

# Methodology for the derivatization and quantification of dialkyl phosphate esters in petroleum samples

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Dialkyl phosphate esters are used as gellants in some oil well fracturing processes for conventional oil production. Residual amounts of these compounds that remain in the well represent a source of potential contamination of the crude oil produced from the well. This contamination results in fouling of refinery equipment. Current methodologies for the analysis of alkyl phosphates have a relatively poor detection limit ( $0.5 \pm 1.0 \mu\text{g mL}^{-1}$ ) and provide no speciation information: only a total phosphorus concentration. Herein, we present an approach that permits speciation of individual alkyl phosphates and quantification of individual compounds with limits of detection and precision that represent an improvement on the existing methodology. The method that we present relies upon derivatization of dialkyl phosphates to their trimethylsilane (TMS) esters followed by a comprehensive two-dimensional gas chromatographic separation. Two dialkyl phosphate esters, dibutyl and bis(2-ethylhexyl) phosphate were used as model compounds. Recovery of spiked samples in pure solvent and a model petroleum mixture ranged from 92% to 120%. This approach represents a significant first step in the development of an analytical solution to the challenge of phosphorus contamination facing the oil industry.

## 1.0 Introduction

Conventional oil production involves extracting oil from underground reservoirs and processing the raw crude into various petroleum products within refineries. Numerous oil extraction methods exist and their implementation relies heavily on the features of the well being processed.<sup>1</sup> Hydraulic fracturing is one of the most commonly used extraction techniques. This method uses repetitive pumping of a fracturing fluid into the well at pressures up to 15 000 psi. This high pressure causes fractures to develop within the rock. The fracture fluid is then withdrawn, leaving a network of fractures through which the oil is extracted. In order to keep the fractures from collapsing on themselves, a proppant (such as glass beads or crushed walnut shells<sup>2</sup>) is added to the mixture. The role of the proppant is to prop the fractures open, while still leaving large enough channels through which the crude can flow.

In order to easily transport the proppant into the fractures and then extract the fracture fluid from the well, one must be able to manipulate the viscosity of the fracture fluid. Fracturing gellants are used as viscosity builders. Initially the viscosity must be quite high such that the proppant remains dispersed in the fluid. The high viscosity also aids in achieving the pressures required for the fracturing process. Once fracturing is completed, the viscosity must be reduced so that the fluid is easily extracted, leaving the proppant behind. This is achieved through the addition of gel breakers which decrease the self-assembly properties of the gel.<sup>3</sup>

In the case of water-sensitive geologies, dialkyl phosphate esters are common components of fracture fluid gellants.<sup>4</sup>

Unfortunately, residual gellant that remains in the well after the fracturing process is completed can contaminate the crude oil that is produced. The presence of these compounds in crude oil has been implicated in several refinery-fouling incidents in both Canada and the United States. Chronic exposure to trace levels of phosphorus can heavily impede the plant's function, resulting in maintenance shutdowns which are often unplanned.<sup>5</sup>

Current methodology for phosphorus analysis involves the atmospheric pressure distillation of a crude sample and collection of the fraction distilling below 250 °C. This fraction is then analyzed *via* inductively coupled plasma optical emission spectrometry (ICP-OES).<sup>6</sup> This method has a limit of detection of  $0.5 \pm 1.0 \mu\text{g mL}^{-1}$  phosphorus; much of the imprecision is due to challenges in sample introduction.<sup>7</sup>

A more precise method with a lower limit of detection would improve operators' ability to predict and manage fouling events. Were the method capable of providing speciation information as well, it would also permit researchers to study the chemistry of alkyl phosphates in a refinery environment and gain some fundamental understanding of fouling processes.

Comprehensive two-dimensional gas chromatography (GC  $\times$  GC) possesses impressive separation power, allowing analysis of highly complex matrices. This technique is proving to be a great asset for all fields of petrochemical investigations. Examples of where this technology has been applied include group-type separations,<sup>8–11</sup> examination of weathering behaviours,<sup>12</sup> identification of biomarkers,<sup>13</sup> characterization of sources of crude oil,<sup>14</sup> and the analysis of biofuels<sup>15</sup> to name but a few.

GC  $\times$  GC is well established in the literature and those readers unfamiliar with the technology are referred to a series of review papers that discuss various aspects of the technique<sup>16,17</sup> and its application to a variety of fields including petrochemical analysis. Briefly, GC  $\times$  GC employs two columns with different

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stationary phase chemistries, coupled by a modulator or interface. Typically, the column used in the first dimension is longer and apolar, with retention being governed by non-specific interactions, and the column used in the second dimension is shorter and has more polar or other specific interactions governing the separation. The modulator acts to control the flow of analytes from the primary column to the secondary column, periodically introducing narrow pulses of primary column effluent into the secondary column. The entire setup is operated in such a manner that each pulse introduced to the secondary column is (ideally) finished its separation in the secondary column before the subsequent modulation pulse begins to elute from the secondary column, thus avoiding so-called wrap-around peaks. Furthermore, the conditions are such that individual peaks eluting from the primary column are sampled multiple times, allowing the preservation of the separation achieved in the primary dimension. Peaks eluting from the secondary column are recorded by a fast detector capable of operating at a rate of at least 50 Hz, preferably 100 Hz for quantitative analysis, identified, and combined by software routines.

When considering the analysis of alkyl phosphates by GC  $\times$  GC, only the trialkyl phosphates are suitable. Due to the acidic protons, mono- and dialkyl phosphates are not amenable to GC analysis without prior derivatization. This manuscript presents a derivatization method for dialkyl phosphates that relies on trimethylsilylation. The optimized derivatization method is then used in a brief recovery study of two dialkyl phosphates spiked into a petrochemical distillate sample, demonstrating the applicability of this approach for the analysis of alkyl phosphates in petroleum samples.

## 2.0 Experimental

### 2.1 Materials and reagents

All solutions were prepared in 5 mL volumetric flasks with standard ground glass stoppers. Prepared samples were then transferred to clear 1.2 mL glass GC vials with PTFE silicone septa (Chromatographic Specialties, ON, Canada) for analysis. Reagents consisted of chlorotrimethylsilane (TMCS), pyridine, and *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (Sigma-Aldrich, ON, Canada). ACS grade hexane (Sigma-Aldrich) was used as the solvent for target analytes bis(2-ethylhexyl) phosphate (Alfa Aesar, MA, USA) and dibutyl phosphate (Sigma-Aldrich). Both dialkyl phosphates were of  $\geq 97\%$  purity. Tetradecane (Eastman, TN, USA) was diluted with hexane to provide a 60  $\mu\text{g mL}^{-1}$  stock solution to serve as an internal standard for use during the derivatization optimization. 87-Octane unleaded gasoline was obtained from a local vendor for use as a model petrochemical mixture.

### 2.2 Instrumentation and experimental conditions

**2.2.1 Derivatization reagent ratio optimization.** The derivatization reagent ratio was optimized using a Pegasus 4D-TOFMS system (Leco, St Joseph, MI, USA). The primary column was a 10 m  $\times$  0.18 mm, 0.2  $\mu\text{m}$  RTX-5 (Restek, PA, USA). A 1.1 m  $\times$  0.10 mm, 0.1  $\mu\text{m}$  Rxi-17 (Restek), served as the second-dimension column. The system was operated in one-dimensional mode

for derivatization optimization experiments. The front inlet was set to 250  $^{\circ}\text{C}$ . 1  $\mu\text{L}$  injections were performed in split mode with a 50 : 1 split ratio. Helium was used as the carrier gas and set at a flow rate of 1.1  $\text{mL min}^{-1}$ . The primary oven temperature program was set to 80  $^{\circ}\text{C}$  to 260  $^{\circ}\text{C}$ ; the secondary oven possessed a constant offset of +20  $^{\circ}\text{C}$ . Both column temperatures increased at a rate of 10  $^{\circ}\text{C min}^{-1}$ . Data were collected over a  $m/z$  range of 35–500 at a rate of 10 spectra per second with a solvent delay of 80 s. The detector voltage was set to 1400 V. The ion source temperature was set to 200  $^{\circ}\text{C}$  and transferline temperature was 240  $^{\circ}\text{C}$ .

### 2.2.2 Optimization of derivatization time and temperature.

Optimization of derivatization time and temperature was conducted using a Consumable-free Leco GC  $\times$  GC system equipped with a flame ionization detector, operated in one-dimensional mode. The column used was a 10 m  $\times$  0.18 mm, 0.2  $\mu\text{m}$  RTX-5. Injector and flow rate settings were identical to those used for the derivatization ratio optimization experiments. The oven was programmed from 50  $^{\circ}\text{C}$  to 280  $^{\circ}\text{C}$  at a rate of 4  $^{\circ}\text{C min}^{-1}$ . Data were collected at a rate of 20 Hz.

**2.2.3 Calibration and recovery study.** To perform a calibration and recovery study, the GC  $\times$  GC-FID system was re-configured in two-dimensional mode, adding a 1.1 m  $\times$  0.10 mm, 0.1  $\mu\text{m}$  Rxi-17, secondary column. The first-dimension temperature program was set to 40  $^{\circ}\text{C}$  to 260  $^{\circ}\text{C}$  and the secondary oven was programmed with a constant offset of +20  $^{\circ}\text{C}$ . Both column temperatures increased at a rate of 4  $^{\circ}\text{C min}^{-1}$ . The modulator was operated with an offset of 30  $^{\circ}\text{C}$  and a 4 s modulation period was used. Data were acquired at 100 Hz. In all cases, data were processed using ChromaTOF software v.4.22 and v.4.24 (Leco).

## 3.0 Results and discussion

### 3.1 Derivatization reagent mixture optimization

An established method for the derivatization of phosphates is silylation with BSTFA, often with the addition of pyridine and TMCS.<sup>18</sup> In the reaction, the TMCS serves to help activate the BSTFA and pyridine acts as a proton scavenger to ensure that the reaction is driven to completion. Though the general

**Table 1** Effect of derivatization reagent ratio on analyte response, normalized to tetradecane

Compound	BSTFA : pyridine : TMCS	Normalized response avg $\pm$ $\sigma$ ( $n = 3$ )
Dibutyl phosphate	1 : 1 : 1	0.263 $\pm$ 0.025
	5 : 5 : 1	0.321 $\pm$ 0.073
	10 : 5 : 10	0.384 $\pm$ 0.052
	10 : 5 : 2	0.441 $\pm$ 0.057
	1 : 0 : 1	0.364 $\pm$ 0.027
	5 : 0 : 1	0.369 $\pm$ 0.028
Bis(2-ethylhexyl) phosphate	1 : 1 : 1	0.188 $\pm$ 0.022
	5 : 5 : 1	0.247 $\pm$ 0.152
	10 : 5 : 10	0.257 $\pm$ 0.113
	10 : 5 : 2	0.241 $\pm$ 0.017
	1 : 0 : 1	0.243 $\pm$ 0.110
	5 : 0 : 1	0.224 $\pm$ 0.061

chemistry has been established, optimization of the ratios of the reagents must be performed for each application. An initial investigation was conducted in order to optimize the ratio of these three components in the derivatization reagent mixture. BSTFA, pyridine and TMCS were mixed to provide separate solutions with ratios of 5 : 0 : 1, 1 : 0 : 1, 10 : 5 : 10, 10 : 5 : 2, 5 : 5 : 1, and 1 : 1 : 1 (BSTFA : pyridine : TMCS) by volume. Solutions of model analytes, bis(2-ethylhexyl) phosphate and dibutyl phosphate, each at a concentration of  $10 \mu\text{g mL}^{-1}$  were prepared in hexane. 500  $\mu\text{L}$  aliquots of these solutions were then taken and placed in GC vials to which 100  $\mu\text{L}$  of derivatization reagent mixture and 10  $\mu\text{L}$  of internal standard solution were added. The vials were sealed, shaken, and placed in an oven to derivatize for 1 h at  $70^\circ\text{C}$ . After derivatization, the samples were analyzed by GC-TOFMS. The results of this derivatization mixture optimization are presented in Table 1.

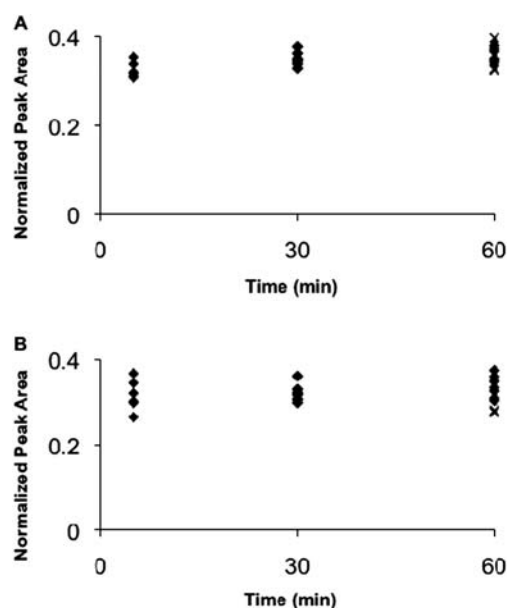
The first observation of note is that at  $70^\circ\text{C}$ , all sample vials experienced some degradation of their septa. The degree of degradation varied from vial to vial, but did not appear to be correlated with any of the ratios being tested. A variety of PTFE-lined septa were tested, and all exhibited degradation. This degradation was believed to be the source of extraneous peaks observed in the chromatograms (data not shown). Fortunately, these peaks did not coelute with either of the model analytes or internal standard being investigated. Consequently, the results at  $70^\circ\text{C}$  were considered to be valid.

The most suitable derivatization conditions were found to use the 10 : 5 : 2 BSTFA : pyridine : TMCS mixture. This ratio demonstrated reasonable abundance for both analytes, combined with the most precision and the least amount of peak tailing. Analyte identities were confirmed by their mass spectra and by repeating the experiment in the absence of derivatization reagents. Without derivatization reagents, no analyte signal was observed.

### 3.2 Optimization of derivatization time and temperature

Having chosen a suitable ratio for the components of the derivatization reagent mixture, the derivatization time and temperature were then optimized. We chose to attempt the derivatization at room temperature (approximately  $21^\circ\text{C}$ ) in the hopes that this would help to preserve the septa of the GC vials. 500  $\mu\text{L}$  aliquots of the model compound solutions were transferred to GC vials, 100  $\mu\text{L}$  of derivatization reagent and 20  $\mu\text{L}$  of internal standard were added. The vials were sealed, shaken, and allowed to sit for the prescribed time before analysis. Samples were not prepared until the chromatographic equipment was in a ready state, so that the time of injection would be as close as possible to the nominal stop time for the derivatization experiment. The times that were tested were 5, 30, and 60 minutes. Each experiment was performed 6 times as there was a large variability that was observed in the results for GC-FID analysis (Fig. 1). Three replicates were also derivatized for one hour at  $70^\circ\text{C}$  for comparison purposes.

The difference between the ratios observed for analyte peak area vs. internal standard peak area in the GC-FID experiments vs. the GC-TOFMS experiments is attributed to changes in the relative responses of the two detectors for the compounds and the different volumes of internal standard that were used in each



**Fig. 1** Effect of derivatization time and temperature on analyte response, normalized to tetradecane. (A) Dibutyl phosphate TMS; (B) and bis(2-ethylhexyl) phosphate TMS. (♦) room temperature and (×)  $70^\circ\text{C}$ .

set of experiments. The high variability observed in the time optimization study was attributed to problems with the injector liner and the autosampler. Though imprecise, the data in Fig. 1 indicated that derivatization at room temperature for 30 minutes was sufficient for complete derivatization of the model compounds, and that the results were essentially identical to derivatization at  $70^\circ\text{C}$ .

### 3.3 Calibration and recovery study

Having chosen optimal conditions for the derivatization of dialkyl phosphate esters, the GC  $\times$  GC-FID system was calibrated in GC  $\times$  GC mode and a recovery study was performed.

Standards of the model compounds at concentrations of 0.05, 0.25, 0.5, 1.25, 2.5, and 5.0  $\mu\text{g mL}^{-1}$  were prepared in hexane. 500  $\mu\text{L}$  aliquots of each standard were taken and derivatized according to the above procedure using 100  $\mu\text{L}$  of the derivatization mixture. Tetradecane was used as an internal standard as it is not present in significant quantities in the gasoline sample used as a model petrochemical mixture. For general use on other petrochemical samples, a different internal standard will need to be chosen.

The calibration equations for bis(2-ethylhexyl) phosphate and dibutyl phosphate were found to be  $y = 0.0223x - 0.0025$  and  $y = 0.0199x - 0.0011$ , respectively, with  $R^2$  values of 0.9967 and 0.9998, respectively. For the calibration, the 0.05  $\mu\text{g mL}^{-1}$  standards were found to be below the detection limit and were excluded. The 0.25  $\mu\text{g mL}^{-1}$  standards showed peaks that were easily quantifiable.

The recovery of spiked samples was also tested. Samples of bis(2-ethylhexyl) phosphate and dibutyl phosphate were prepared to the concentrations shown in Table 2 in both hexane and gasoline, which served as a model petrochemical sample

**Table 2** Results of recovery study

Matrix	Spike/ $\mu\text{g mL}^{-1}$	Recovered/ $\mu\text{g mL}^{-1}$	Recovery (%)
<i>Dibutyl phosphate</i>			
Hexane	0.40	$0.40 \pm 0.03$	100
Gasoline	0.25	$0.23 \pm 0.03$	92
<i>Bis(2-ethylhexyl) phosphate</i>			
Hexane	0.25	$0.30 \pm 0.15$	120
Gasoline	0.25	$0.27 \pm 0.15$	108

having no components that coeluted in GC  $\times$  GC mode with the model analytes (and hence could be analyzed by GC  $\times$  GC-FID). These samples were then derivatized using the established protocol and analyzed by GC  $\times$  GC-FID. Recoveries for the analytes were all satisfactory, ranging from a low value of 92% to a high value of 120%.

A strict definition of detection limit for modulated multidimensional separations (GC  $\times$  GC, LC  $\times$  LC, etc.) is as yet elusive;<sup>19</sup> however from our results we can determine that under these conditions, the detection limit is between 0.25 and 0.05  $\mu\text{g mL}^{-1}$  for both model compounds. As we are presently concerned with the derivatization method, a more precise and thorough study of the detection limits for these compounds is left for future study. Nevertheless, we can say for certain that the approach detailed herein represents a significant improvement in detection limits over the currently used ICP-OES methodology which has a detection limit of  $0.5 \pm 1.0 \mu\text{g mL}^{-1}$  total phosphate.

#### 4.0 Conclusions

Derivatization of mono- and dialkyl phosphates is required for their analysis *via* gas chromatography. 100  $\mu\text{L}$  of a derivatization reagent mixture of BSTFA, pyridine, and TMCS in a ratio of 10 : 5 : 2 (BSTFA : pyridine : TMCS) by volume added to 500  $\mu\text{L}$  of petrochemical sample and reacted for 30 minutes provided excellent results for the model compounds tested. This provides a simple, relatively quick methodology for the derivatization of these compounds prior to GC ( $\times$ GC) analysis. The analytical approach used here yielded satisfactory recoveries with detection limits and a level of precision that exceeds the capabilities of current methodologies for the analysis of dialkyl phosphates in petroleum samples. This represents a significant step towards the routine quantification and speciation of alkyl phosphates in petrochemical samples and the ability to study the chemistry of these mixtures in greater detail.

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