Journal of Chromatography A, 1252 (2012) 171–176

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

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

Analysis of alkyl phosphates in petroleum samples by comprehensive two-dimensional gas chromatography with nitrogen phosphorus detection and post-column Deans switching[☆]

Katie D. Nizio, James J. Harynuk*

Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2, Canada

ARTICLE INFO

Article history:
Received 8 May 2012
Received in revised form 18 June 2012
Accepted 19 June 2012
Available online 27 June 2012

Keywords:
GC×GC
NPD
Deans switch
Alkyl phosphates
Fracturing fluid
Petroleum

ABSTRACT

Alkyl phosphate based gellants used as viscosity builders for fracturing fluids used in the process of hydraulic fracturing have been implicated in numerous refinery-fouling incidents in North America. In response, industry developed an inductively coupled plasma optical emission spectroscopy (ICP-OES) based method for the analysis of total volatile phosphorus in distillate fractions of crude oil; however, this method is plagued by poor precision and a high limit of detection (0.5 ± 1 μg phosphorus mL^{-1}). Furthermore this method cannot provide speciation information, which is critical for developing an understanding of the challenge of alkyl phosphates at a molecular level. An approach using comprehensive two-dimensional gas chromatography with nitrogen phosphorus detection (GC×GC–NPD) and post-column Deans switching is presented. This method provides qualitative and quantitative profiles of alkyl phosphates in industrial petroleum samples with increased precision and at levels comparable to or below those achievable by ICP-OES. A recovery study in a fracturing fluid sample and a profiling study of alkyl phosphates in four recovered fracturing fluid/crude oil mixtures (flowback) are also presented.

1. Introduction

Oil production involves both the extraction of crude oil from underground reservoirs as well as the processing of raw crude within refineries in order to produce the many petroleum products upon which we are dependent. The choice of oil extraction technique relies heavily on the features of the well being processed [1]. Hydraulic fracturing is one of the most common, particularly in partially depleted reservoirs. This process uses the repetitive pumping of a fracturing fluid into the well at pressures on the order of 15,000 psi [2]. These high pressures create a network of fractures within the rock that provide channels through which the oil can flow to the wellhead. A propping agent (proppant) such as advanced ceramics [3], sand grains, walnut shell fragments, tempered glass beads, aluminum pellets, nylon pellets or a mixture thereof [4] is introduced with the fracturing fluid. The proppant serves to prevent a collapse of the fracture network once the pressure is removed, ensuring clear passages to the wellhead.

During the fracturing process the fracturing fluid must be viscous in order to both maintain the proppant particles in suspension and to effectively transmit the fracturing pressure into the rock. Gellants are added to the fracturing fluids as viscosity builders. Once the fracturing process is complete, the viscosity of the fracturing fluid must be reduced such that it can be easily withdrawn from the well while leaving the proppant in place. This is achieved through the addition of a gel breaker that disrupts the self-assembly properties of the gel, greatly decreasing its viscosity [2].

As previously mentioned, choice of fracturing fluid and gellant are influenced by the geology of the well being processed. In the case of water-sensitive geologies, like those found in the Western Canadian Sedimentary Basin, oil-based fracturing fluids containing a dialkyl phosphate ester gellant are typically required [5]. Metal cations with a coordination number of 6 (e.g., Fe^{3+} and Al^{3+}) are added along with the dialkyl phosphates in order to establish a viscous, cross-linked gel. This gel can be disrupted by the addition of water, alcohols, surfactants, or by adjusting the pH [2].

The gellants added to oil-based fracturing fluids are typically dialkyl phosphates with alkyl chains 2–30 carbons in length [6,7]. However, these gellants are manufactured as a technical mixture formed from the reaction of either phosphorus pentoxide, phosphorus pentachloride, or phosphorus oxychloride with selected alcohols, resulting in a mixture containing dialkyl phosphates as the major components with lesser amounts of mono- and tri-alkyl phosphates [2,5].

[☆] Presented at the 36th International Symposium on Capillary Chromatography and Electrophoresis and 9th GC×GC Symposium, Riva del Garda, Italy, May 27–June 1, 2012.

* Corresponding author. Tel.: +1 780 492 8303; fax: +1 780 492 8231.
E-mail address: james.harynuk@ualberta.ca (J.J. Harynuk).

0021-9673/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chroma.2012.06.070

After fracturing, spent fracturing fluid mixed with crude oil (flowback) is ideally diverted prior to the well going into production. However, it is a challenge to identify when the majority of the phosphates have been removed, and traces of gellant will inevitably contaminate the oil. Phosphate gellants have been implicated in numerous refinery-fouling incidents in North America costing tens of millions of dollars as a result of unplanned shutdowns. It is believed that these compounds volatilize or form volatile species through some unknown chemical reactions. These species then damage equipment (e.g., deposits on distillation tower trays or deactivation of catalysts). The potential also exists for these compounds to contaminate final products, affecting consumers. Overall, this contamination results in decreased and unpredictable lifespans of refinery equipment in addition to more recurrent maintenance shutdowns.

An inductively coupled plasma optical emission spectroscopy (ICP-OES) based method for the analysis of total volatile phosphorus in distillate fractions of crude oil has been developed [8]. However, this method is plagued with poor precision and a high limit of detection (0.5 ± 1 μg phosphorus mL^{-1}). Additionally, this cannot speciate the phosphates, leaving industry incapable of studying this chemistry at a molecular level. Recently, we have approached this challenge using comprehensive two-dimensional gas chromatography (GC×GC) [9].

GC×GC is a separations technique with numerous applications in many fields, especially petroleum. Its application to the petroleum field has been reviewed recently [10] and several other cover broader aspects of the technique [11–18]. We recently introduced a method based on trimethylsilylation derivatization followed by GC×GC separation using a flame ionization detector (FID) for the speciation of di- and tri-alkyl phosphates in petroleum samples [19]. Although this analytical approach yielded detection limits and a level of precision that exceeded the capabilities of the currently accepted ICP-OES methodology, our research demonstrated the necessity for selective detection in this application, which we achieved through the use of time-of-flight mass spectrometry (TOFMS) [20]. Overall this method was capable of both speciating and quantifying alkyl phosphates in petroleum samples with better precision and lower limits of detection when compared to ICP-OES. However, the TOFMS is a very expensive instrument which is not suitable for use in on-line or at-line monitoring in a refinery environment. Herein, we present the use of nitrogen–phosphorus detection in conjunction with GC×GC for alkyl phosphate measurement in petroleum samples. This is a much more rugged and less expensive detector than the TOFMS, making the new method more attractive for implementation in an industrial setting.

2. Experimental

2.1. Materials and reagents

Stock solutions were stored in glass vials and refrigerated at ~7 °C. Calibration, recovery study, and industrial petroleum sample solutions were prepared in 1.8 mL glass GC vials with PTFE-lined silicone septa (Chromatographic Specialties, Brockville, ON, Canada) for analysis by GC×GC-FID/NPD.

All reagents were used as received unless otherwise stated. Derivatization was performed according to a previously established protocol [19] using a mixture of *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (Sigma–Aldrich, Oakville, ON, Canada), pyridine (Caledon, Georgetown, ON, Canada), and chlorotrimethylsilane (TMCS) (Sigma–Aldrich) in a 10:5:2 ratio by volume. 50 μL of the derivatization reagent mixture was added to 500 μL of sample and left to derivatize at 30 °C for at least 30 min before analysis. Vials were maintained at temperature using the GC autosampler tray which was kept at 30 °C by circulating heated water through the trays.

The alkyl phosphate standards utilized for the calibration and recovery studies consisted of triethyl, triisopropyl, tripropyl, dibutyl, and tributyl phosphate (Sigma–Aldrich) and bis(2-ethylhexyl) phosphate, trihexyl phosphate, and trioctyl phosphate (Alfa Aesar, Ward Hill, MA, USA). CHROMASOLV® grade hexane (Sigma–Aldrich) was used as a solvent. Triphenyl phosphate (Sigma–Aldrich) was dissolved and diluted in reagent grade acetone (Caledon) to give a 1020 μg mL^{-1} stock solution that was used as an internal standard. A fracture fluid sample distilling <250 °C (Wilson Analytical, Sherwood Park, AB, Canada) was diluted 10 times in hexane (Sigma–Aldrich), spiked with ~50 μg mL^{-1} of each alkyl phosphate, and derivatized for the recovery study. Four different industrial flowback samples (Imperial Oil, Sarnia, ON, Canada) each comprising a mixture of crude oil and fracturing fluid, were derivatized and spiked with internal standard before analysis.

2.2. Instrumentation and experimental conditions

2.2.1. Calibration and recovery study

Analysis was conducted using a Consumable-free LECO GC×GC system (Leco Instruments, St. Joseph, MI, USA) equipped with a CFT Deans switch (Agilent Technologies, Mississauga, ON, Canada) and both FID and NPD detectors (Fig. 1). The NPD utilized a modified capillary-optimized jet (DETector Engineering &Technology, Inc., Walnut Creek, CA, USA) and a TID-2 black ceramic bead (DETector Engineering &Technology, Inc.). This NPD jet has a large enough bore to permit the capillary column to pass through the jet and be positioned a few mm from the detector bead, improving the response characteristics of the detector over the conventional design [21]. The column configuration consisted of a 10 m × 0.18 mm, 0.18 μm Rxi-5Sil MS (Restek, Bellefonte, PA, USA) column in the first dimension and a 0.5 m × 0.18 mm, 0.18 μm Rxi-17Sil MS (Restek) column in the second dimension. The transfer lines consisted of 0.18 mm ID deactivated fused silica (Agilent Technologies), 16 cm connected the secondary column to the Deans switch and 20 cm sections connected the Deans switch with the detectors. All injections were performed in triplicate using 1 μL of sample with an Agilent 7683B Series autosampler and a split ratio of 50:1. The inlet temperature was 250 °C. Helium was used as the carrier gas with a ramped pressure program of 129.7 (held for 2 min)–249.3 kPa at 15.0 kPa min^{-1} for the inlet and 36.5 (held for 2 min)–62.8 kPa at 3.3 kPa min^{-1} for the Deans switch plate. The pressure programs were calculated using the Agilent Deans Switch Calculator and HP Flow Calculator. The primary oven temperature program was 40 (held for 2 min)–280 °C at 30 °C min^{-1}. Relative to the primary oven, the secondary oven was programmed to have a constant offset of +30 °C and the modulator a constant offset of +45 °C. A modulation period of 1.5 s was used. The Deans switch initially directed solvent and any excess derivatization reagents exiting the secondary column to the FID. After 3.3 min, the valve was actuated to direct the effluent to the NPD for selective detection of the alkyl phosphates. Both detectors were kept at 325 °C. Data were acquired at a rate of 100 Hz and processed using ChromaTOF software (v.4.42; LECO). The data processing method used a baseline offset of 0.5, auto smoothing, expected first-dimension peak width of 4.5 s, expected second-dimension peak width of 0.2 s, and a minimum S/N of 5 for peak detection.

2.2.2. Industrial petroleum samples

Analyses were conducted using the same instrumental set-up and column configuration as previously stated. The method was modified as follows while all other parameters remained the same. Helium was used as the carrier gas with a ramped pressure