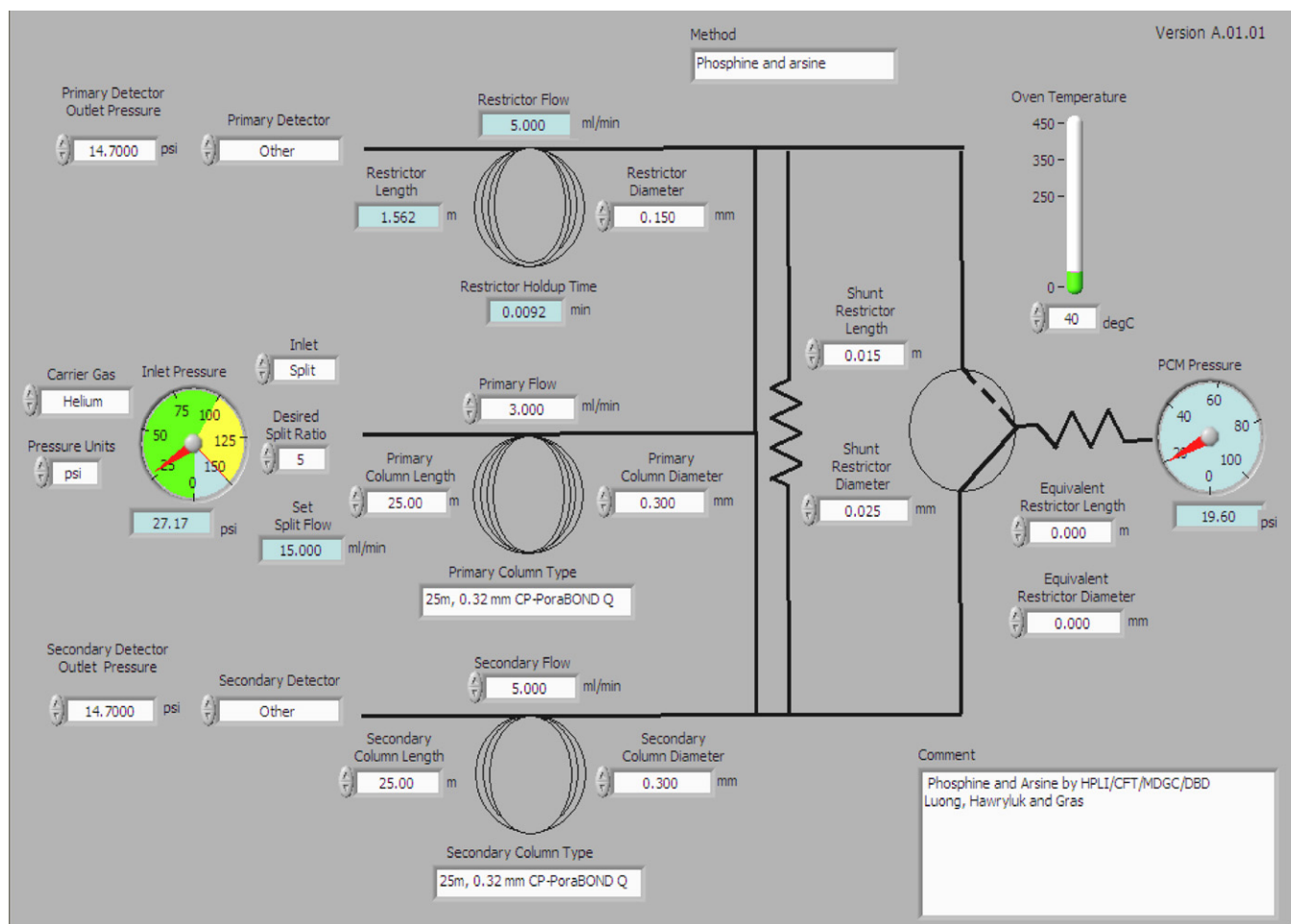
Fig. 1. Deans switch flow configuration diagram.

capillary flow technology, back-flushing through the inlet vent can be carried out simply by decreasing the inlet pressure while simultaneously increasing the auxiliary pressure as illustrated in Fig. 1. By employing the back-flushing technique, a complete analysis can be conducted in less than 4 min. Fig. 5 shows an overlay of arsine and phosphine in propylene with and without back-flush. Back-flushing improves analytical time as well as keeping the detector in a cleaner state as shown by the steady, unchanged detector signal baseline in repeated analysis.

3.4. Impact of matrices

With the DBD operating in argon mode, the detector has very low or no sensitivity for the presence of O_2, N_2, H_2O, CO, CO_2, or CH_4. Therefore, this analytical procedure can be used for the measurement of phosphine and arsine in said matrices without significant re-optimization. Other impurities encountered in light hydrocar-
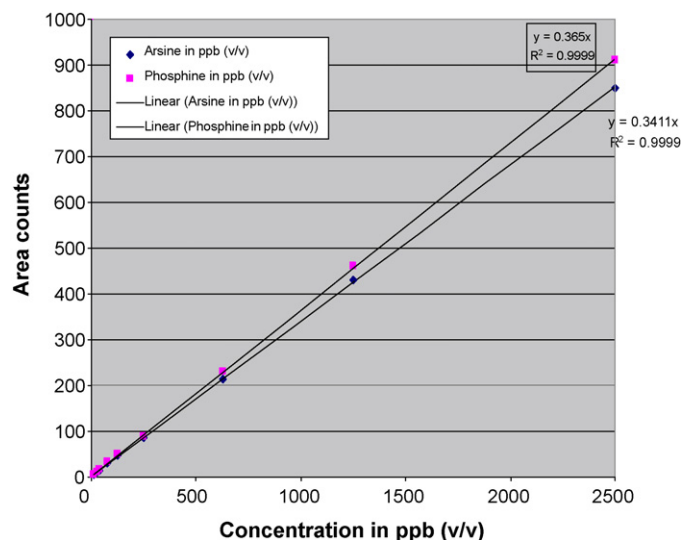

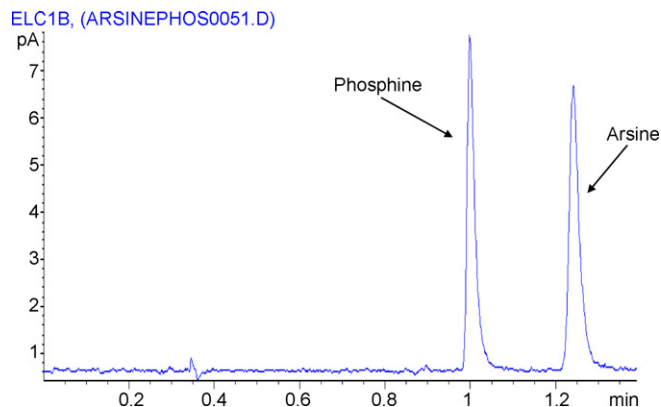Fig. 2. Linear range of phosphine and arsine from 10 to 2500 ppb (v/v).

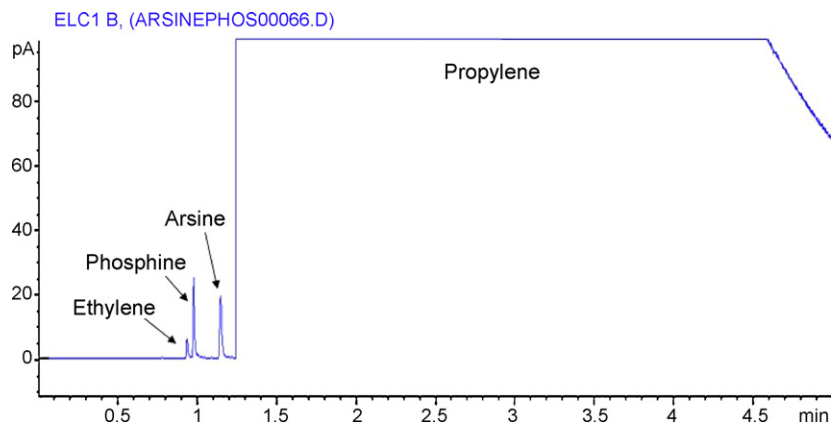Fig. 3. Chromatogram of 25 ppb (v/v) each of phosphine and arsine in nitrogen.

ELC1 B, (ARSINEPHOS00066.D)

Fig. 4. Separation of phosphine and arsine from propylene with propylene through detector.

bons include hydrogen sulfide and carbonyl sulfide. Hydrogen sulfide, if present can be separated and detected by the technique described. Carbonyl sulfide, while can be detected at the ppm level using the DBD in argon mode, co-elutes with the matrix (propylene) under the conditions used.

The detector also has response for alkanes greater than n-propane, alkenes and alkynes. For hydrocarbons that are longer chains than propylene, the matrix can be handled by either venting or back-flushing through the inlet vent as illustrated with propylene. A more difficult matrix would be ethylene since ethylene elutes just before phosphine on the column used. An approach one could take would be the employment of capillary flow technology Deans switch to, instead of back-flushing, "heart-cut" arsine and phosphine onto the second dimension. An added advantage associated with the "heart-cutting" approach is that the analytical column (2nd dimension) is kept clean of the potential heavier contaminants since it only gets exposed to only arsine and phosphine. The contaminants and matrix are quarantined in the first column (1st dimension). They either can be back-flushed or allow to elute via a restrictor as shown in Fig. 1.

By incorporating capillary flow technology either by back-flushing or heart-cutting, extra analytical flexibility has been integrated.
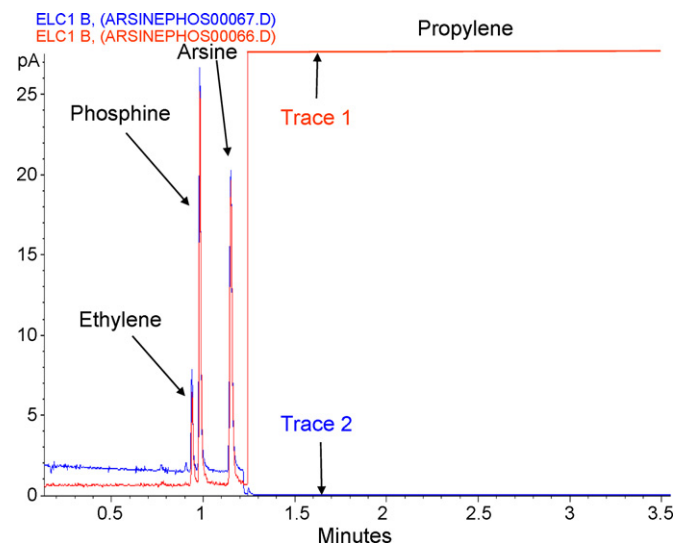

Fig. 5. Overlay of chromatograms of phosphine and arsine in propylene. Trace 1: Without back-flush (propylene through detector). Trace 2: With back-flush (propylene back-flush through inlet vent).

4. Conclusions

A gas chromatographic procedure has been successfully developed and implemented for the measurement of parts-per-billion level of phosphine and arsine in hydrocarbons such as propylene. The successful measurement of phosphine and arsine at the levels mentioned was attained by incorporating proven GC sub-components including a large volume injection technique to increase the mass of solutes delivered for sensitivity improvement, capillary flow technology to keep the matrix from entering the detector by back-flushing or by heart-cutting if required, and dielectric barrier discharged detector operating in argon mode for sensitivity enhancement as well as offering improved selectivity towards the solutes cited. The analytical procedure can be leveraged to analyze for phosphine and arsine in a variety of matrices and has been proven to be reliable in continuous operation during the first 6 months of deployment.

Acknowledgements

CP-Lowox, CP-SilicaPLOT, CP-PoraBOND Q are trademarks of Varian Inc, Middelburg, The Netherlands.

FocusLiner is a trademark of SGE Analytical Sciences, Victoria, Australia.

GasPro is a trademark of Agilent Technologies, Folsom, CA, USA.

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