Improving oil classification quality from oil spill fingerprint beyond six sigma approach

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ABSTRACT

This study involves the use of quality engineering in oil spill classification based on oil spill fingerprinting from GC-FID and GC–MS employing the six-sigma approach. The oil spills are recovered from various water areas of Peninsular Malaysia and Sabah (East Malaysia). The study approach used six sigma methodologies that effectively serve as the problem solving in oil classification extracted from the complex mixtures of oil spilled dataset. The analysis of six sigma link with the quality engineering improved the organizational performance to achieve its objectivity of the environmental forensics. The study reveals that oil spills are discriminated into four groups' viz. diesel, hydrocarbon fuel oil (HFO), mixture oil lubricant and fuel oil (MOLFO) and waste oil (WO) according to the similarity of the intrinsic chemical properties. Through the validation, it confirmed that four discriminant component, diesel, hydrocarbon fuel oil (HFO), mixture oil lubricant and fuel oil (MOLFO) and waste oil (WO) dominate the oil types with a total variance of 99.51% with ANOVA giving $F_{stat} > F_{critical}$ at 95% confidence level and a Chi Square goodness test of 74.87. Results obtained from this study reveals that by employing six-sigma approach in a data-driven problem such as in the case of oil spill classification, good decision making can be expedited.

1. Introduction

Accurate analysis and validation of oil classification from the spilled oil samples has become paramount in order to comply with global market competition, needs and market conditions. Appropriate methodology applied in the analysis and validation that enables oil classification based on oil spill fingerprinting can be successfully established in the field of environmental forensics. Moreover, only a few researchers have included prevalent techniques such as non-linear regression in oil spill fingerprinting. Many researchers continuously search for improvement (Jacobs et al., 2015) in various innovative statistical control and analysis methodologies such as quality engineering via six-sigma approach to procure promising results in a short time with significant reduction in operational cost. In this study, we focus on the application of six-sigma as an innovative statistical analysis approach in oil spill fingerprinting. Six-sigma is prevalent in adminis-

trative problems (Westphal et al., 1997), however, in oil spill problems statistical control and analysis approach or tools viz. identifying and quantifying, controlling sources of variation, reducing sources of variation and anticipating sources of variation (Ian et al., 2010) are prevalent. Six-sigma can be defined as the management of variation sources in relation to performance requirements (Teece, 2003; Ian et al., 2010). Six-sigma has been defined as the improvement comprising of both economic activity in the organization and administrative techniques. Through the methodologies of six-sigma, firms are able to achieve good development and minimize the action that needs to be taken to resolve problems or defects (Tekin, 2013). Through the six-sigma approach, many firms are able to maintain the same levels of production, delivery and management processes every time with substantial elimination of damages. Moreover, six-sigma methodologies have been successful in assisting problem-solving of HPC plant corrosion (Harjac et al., 2008). As stated by Jacobs et al., 2015 the adoption

of six-sigma improve the financial performance prior to adoption. The adoption of six-sigma application in administrative sectors is successfully achievable as a technology transfer with the availability of both physical proof benefits through customizes the six-sigma adoption to best fit organizational context and full adoption of the six-sigma knowledge as dependent (Williams, 2007).

Analyses and validation of the oil classification from gas chromatography/flame ionization detector (GC-FID) and gas chromatography/mass spectrometry (GC–MS) allow the study of physicochemical characteristics and ultimately enable the determination of the origin of oil spill samples. This study briefly presents the oil spill fingerprinting process and data interpretation process and its validation through the use of several multivariate techniques and six-sigma analyses. A work by Juahir et al., 2011a, 2011b have demonstrated that multivariate tools can be successfully utilized for meaningful data reduction and interpretation. Multivariate tools such as principal component analysis (PCA), cluster analysis (CA) and discriminant analysis (DA) are important as pattern recognition tools and can be used for oil classification based on oil spill variables from different pollution sources. By integrating multivariate techniques in a quality framework, this study aims to show that six-sigma approach could improve and enhance the classification of oil spills recovered from Peninsular Malaysia and East Malaysia (Sabah).

2. Materials and methods

2.1. Chemicals

Dichloromethane (DCM) and hexane are the two types of solvents used in oil spill fingerprinting analysis for oil type classification. Internal reference standards of PAHs, biomarker and n-alkane were purchased from Chiron and these are commonly used in oil fingerprinting. The standard include Terphenyl-d_{14}; $C_{30}17 \beta$ (H), 21β(H)-hopane and 5α-androstane. The surrogate standards for oil classification, Phenanthrene-d_{10}, Perylene-d_{12}, Acenapthene-d_{10}, Benz(a)anthracene-d_{12} and o-terphenyl were obtained from AccuStandard Inc.

2.2. Oil samples collection

Oil samples were obtained from Department of Environment (DOE), Malaysia covering the period of year 2013 until 2014. The samples were collected from thirty-two spilled oil from distinct location-selected water areas of Peninsular Malaysia and Sabah (East Malaysia) (Fig. 1). Table 1 provides the detailed sample description and the thirty-two distinct sampling locations. Upon arrival, the samples were registered and stored at 4 °C prior to analysis. All the organic solvents were of analytical grade A type or higher.

2.3. Laboratory method

The surrogates and all standards for *n*-alkanes and polyaromatic hydrocarbon (PAH) were purchased from AccuStandard Inc. The standards for internal and biomarkers were purchased from Chiron. The solvents used for this oil fingerprinting are dichloromethane (DCM) and hexane. Various internal reference standards selected to specifically identify PAH, Terphenhyl-d14 and *n*-alkanes in the complex mixture of hydrocarbon, are Terphenyl-d_{14}, $C_{30}17 \beta$ (H), 21β(H)-hopane and 5α-androstane. The surrogates used in the oil fingerprinting were made up of the mixture of four PAH compounds, Perylene-d_{12}, Acenapthene-d_{10}, Benz(a)anthracene-d_{12}, Phenanthrene-d_{10}, and o-terphenyl for n-alkanes.

2.3.1. Preparation of samples and column clean-up

The laboratory analysis was conducted for two types of oil samples viz. uncontaminated oil and oil-water. The results obtained from lab analysis were then analyzed statistically to ascertain the presence of the relevant oils. In this work, for the first sample, approximately 0.8 g of oil sample was prepared, weighed and dissolved in 10 ml of hexane to achieve an 80 mg/ml final concentration. For the second sample of oil-contaminated water, the sample is transferred into a pre-cleaned separating funnel. The bottles containing samples of oil-contaminated are serially cleaned (three times) with 10 ml dichloromethane (DCM) to complete transferring into the separating funnel. For oil type determination, 60 ml of DCM was repeatedly added (twice) into the separating funnel with subsequent vigorous agitation to further extract the oil from water. Subsequently, the extracts from the separating funnel were combined, dried and filtered under a pre-cleaned sodium sulphate layer. To these dried extracts were added 5.0 ml of hexane by rotary evaporation to achieve oil concentration of 10 ml of oil phase per 5.0 ml of solvent. Consequently, total solvent extractable material (TSEM) was measured to determine the oil concentration extracted of 16.0 mg and quantified prior to column clean-up analysis.

The oil extraction was spiked with surrogates (Mixture of 4 PAH compounds and o-terphenyl) in the clean-up glass column prior to analysis to enable extract quantification and clean glass column (30 cm × 10.5 mm I.D.) analysis by GC–MS. The clean-up process was repeatedly preceded with 3.0 ml of hexane into the column. A pre-cleaned glass column containing approximately 6.0 g pre-cleaned silica gel (100–200 mesh, Davisil grade 923) topped with 0.5 cm pre-cleaned sodium sulphate and conditioned with 20 ml hexane were utilized for GC–MS. Approximately 12.0 ml of hexane consisting of *n*-alkanes and biomarkers (addressed as F1) was added into the column to elute aliphatic compounds. For eluting aromatic compounds (addressed as F2), approximate 15 ml of 50% DCM in hexane was used. Both fractions (F1 and F2) are subsequently concentrated by bypassing the gentle stream of N_2 to achieve the volume of fraction < 0.5 ml. Subsequently, the F1 was spiked with 1.0 ppm of $C_{30}17 \beta$ (H), 21β(H)-hopane and 20 ppm of 5α-androstane. The F2 was spiked with 1 ppm of d_{14}-terphenyl. The total volume of fractions brings the final injection volume to 1.0 ml prior to analysis.

2.3.2. GC-FID and GC–MS analysis of oil spill fingerprints

The extended use of GC-FID and GC–MS in oil spill fingerprinting enable oil type classification of highly complex samples of spilled oil. According to Ramsey et al. (2014), steranes, sesquiterpanes and terpanes are the petroleum biomarker compounds and recalcitrant to the environment, but widely used in oil spill fingerprinting due to its unique characteristics to the oil's source. The unique characteristics of biomarkers can generate the oil-specific fingerprint and distinctive oil hydrocarbon compositional ratio for each petroleum compound. Besides, the biomarkers can be used to compare oil composition for each specific oil source present in the environment. In this study, the ratios of steranes and terpanes and the retention times were fixed. The GC–MS chromatogram determined the petrogenic biomarker, steranes (m/z 191, m/z 218) and terpanes (m/z 276, m/z 278, m/z 191) in the oil samples. Thus, the results obtained can be used in quantitative analysis and the statistical results compared using repeatability limits for future oil type classification interpretation of the samples. Wang et al. (2005) explained the correct methods for accomplishing separation and analyses process of diesel, HFO, MOLFO and WO through chromatographic methods, and Wang et al. (1994); Wang and Stout (2007) provides the correct procedures for analysis *n*-alkanes, biomarkers and PAHs. Perkin Elmer Clarus 680 equipped with flame ionization detector and PE AutoSystem GC with built-in Autosampler were used to analyze *n*-alkane distribution and TPHs. Agilent 7890A GC System equipped with mass-selective detector and CTC PAL ALS autosampler was used to perform the analyses of biomarkers viz. sesquiterpanes, terpanes and steranes and target PAH compounds (including five alkylated PAH homologous groups and other EPA priority PAHs). In addition, the capillary column of 30 m × 0.25 mm HP-5MS fused silica was used in oil fingerprints. The oven temperature was programmed at; a) *n*-alkanes fragmentation (GC-FID) retained for 2 min at 50 °C, and then pro-