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Simple and sensitive method for the measurement of volatile alkyl mercaptans in gasoline for remote field deployment

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ABSTRACT

Trace sulfur species, such as elemental sulfur, hydrogen sulfide, and volatile alkyl mercaptans, adversely affect silver based devices, such as gasoline level sensors, used in most vehicles. Identification and measurement of the sulfur species are key to developing a process control and/or treatment system to solve the problem at the refinery, prior to product distribution. A new and innovative method was developed for the analysis of specific mercaptan species in gasoline, and is reported here. The initial sample treatment stage is precipitation and stabilization of mercaptans as silver mercaptides. This stabilization could be successfully utilized in the field to mitigate the instability of mercaptans in gasoline samples. Another advantage of this step is that silver nitrate ($AgNO_3$) precipitation concentrates the mercaptans allowing for trace level detection. The silver mercaptides are converted to pentafluorobenzyl derivatives and analyzed by gas chromatography (GC) with mass spectrometric (MS) detection. Results based on this technique show that alkyl mercaptans can be accurately measured in the full scan mode of MS with a limit of detection (LOD) of 0.02 mg/L when a 100 mL gasoline sample is used. The recovery of mercaptans spiked into gasoline was 85 to 120% (n = 5). Gasoline producers will find knowing the exact levels of mercaptans in their products a useful tool to avoid distribution delays.

1. Introduction

Incidents of vehicle fuel level sensor/sender failures have been reported worldwide since 1999 and thousands of motorists have been affected by it. Electrical contacts in fuel level sensors made of silver (Ag alloys) are vulnerable to corrosion by certain commonly occurring trace sulfur species found in gasoline. This corrosion can lead to inaccurate/false dash board fuel level readings. Silver-plated bearings used in some gas station fuel pumps are another example of components that may be adversely affected by the sulfur species in fuel.

The corrosion mechanisms are not fully understood but thought to be due to synergism between elemental sulfur, hydrogen sulfide, and specifically low molecular weight mercaptans [1,2]. Levels of contamination in the low ppm range may cause this problem — although the specifics are not entirely understood. Gasoline with this sulfur contamination cannot be distributed and sold, posing a logistical problem for refineries. Total sulfur measurements at the refinery are not useful in predicting mercaptan concentration or species in gasoline. The Petro Canada silver wool test [3] works well as a predictor of the likelihood of mercaptan containing gasoline to damage automobile sensors, but does not identify the specific sulfur species. Identification of the sulfur species (in this case mercaptan) is key to developing a process control and/or treatment system to solve the problem at the refinery level.

While there are several analytical methods that can be employed for the measurement of total mercaptans in gasoline [4–8], to the best of our knowledge, there are no reports on reliable measurement of specific mercaptans in gasoline at concentrations lower than 1 ppm. The short holding time of low molecular weight mercaptans in the samples is also one limitation of most available methods. Several studies have described analysis methods for sulfur components in gasoline using GC coupled with sulfur-specific detectors [9,10]. However, these methods only determine that sulfur-containing compounds are present in gasoline and do not specify any molecular structures or distinguish peaks corresponding to specific mercaptans. Derivatization of mercaptans for analysis by GC or HPLC was found to be a reliable approach for identification and quantification of mercaptans [11–13]. Measurement of mercaptans after derivatization with pentafluorobenzyl p-toluenesulfonate was reported for mercaptan standards dissolved in dichloromethane by Funazo et al. [11]. Wu et al. [12] used pentafluorobenzyl bromide (PFBBr) for derivatization and measured both n-butyl and phenyl mercaptan standards in acetone. These methods introduced the concept of derivatization, and used low volumes (no more than 0.5 mL) of pure standards as analyte. They did not suggest any methodology for measurement of entrained mercaptans (i.e. in gasoline). Nishikawa et al. [13] determined levels in air samples by derivatization of low molecular weight mercaptans with 7-chloro-4-nitro-2,1,3-benzoxadiazole and measured them by HPLC. These kinds of derivatizations and measurements by HPLC or GC would be useful for the development of methods for the determination of mercaptans in gasoline if we include extraction steps for

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gasoline samples to achieve a detectable amount of mercaptans. To determine trace amounts of mercaptans in gasoline (in the range of 0.1 ppm), an extraction of at least 25 mL of gasoline is needed. In recent years the technology for determination of mercaptans in evaporated samples or gas (state) has been greatly improved. The specialized sampling filters [14] and/or sophisticated GC systems and GC columns [15,16] allowed identification and measurement of a large number of mercaptans in gas (state) samples without any derivatization and with detection limits as low as 0.2 ppm (v/v). Several GC based instruments, as sulfur compound or mercaptan analyzers, have become commercially available for analysis of ambient air (e.g.: TRSMEDOR — H2S, mercaptans' analyzers M52022 or the Syntech Spectras GC955 series 800). These methods all use large volumes of gas (state) samples and, therefore, are not useful or sensitive enough for analyzing liquid gasoline samples.

This report introduces a method for stabilizing and analyzing mercaptans in gasoline with consideration of three critical aspects of this kind of analysis:

I) The mercaptans in gasoline samples should be stabilized at the time of sampling as they may degrade or evaporate.
II) The mercaptans need to be concentrated in the samples to be at measurable levels.
III) A method for the analysis should be selected, which is highly sensitive, selective and deals with stable derivatives of the mercaptans.

A novel, simple, practical, easy-to-implement method was developed to quantify the specific mercaptan species in gasoline at low ppm (mg/L) levels for remote field deployment. The idea was adapted from Wu et al. [12], who analyzed standard n-butyl and phenyl mercaptans by silver precipitation and derivatization. The method [12] was modified by adding an extraction step for high volumes of gasoline, using mass spectrometric (MS) detection, which offers positive identification and sensitive quantification ability, and some other adjustments described in this paper. The method was thoroughly validated for work with gasoline samples from refineries. It was demonstrated that when mercaptans in gasoline are precipitated by silver nitrate, the precipitation step served to stabilize and concentrate the mercaptans in the precipitate. Two model mercaptans, ethyl and n-propyl mercaptans, were analyzed.

2. Materials and methods

2.1. Materials

Ethyl and n-propyl mercaptans were purchased from Sigma-Aldrich. Pentafluorobenzyl bromide (98%) was purchased from Alfa Aesar. Other reagents (e.g. n-hexanes, xylenes, and silver nitrate) were of analytical reagent grade. Mercaptan standard solutions were prepared in xylenes. n-Tetradecane-d_{30} (purchased from C/D/N Isotopes Inc.) was used as an internal standard.

2.2. Preparation of Clean Gasoline

A regular grade gasoline sample was provided by Suncor Energy Inc. Any existing mercaptans were removed from the gasoline sample by two sequential manual extractions with 3 N NaOH [17] followed by three sequential manual extractions with pure water (to ensure no NaOH remained in the gasoline). This extracted sample was referred to as Clean Gasoline and was used as a control. Ethyl and n-propyl mercaptan standards were spiked in sub-samples of Clean Gasoline. These samples were treated and analyzed as per the method and their analytical results were used to calculate the recovery of mercaptans in gasoline. (Note: The mercaptan standards in gasoline were unstable. All spiked solutions were used within 6 h of preparation.)

2.3. Extraction and derivatization procedure

Ethyl and n-propyl mercaptans were precipitated as silver mercaptides, derivatized, and analyzed by GC/MS. For the calibration curve, an aliquot of the standard solution was added to 6 mL of 0.02 M $AgNO_3$ (dissolved in isopropanol) solution in a 15 mL glass test tube with a Teflon lined cap. After the test tube was shaken by hand to attain the complete formation of silver mercaptide precipitate, it was centrifuged at 670 *g* for 5 min. The supernatant was removed and 1 mL of deionized water was added to the precipitate. After shaking, 0.1 mL of Na_2S (0.1 M), 0.125 mL of $ZnSO_4$ (0.04 M) and 0.1 mL of NaOH (8 M) solutions were added in succession. Then, 2.0 mL of the internal standard solution (0.127 mM in n-hexane) and 10 μL of PFBBr were added. The reaction mixture was shaken for 1 h in a water incubator at 60 °C. An aliquot of 1 mL of the clear n-hexane layer was transferred to a 4 mL vial, dried by blowing nitrogen on it, and the precipitate was dissolved in 100 μL n-hexanes. One microliter of this solution was injected into the GC.

To analyze gasoline samples, 40 mL of gasoline was added to 6 mL of 0.02 M $AgNO_3$ (dissolved in isopropanol) solution, the mixture was centrifuged at 670 g for 5 min and the supernatant was removed. 1 mL deionized water was added to the final precipitate and it was treated as described above.

2.4. Gas chromatographic conditions

Both pentafluorobenzyl derivatives of ethyl and n-propyl mercaptans were analyzed by GC/MS. The GC/MS was comprised of a Hewlett Packard (HP) 5890 Series II GC and a HP 5970 Series Mass Selective detector. The column (length: 30 m, diameter: 0.250 mm) was a DB-5 ((5%-Phenyl)-methylpolysiloxane column; 300/320 °C temperature limit; 0.25 μm coating thickness; from Agilent J & W). The injector temperature was kept at 250 °C. The oven temperature program was 3 min isothermal at 50 °C and then a 10 °C/min ramp to 300 °C, held for 2 min. Helium was used as carrier gas. A split flow was used. The interface temperature was 250 °C and peak areas were measured by a computer using the program HP Chemstation. The MS was operated in full scan mode, screening from 50 to 400 amu with 1.7 scans per second. To improve the separation and detection, selected single ions (e.g. parent ions at $m/z = 242$ and $m/z = 256$, which correspond to pentafluorobenzyl ethyl thioether and pentafluorobenzyl n-propyl thioether, respectively, and $m/z = 82$ to correspond with the internal standard) were monitored and areas under those peaks were used for quantification.

3. Results and discussion

3.1. Analytical calibration

A calibration graph for ethyl and n-propyl mercaptans, plotting the peak area ratio of the derivative to the internal standard against the mercaptan weight is shown in Fig. 1. This graph covers the range of 3.5–280 μg (0.035–2.8 mg/L when 100 mL gasoline was analyzed). The linear regression equations, $y = 0.0014x + 0.0038$ with a correlation coefficient of 0.999 for ethyl mercaptan and $y = 0.0007x + 0.0036$ with a correlation coefficient of 0.990 for n-propyl mercaptan, were obtained. The results indicate linearity over the range analyzed. The observed limit of detection (LOD) was 1.7 μg. The LOD was also calculated from the results of seven independently prepared 13.9 μg mercaptans in Clean Gasoline standards by using the following formula [18].

$$\mathrm{LOD} = t(n-1) \times \mathrm{SD}.$$

Where t (n − 1) is the value of the 95% one-side Student's distribution for n − 1 degrees of freedom, and SD is the standard deviation obtained for seven replications. The LOD calculated for the mercaptan