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THOUGHTS ON MANUFACTURING CHANGES IN THE US PETROLEUM INDUSTRY: IMPLICATIONS FOR AGE-DATING, CALCULATING WEATHERING INDICES AND HYDROCARBON FINGERPRINTING

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ABSTRACT

Techniques for the hydrocarbon fingerprinting and age-dating of petroleum contamination in environmental matrices are undergoing major advancements in the environmental forensic community at the present time. Techniques that were reliable in the past to age-date gasoline may not be that reliable in the reality of today's modern refinery practices. Within the forensics community, age-dating of gasolines undergoes routine application using a variety of approaches. Not so for distillate fuels. Age-dating of distillate fuels is experiencing a major debate within the forensics community. Forces working to expand the use of hydrocarbon degradation models from soils to other matrices may have pushed the most widely-used age-dating approach too far, creating the current two-sided debate. Moreover, a newly-emerging problem with age-dating of distillate fuel contamination is outlined, examined, and discussed. It is recommended that the forensics community critically examine age-dating and environmental weathering calculation techniques to a degree that currently is missing.

Keywords: Hydrocarbon fingerprinting, petroleum refining, age-dating, gasoline, distillate

1. INTRODUCTION

Changes within the US petroleum refining business structure have induced corresponding changes in the way hydrocarbon fingerprinting investigations should be conducted. Consolidation within the refinery industry has reduced the number of refiners selling branded and unbranded gasolines. It is changes within the branded gasoline area that are most interesting to follow. Such changes as we have seen make it incumbent upon a forensics investigator to make certain of the original source of the gasoline before coming to conclusions regarding the type(s) of gasoline, performance-based parameter evaluations, assessment of potential release date(s) and source-relationship assessment.

Determination of the type of gasoline and the manufacturing processes employed proceed along several lines of investigation. Hydrocarbon fingerprinting laboratory analyses for characterizing alkyllead species, hydrocarbon distribution and defining various classes of gasoline components are usefully and routinely employed. Similarly, distillate fuels can be analyzed to determine major hydrocarbon components, likely initial formulation composition,

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data on the performance-based parameters, the number of contaminant source(s), and weathering-induced changes as well. In such cases, data are what data are. Not so for age-dating of petroleum products, however. Age-dating of petroleum product releases can be impacted simply by initial composition of the product. For the most part, age dating of petroleum products really is describing the composition of products within the degree of hydrocarbon weathering found in samples collected. Age dating assumptions currently being made by some within the forensics community need to be re-examined. It is clear that the forensics community is not of one mind regarding age-dating of petroleum product releases. This is especially true for distillate fuels. New developments in the commercial practice of age-dating of distillates threaten to take issues even further away from reliable science and deposit them squarely in the guesswork category.

What we truly are discussing when we talk about hydrocarbon fingerprinting and age-dating of petroleum products is examining the effects of environmental weathering on petroleum hydrocarbon distribution. There should be ways in which simple weathering indices for gasoline and distillate fuels could be easily calculated then that can be widely available to the community. Development of such indices will remove the qualitative descriptive terms we all have seen coming from forensic geochemical laboratories for years.

2. GASOLINE REFINING APPROACHES AND HYDROCARBON FINGERPRINTING

Not all gasolines are created equal. Indeed, that is the fundamental hypothesis that is tested when performing forensic hydrocarbon fingerprinting investigations. However, these days, some gasolines, it seems, are more equal than others. And, depending upon your viewpoint, it may or may not be deliberate that some gasolines are more equal than others. The former is especially true today as more and more refineries are coming under the same new management, through the process of acquisition by growing refinery based companies and/or by consolidation within the oil and gas industry. As for the latter, the fact that it was not deliberate may simply be a consequence of market forces much stronger than science alone.

Certainly we have seen unprecedented consolidation in the oil industry in the past decade, in some respects almost the start of an industry-wide reversal of the Standard Oil dissolution under the Sherman Antitrust Act of 1890. Thus, we now have ExxonMobil, ChevronTexaco, ConocoPhillips and BP, which has become combination of the acquiring company, British Petroleum, ARCO and Amoco. Royal Dutch/Shell has remained and Gulf has been acquired, broken apart and various assets have been incorporated into other companies. It is now ConocoPhillips. The "Seven Sisters" have changed form. There are, however, other players as well.

How gasoline refiners operate during this period of oil industry consolidation directly bears on the science of hydrocarbon fingerprinting. A combination of factors have made hydrocarbon fingerprinting investigations even more challenging. Because of industry requirements for performance standards, the general range of gasoline products remains set. We can differentiate types of gasolines through laboratory analyses. Assessment of the type of gasoline sometimes fully addresses issues of source identification, transport and product mixing. However, due to changes in the petroleum refining business, not always. At times, one or more refinery companies have manufactured and marketed not only their own gasolines, but also they have manufactured gasolines for their wholesale clients (the self same former "Seven Sisters") who have, in turn, marketed the products as their own branded gasolines as before. Therefore, there are times when regional gasoline supplies have been dominated by a single manufacturer, with the expected consequences for hydrocarbon fingerprinting.

Historically, gasolines were refined and branded gasolines marketed by a company using company-owned refineries strategically placed within its geographic market. Hence, within the market serviced under such an arrangement, be it local or be it supplied by some type of bulk transport system, the expectation could be advanced that a company's gasoline chemical composition (its hydrocarbon backbone, if you will) would be the same in that particular geographic market. And, further, that different refining companies servicing the same geographic market would not be marketing gasoline with the same chemical composition. Here, in this situation, the hydrocarbon backbone would be expected to remain consistent in the products being marketed, and laboratory-based hydrocarbon fingerprinting techniques were expected to be able to distinguish among the different possible origins. Today, some major refiners still operate using this first type of business structure. But not all. There are two other types of business operations at work in today's gasoline refinery business.

Over the past few years, as a consolidation within the refining industry proceeded, refineries have been sold to refiner-only companies, giving rise to a second type of refinery business structure. However, changeovers to the new company brand were not made instantly, and the acquired company branded gasolines were marketed by the new company for some period of time. Eventually, however, the changeovers were made and those branded gasolines faded from the marketplace and were replaced by branded gasolines from the newly formed company. Review of company-specific government filings confirms such occurrences in the late 1990s and early 2000s. The consequent changeover to different refineries supplying the same branded service station over time directly impacts the use of hydrocarbon fingerprinting for source determination, not for simple product identification.

A third type of refining business plan exists in the US today. In this type of plan, one refinery manufactures gasolines for multiple marketed brands. And, unlike the first or second type of operation, manufacture of multiple gasoline brands is part of the strategic arrangement within these companies. Hence, even though branded gasolines can be found at branded service stations, different gasolines with the same basic hydrocarbon backbone are being sold throughout the geographic service region. While the addition of company-specific gasoline additives offers hope for hydrocarbon fingerprinting investigations, the facts are that the same hydrocarbon backbone is used in all gasolines manufactured by this type of refinery. For example, a major east coast refinery recently reported the manufacture of gasolines for consumption under the Sunoco, Sun, Shell, Coastal, Mobil, Texaco, Amoco, and Gulf brands. Such an arrangement offers the greatest challenge to hydrocarbon fingerprinting investigations, especially when two or more potential sources may, in fact, come from the same refinery but are branded differently.

It almost goes without saying that understanding the supply of gasoline to a site is terrifically important, no more so than today, when working at a branded gasoline service stations selling branded gasoline is not an automatic guarantee that the hydrocarbon backbone of the branded gasoline has remained the same. A prudent forensic investigator will track the origins of the petroleum hydrocarbon product thought to be present at a site as far back as possible in time to assure that fingerprinting conclusions to be reached are based upon site-specific results and not refinery-induced differences. Such tracking of the refinery origin of gasoline or gasolines involved in release investigations should identify if multiple gasolines potentially will have the same gasoline hydrocarbon backbone.

3. AGE-DATING CONSIDERATIONS - NO CONSENSUS AND A NEW DANGER

In light of the changes in the petroleum refining industry today, and considering what may well be a lack of consistency in gasoline composition even among branded gasolines over time, it is not surprising that the subject of age-dating petroleum hydrocarbon product contamination should come up often. In thinking about such things, it seems as through there has been serious rush to judgement regarding the ability to age-date hydrocarbon contamination. In point of fact, there are several ways to age-date chemicals in the environment (Kaplan 2003). Age-dating different types of gasolines presents its own set of challenges to the forensic investigator: fortunately, there are tools which can be used (Kaplan et al. 1996, 1997; Schmidt et al. 2002; Hurst 2002) to assist in a gasoline age-dating investigation and the use of PS-6 gasoline to age-date certain gasolines has been effectively constrained (Wade 2003). Such tools routinely undergo close examination within the forensics community, but are widely accepted.

Such acceptance is not the case, however, when the subject turns to age-dating of distillate fuels. Age-dating distillate fuels almost always relies on a single technical work found in the peer-reviewed literature. This single paper is the Christensen and Larsen (C&L) paper (Christensen and Larsen 1993) that dealt with distillate fuel releases in the Netherlands and Denmark. The approach takes advantage of the time differences between degradation of normal alkanes commonly found in distillate fuels, and isoprenoid hydrocarbons (IP13 - IP20) also found in distillate fuels. The work was strictly empirical in nature, tracking changes in the n-C17/IP19 ratio over a known number of single distillate fuel releases of varying dates.

It borders on the trite to say that this particular paper has received its fair share of attention. The C&L paper is often cited as a work of wide ranging applicability. While a limited amount of closer review of this approach's applicability in the US has been published (Wade, 2001a; Hurst and Schmidt, 2005), a broad-based examination of the applicability of the C&L model in the United States of America is overdue. Examining the sheer volume of technical reports prepared, a single great truth comes out - there is almost no consideration of the very specific set of conditions established in Christensen and Larsen's paper in the vast majority of works using the C&L age-dating model.

There is a great lack of consensus regarding the applicability of the C&L age dating approach in the environmental forensic community today. To some, it seems as though the C&L approach has been hijacked and is being used widely and most inappropriately by a limited number within the forensic community. Those who are misusing the C&L approach ignore basic science in their rush to arrive at an outcome. Others have been cautious in their examination of the C&L approach (Murphy and Morrison 2001). The lack of consensus within this community can be traced, appropriately or inappropriately, to the ability to track a true scientific endeavor compared with simply offering a commercial service to an unwitting and easily deceived client base. The following needs to be said: the C&L approach may be applicable to sites here in the USA, but only after a rigorous scientific evaluation of all facets of hydrocarbon degradation within a specific study site. And it is the sad fact that in case after case, a rigorous scientific evaluation of hydrocarbon degradation is not present. Single samples should not be age-dated. Any uncertainty that is to be attached to a single value date result based upon a literature work, or guesswork, and not on site-specific findings is almost certainly wildly unscientific. Such a lack of scientific approach to the subject of age-dating in general and case after case in particular should be disturbing enough to scientists in the field, but there is an even more disturbing trend emerging from the misuse of the 1993 C&L paper.

The trend concerns the combined use of the C&L distillate fuel age-dating approach and aquarium-based crude oil hydrocarbon degradation studies in seawater to estimate the time for the degradation of isoprenoid hydrocarbons in the subsurface environment. Based upon degradation studies of floating crude oil in a seawater aquarium completed by Kennicutt in the late 1980s (Kennicutt 1988), today an extrapolation is being made to estimate the degradation time of (i.e., age-date) isoprenoid hydrocarbons in soils. In his experiments, Kennicutt showed that the n-C17/IP19 and n-C18/IP20 ratios were constant in Arabian Light Crude Oil (100 ml) floated in an all glass 150 liter aquarium of sea water for a period of 40 days, and then underwent changes between 40 and 120 days before falling to zero at 120 days into the study (see Kennicutt 1988, Figure 4). While the logic of the abstraction is not stated and Kennicutt is simply cited as though the paper is an authoritative source for the age-dating of isoprenoid hydrocarbons in the environment, there has to be more to this than is being stated presently.

Apparently, the line of logic has to go something like this: if 20 years were required for the n-C17/IP19 ratio to fall to zero, it should take one to three times as long for the isoprenoid hydrocarbons to fall to zero also according to Kennicutt's aquarium seawater studies. Therefore, it is said that isoprenoid hydrocarbon degradation in a soil matrix should take from 20 to 60 years. And, therefore, following this line of logic to its absurdum, certain distillate fuels with isoprenoid hydrocarbon degradation will have been released to the environment X number of years previous, for example. Now, if the subject weren't so serious, this approach almost would be laughable. But this subject is no laughing matter.

No consideration of possible effects for experimental conditions is mentioned in this leap to a "Burning Conclusion." The Kennicutt (1988) paper simply is cited as the authoritative source for age-dating isoprenoid hydrocarbon degradation. So, we are lead to believe that the conditions extant in soils (soil depth, temperature, eH/pH, moisture, micro-nutrients, redox potential, and other physical parameters unknown) must be identical to those achieved in a careful aquarium experiment with Arabian Light Crude Oil and seawater? Apparently the answer is yes, that is what is expected by the combination of the results of Christensen and Larsen (1993) with Kennicutt (1988). Again, as we have seen in the misuse of the C&L approach, scientific facts are ignored in favor of commercial results. And it is the unwitting and easily deceived client base that stands to loose the most in use of this latest wrinkle now being offered by commercial petroleum age-dating enterprises. Such work needs to be critically examined, not simply accepted. Currently, clients using such services are not examining such work effectively, to their ultimate peril.

4. WEATHERING OF PETROLEUM PRODUCTS - QUANTITATIVE NOT QUALITATIVE

What forensic geochemical tools dealing with hydrocarbon fingerprinting and age dating have in common is to take advantage of the study of some aspect of petroleum product composition or weathering reactions in the environment. Fine, let's take advantage of the known facts of the petroleum hydrocarbon weathering in the environment, but let's stick to just the facts of the situation. Let's not forget that the Scientific Method is the basic process which we all should use. And let's leave the supposition and the outright guesswork out of this process completely.

When working with compliance based chemical data where only BTEX data (benzene, toluene, ethylbenzene, and the three xylene isomers) are required and only BTEX data are produced, a useful weathering index has been proposed in the chemical literature taking advantage of the relative changes in benzene and toluene compared with ethylbenzene and the xylene isomers (Kaplan et al. 1997). Ratio analysis has been offered for this type of data as well (Yang 1995). In the absence of other information, working with compliance monitoring analytical data only, calculation of BTEX ratios can be useful or perhaps the only method open to the investigator. However, industry efforts to reduce the amount of benzene in blended gasolines may render such a ratio analysis somewhat less accurate over time. Further, a cautionary note has been sounded when dealing with the BTEX ratio in the technical literature (Alvarez et al 1998). If all that are available are BTEX data, use of ternary analysis techniques offers additional ways to examine such limited data (Wade 2001b).

Weathering of petroleum products can be documented by a comprehensive gas chromatographic analysis of contaminated samples. However, let's remember, soils are soils, water is water, and separate phase product is separate phase product, and the matrix in which the contamination is found makes a big difference in the fate of petroleum hydrocarbons released to the environment (Kaplan et al. 1997). For gasoline range products, chemical analysis of more than just the BTEX compounds is available using capillary column gas chromatography. Analysis for PIANO compounds (paraffin, isoparaffin, aromatic, naphthene, and olefin) provides data which lend themselves nicely to hydrocarbon fingerprinting inquiries. PIANO analyses typically provide data on 180-220 different gasoline range hydrocarbons. Data on the chemical composition of alkylate in blended gasolines can be used to determine the refinery used to manufacture the gasoline. The PIANO analysis approach adequately defines the hydrocarbon backbone of the blended gasolines.

Moreover, such GC-based data reasonably can be used to analyze weathering patterns in gasoline range products that have been released to the environment. Using the PIANO data, analysis of the changes in the relative proportions of typical classes of blended gasoline hydrocarbons, from the most volatile C4/C5 hydrocarbons to the C3-, C4-, C5-alkylbenzenes, to allow calculation of new weathering ratio analyses would be clearly better than verbal descriptions of weathering as "moderate" or "extensive."

A comparable analytical approach to PIANO analysis of gasoline range products is available also for distillate range products using comprehensive two-dimensional gas chromatography (Frysinger et al. 2003; Nelson et al. 2006). GCxGC has the ability to resolve thousands of individual petroleum-based hydrocarbons, separating branched alkanes and cycloalkanes, mono-aromatic, naphthalenes, and multi-ring aromatic hydrocarbons. While such an analytical approach facilitates a greater understanding of natural petroleum weathering processes, its use is not available routinely to the wider forensic community. However, all is not lost. There are techniques that can be applied to quantitatively measure the degree of weathering of distillate fuels using widely available GC techniques. There should be no reason to accept a characterization of "mildly weathered" or "severely weathered" from an analytical laboratory. It is possible routinely to measure the amounts of normal alkanes, isoprenoid hydrocarbons and major aromatic hydrocarbons in distillate products found in environmental matrices. From such data, weathering indices easily can be calculated.

5. CONCLUSIONS

Hydrocarbon fingerprinting and petroleum product age-dating forensic techniques are really all about understanding and describing the natural weathering changes petroleum products of a

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certain composition undergo after release to the environment. In today's refining marketplace, assumptions regarding source(s) of refined gasoline products should be re-examined in light of industry-wide changes in business practices. The source of a branded gasoline marketed by a major company and sold at a retail service station may change over time, all the while being sold as the same branded gasoline by the same branded service station. Implications for the application of hydrocarbon fingerprinting techniques at such a location are important as changes in hydrocarbon distribution may be encountered which have nothing to do with weathering and everything to do with changes in the original source (and manufacturing practices) of the refiner. Data show that for some brands nothing has changed and the same refineries manufacture the same branded gasolines. However, for other refiners, the situation has changed and a prudent investigator with evaluate the implications of such changes when applying various hydrocarbon fingerprinting approaches.

For distillate petroleum product age-dating, the forensic community is not in agreement about what approaches to accept. Clearly, application of the Christensen and Larsen approach has become muddled and has resulted in conclusions regarding dates of releases that can be simply wrong. Now, further extensions of the C&L approach by coupling with Kennicutt's limited isoprenoid hydrocarbon weathering data threatens to extend the confusion further and represents the very real probability of proffering wrong age-dating results to an uneducated and less sophisticated audience. Remember, the C&L approach was an empirical result only. The C&L approach is being taken wide afield from its beginnings by some in the forensic community. The unscientific extension and misapplication of the C&L relationship needs to stop. Single samples should not be age-dated. It appears that application of the C&L empirical relationship awaits confirmation from a more rigorous examination within the USA. Further, it should be possible to confirm or refute such an empirical relationship from strictly a theoretical argument and such work is overdue.

Finally, quantitative weathering indices need to be developed to move the forensic community away from verbal descriptive terms such as "mildly weathered" and so forth. With very little additional computational effort, qualitative weathering indices can be developed which will allow rapid comparisons among data points within a data set as well as among different data sets. Given the proper software programming changes within the commercial analytical community, reporting of useful weathering indices is possible and sorely needed by the forensic geochemical community.

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