



National Environmental Monitoring Conference 2016



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Hanby PetroAnalysis - Hanby Environmental

Hanby PetroAnalysis and Hanby Environmental Introduce:

Using Chemical Reaction Spectrophotometry ("CRS") to Fingerprint Hydrocarbons and Crude Oils to Create a Hydrocarbon Smart Grid to Stop Funding of Terrorist Organizations

National Environmental Monitoring Conference 2016, August 8-12, 2016, Hyatt Regency - Orange County, California

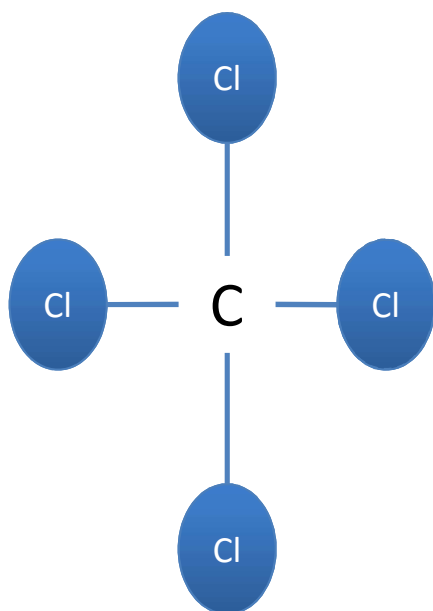
John David Hanby

- Academic: BS Chemistry, LSU, 1970 (GEAUX TIGERS!)
- 1970-1973: Pollution Research, Cambridge MA
- 1973-1974: Europe, Mideast travel
- 1974-1976: Tulane University Medical School, Graduate work, PhD, Physiology (unfinished).
- 1976-1985: Supervisor of Environmental Health Laboratory, NASA, LBJ Houston
- 1986: With wife Barbara incorporated Hanby Analytical Laboratories, Houston. Began R&D to develop colorimetric field test kits based on Friedel-Crafts (FC) reactions.
- 2012: Re-incorporated as Hanby International, LLC to develop spectrophotometer based on FC chemistry.

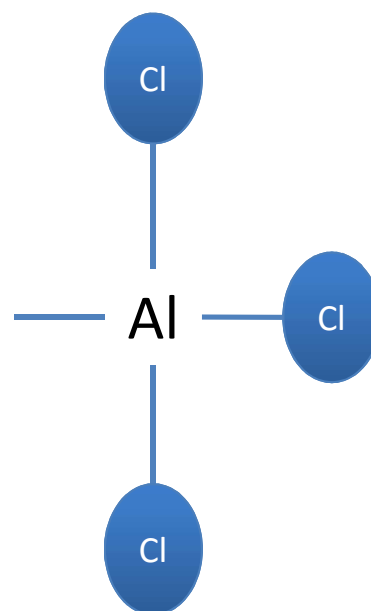
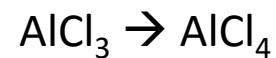
Charles D. Fator

- Academic: BBA Finance,
Sam Houston State University, 1999
- 1990-1994: Hanby Lab Work
- 1999-2012: Bank President and Lending Officer
- 2012-2016: Hanby International, LLC – Partnered with Grandfather John D. Hanby to complete the development of the Hanby **Hydrocarbon ID** utilizing the new Hanby Chemical Reaction Spectrophotometry (**CRS**TM) Technology.

Friedel-Crafts Reaction



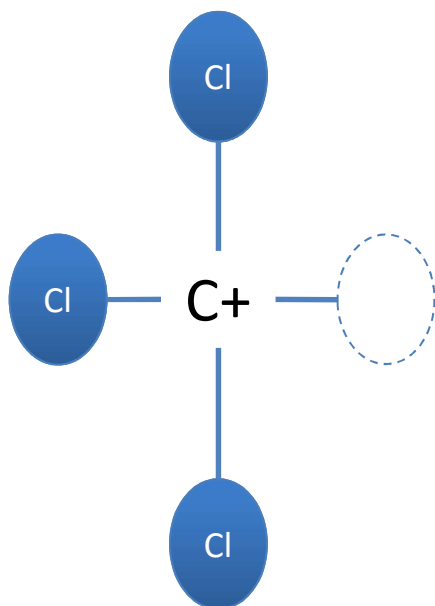
Carbocation Ion



AlCl_4^-

Friedel-Crafts Reaction

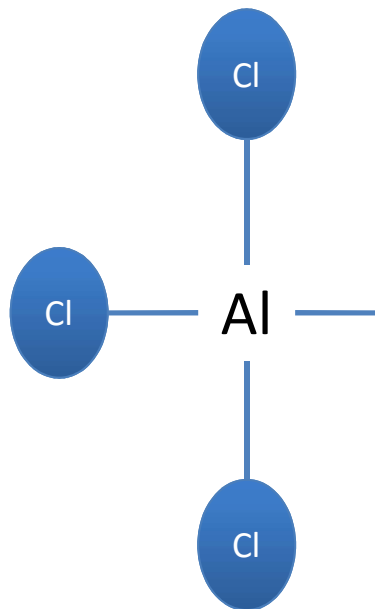
Carbonium Ion –
Positive Charge (+)



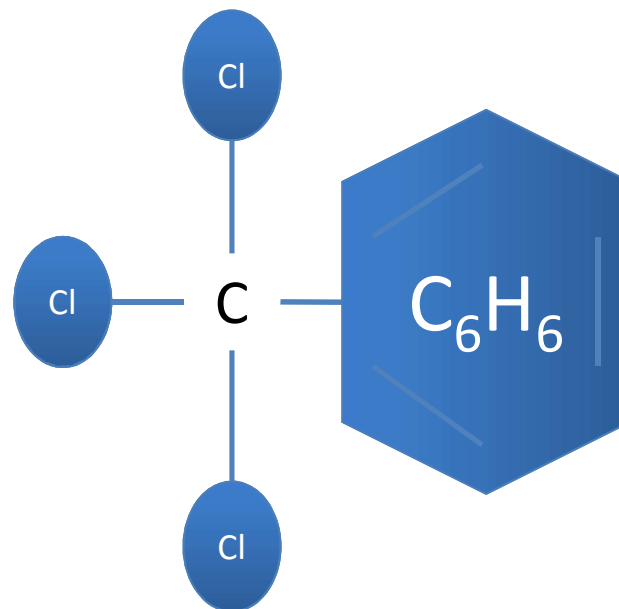
Benzene – Negative
Charge (-)



Friedel-Crafts Reaction



Carbonium Ion

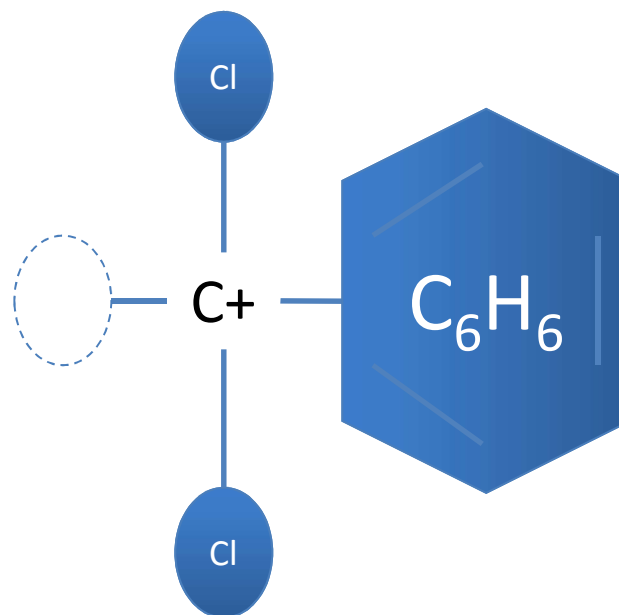


Friedel-Crafts Reaction

Benzene – Negative
Charge (-)

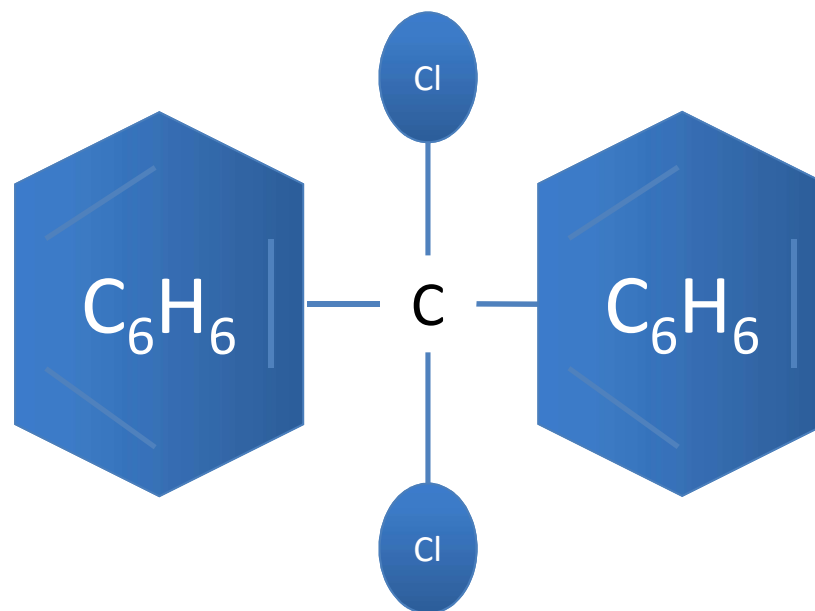


Carbonium Ion –
Positive Charge (+)



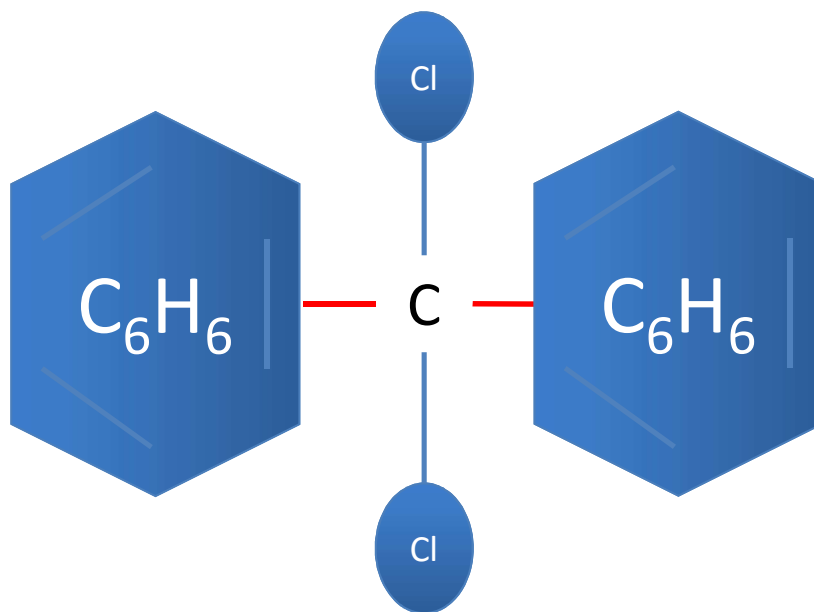
Friedel-Crafts Reaction

The Chromophore



Friedel-Crafts Reaction

The Chromophore



Hanby PetroAnalysis

A graphic showing a molecular structure with blue and white spheres connected by rods, set against a background of blue circles and lines.

Fingerprint Hydrocarbons With Our
Chemical Reaction Spectrophotometer HYDROCARBON ID



National Environmental Monitoring Conference 2016, August 8-12, 2016, Hyatt Regency - Orange County, California

FRONT & CENTER



Hanby Environmental

The Utilization of Strong Chemical Reactions to Enhance the Spectral Signature of Petroleum Substances Chemical Reaction Spectrophotometry

By: John D. Hanby

A new method for the spectral analysis of petroleum compounds in the environment is described that utilizes a combination of chemical (bond) energy and UV/vis light energy.

The correspondence of chemical bond energy levels (10^4 – 10^5 Cal/mol) with UV/visible frequencies (10^{14} – 10^{15} cps) results in a robust spectral resonance that provides a new spectrophotometric technique for the qualitative and quantitative analysis of complex organic substances such as crude oils. Particularly strong spectral signals in the UV/vis region are produced by certain chemical reactions. This strong spectral energy is related to the electronic population inversion achieved in the course of these exothermic chemical reactions, which is in line with the definition of a chemical laser as “a laser operating on a population inversion produced—directly or indirectly—in the course of an exothermic chemical reaction.”¹

The discovery of the analytical capability of this technique was made by the author shortly after he left a 10-year position as Environmental Health Lab Supervisor at NASA, JSC, Houston in 1985. One of the methods for the analysis of Space Shuttle drinking water was the visual determination of the disinfectant used, bromine, utilizing Nessler tubes. The significance of this new technique lies in the enhancement of the signal-to-noise ratio (SNR) resulting from the strong spectral signals achieved by specific chemical substances, particularly aromatics, that are present (3% to 30%) in crude oils and readily undergo the FC reactions. This is analogous to having relatively few “marker compounds” present in a complex substance that provide definitive identification of the substance. Crude oil, petroleum, is the most complex organic substance on the planet. This is understandable given that it is derived from the biota that have accumulated on the earth for about 100 million years and, through sedimentation and geological processes, has “cooked” at high temperature and pressure through this time. Accordingly, the precise, definitive analysis of the hundreds of components in petroleum, or “TPH,” is the most daunting task facing environmental chemists. Hanby patented a field test kit for water and soil samples that utilized the discovery in 1991.

Spectrometry is based on the fact that certain electronic configurations in molecules undergo harmonic resonances with specific frequencies in the electromagnetic spectrum. These frequencies range from extremely powerful energies such as X-rays to relatively low-energy frequencies such as microwave and infrared (heat). Ultraviolet and visible (UV/vis) frequencies have precisely the frequencies that resonate with the electronic structures of molecules. This spectral resonance is captured by the field device, called “Hydrocarbon ID,” and compared with a spectral library stored in the computer of the device. These bonds are composed of electron pairs that strongly resonate with UV/vis spectral energy especially when the newly formed products, called chromophores, are still in close contact (adsorbed) with the catalyst. The first publication concerning this new utilization of the relationship between spectral energy and chemical energy was first described by Hanby in the proceedings of an environmental conference held in Newport Beach, California in 1990.



¹Gross, R.W. 1976. *Handbook of Chemical Lasers*. New York. John Wiley and Sons..

Chemical Reaction Spectroscopy (CRS)

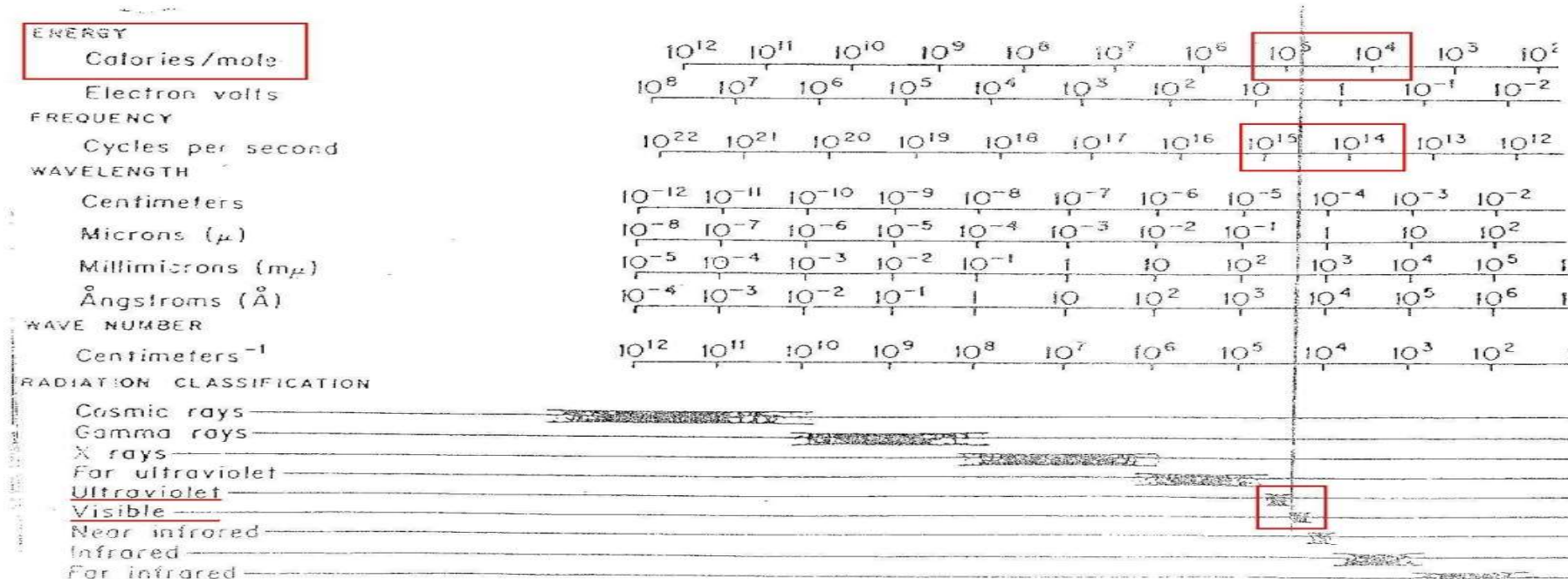
- The correspondence of **chemical bond energy levels** (10^4 - 10^5 Cal/mol) with **UV/visible frequencies** (10^{14} - 10^{15}) results in a robust spectral resonance that provides a new spectrophotometric technique for the qualitative and quantitative analysis of complex organic substances such as crude oils. Friedel-Crafts (FC) electrophilic alkylations exhibit particularly strong spectral signals in this region especially as the chromophores produced are briefly adsorbed to the strong Lewis acid catalyst, $AlCl_3$. This strong spectral energy is related to the electronic population inversion achieved in the course of these exothermic chemical reactions, which is in line with the definition of a chemical laser as, **“a laser operating on a population inversion produced-directly or indirectly- in the course of an exothermic chemical reaction”**. i

Chemical Reaction Spectroscopy (CRS)

- The significance of this new technique lies in the **enhancement of the signal-to-noise ratio (SNR)** resulting from the **strong spectral signals** achieved by specific chemical substances, particularly **aromatics**, that are present **(3-30%) in crude oils** and readily undergo the FC reactions. This is **analogous** to having a **relatively few “marker compounds”** present in a **complex substance** that **provide definitive identification** of the substance. It can be thought of as **converse to the mass spectrometer analytical approach** in which the molecular components of a complex analyte are **further broken into ionized fragments**, which are then **sorted according** to their **mass/charge ratio**.

Chemical Reaction Spectroscopy (CRS)

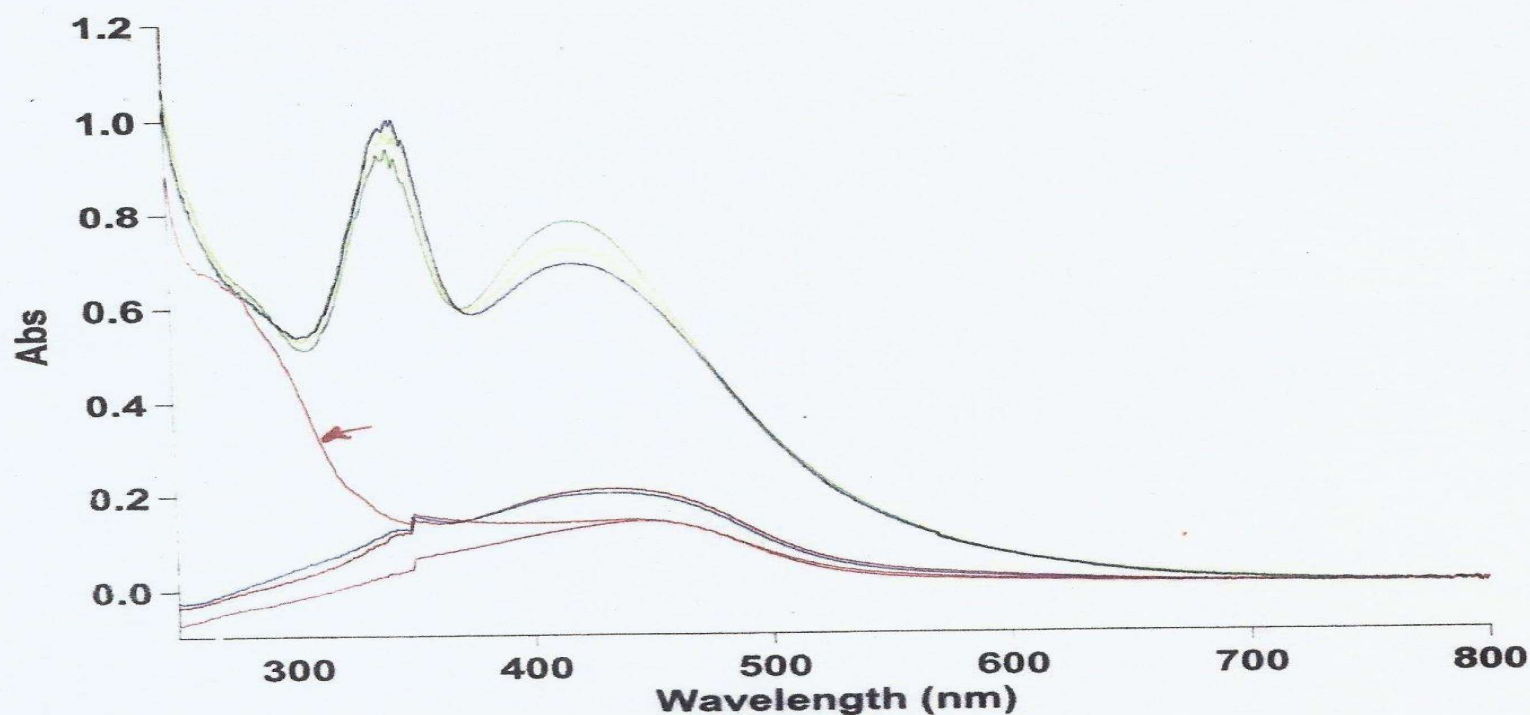
- Certainly the **most widely employed spectro-analytical technique employed in the analysis of formation fluids (crude oils) in the past few decades** has utilized **infrared (IR) and near infrared (NIR) frequencies** of the spectrum. **IR energies are 2-4 orders of magnitude less than UV/visible energies** and consequently do not have the penetrating and ionizing power to cause the chemical changes seen with the latter. The **lower frequencies of IR (heat) cause “bending”, “wagging”, “stretching”, etc.** that describe the **movement of parts (moieties) of molecules** in relation to each other. As with **mass spectrometry, comprehensive and detailed interpretation** of these **spectrograms is far easier** to perform when analyzing **less complex substances than crude oils**. **Another greatly complicating factor** in the use of **IR frequencies**, particularly in the analysis of crude oil, is the **presence of large amounts of water** in the sample. **H₂O has very strong absorbance in the infrared and therefore masks other IR absorbing compounds** that may be in the sample.
- i Gross, R.W. (1976) Handbook of Chemical Lasers, New York: John Wiley and Sons.



The Electromagnetic Energy Spectrum

This table represents the correlation of various units of energy and the names ascribed to the different regions of radiation. Of particular interest in regard to Chemical Reaction Spectrophotometry (CRS) is the correspondence of the relatively narrow regions designated "ultraviolet" and "visible" with the "Calories/mole" units (indicated by the vertical line).

Calories/mole designates the energy content of the electronic bonds that are formed in chemical compounds. As is seen by the vertical line, the calories/mole range corresponding to UV and visible light is 10⁵. The chromophores that are produced in CRS are compounds that have chemical bonds that are in this range. The robust spectral signals evident in CRS are inferred to be the result of the "photon/electron" resonance provided by this "chemical reaction/spectral" phenomenon.



Seven spectrograms of two crude oils (Wolfcamp and Tansill Yates) are shown here. Six of the seven represent the unique absorption extending from ~320 nm to ~500 nm produced by Chemical Reaction Spectrophotometry (CRS). The seventh curve (indicated by the arrow) is typical of the rather featureless absorption spectrogram that is produced in this region by essentially all crude oils using regular UV/vis spectrophotometry. Friedel-Crafts reactions of the CRS method used on the crudes cause the formation of robust UV and visible Chromophores. The top three curves are three repetitions of scans of the Wolfcamp, and the bottom three are scans of the Tansill Yates. Instrument: Cary 5000

LEGALOIL.COM INFORMATION PAPER NO. 2
FINGERPRINTING OIL
 January 2004

Introduction

"Fingerprinting" oil is a process that refers to analytical chemistry techniques by which crude oil is defined into its components in such a way as to permit the identification of a particular sample of crude oil by the uniqueness of its composition.

Originally, star diagrams graphically depicting the relative quantities of specific aromatic compounds were used as oil fingerprints. Within one compartment of an oil field, star diagrams were usually identical since the oil composition is completely homogenized.

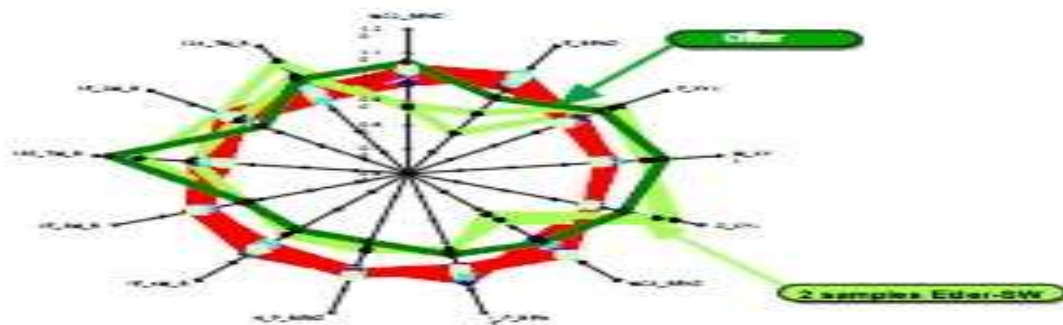


Figure 1-Star fingerprints of oil in Eider, Eider-SW and Otter fields. (source: Ganz, H.H., Hempton, M., Knowles, W., Van der Veen, F., and Kreulen, R., Integrated Reservoir Geochemistry: Finding Oil by Reconstructing Migration Pathways and Paleo Oil-Water-Contacts., *Society of Petroleum Engineers, Paper SPE 56896.*)

Purpose

The process of "fingerprinting" oil was developed to assist oil companies identify the source reservoirs from which oil is taken. When a new well intersects oil, for example, it is useful to know whether this is a new source of oil or the extension of a previously discovered source. In this manner the extent of a reservoir can be mapped and the size of the estimated.

The process came into further use in the economic exploitation of reservoirs by facilitating the commingling of oil from more than one reservoir through a common well. In such instances, reservoirs lie on top of each other and hence one well can pass through multiple reservoirs. Prior to the development of oil fingerprinting technology commingling of oil through a common well was not

feasible, thus entailing a new well for each reservoir. Fingerprinting technology allows the oil from multiple wells to be commingled and the respective contributions identified by source and proportion.

The economic savings available through wells designed for commingling could be as much as US\$1 million US\$ per well less expensive than conventional wells.¹ Fingerprinting Technology also provides information on the history of a particular crude oil accumulation and its original source. This information can be used to inform exploration came from and this information can increase the chances of exploration success.

In defining the size of a reservoir Fingerprinting Technology can help determine if the reservoir penetrated by a particular well is the same reservoir as has been penetrated by other well. Accumulated knowledge from the application of Fingerprinting Technology in region will assist in determining the size of the extent and volume of the field. Such information is also useful in planning the development of the field and specifically the number and location of wells required to drain the field.

In respect to oil theft, at its most basic level fingerprinting can be used to quickly distinguish between natural crude oil, kerosene and artificial products. A more detailed analysis can determine the source reservoir and therein test the bona fides of the person in possession.

Analysis

No common analysis basis or criteria for fingerprinting oil has yet been established among analysts. Therefore, analysis by different companies may (and probably will) produce a different fingerprint (or profile). However, such analyses will be internally consistent. SPDC currently uses 10 components as the basis for its analyses. Other companies may not only use a different number of criteria but may also use different criteria.

Experience

Chevron has the longest experience in fingerprinting oil. It has a laboratory in Lagos that conducts analysis. Shell routinely conducts analysis in Nigeria and the Netherlands. It is understood (but yet to be confirmed) that all major oil companies have developed fingerprinting technology.

Extent of Application

The extent of application and accuracy of fingerprinting technology is related to the size of the database used for comparison with the target sample. Individual companies are each building their own databases.

SPDC² currently has an 800 samples database from reservoirs plus samples from 40 trunk lines in Nigeria. This is likely the most extensive database yet developed by any company.

¹ Shell Bulletin Number 4

² SPDC – Shell Petroleum Development Company of Nigeria Limited

Companies could exchange oil samples to build up a national database. They would then test the samples to develop fingerprints based on their own proprietary analytical techniques. This would protect the analytical technology of each company.

A national "library" of reference samples could also be established. This would be cumbersome and have limited usage, as the national reference samples would have to be analysed using the technical process of the enquiring body analysing the target sample.

The most practical step would be for general agreement on the analytical process used to identify the oil source and the widespread adoption of that process. Of course there is the issue of proprietary rights and the competitive advantage of each company that has developed their own analytical processes thus far.

With the widespread use of an agreed analytical process, an international database of oil fingerprints could be developed. This would provide a quick and readily accessible register of known oil sources against which samples of suspect crude oil could be compared.

Limitations

Currently there is no commonality in the type and number of components used by various oil companies to identify crude oil.

Oil Spills: Oil that is spilt degrades and source identification is not accurate unless a sample is taken early in the spill.

Blending: There is a question as to whether the blending or mixing of crude oil that occurs in tankers when transporting crude oil will disguise the source of the individual crude oils. This is not dissimilar to the commingling that occurs when oil is transported through trunk lines or more than one well is tapped by a well (to be confirmed).

Conclusion

Fingerprinting technology has been developed by most of the large oil companies and is routinely being used to identify the source of crude oil to assist in tracing sources of oil spills, defining reservoir extents and volumes, commingling to facilitate extraction and transport of crude oil. It is also currently being used at the request of police in Nigeria to identify the cargoes of suspected oil thieves. The use of oil fingerprinting technology can be extended (and standardised) as an essential tool in identifying the source of suspected stolen oil.

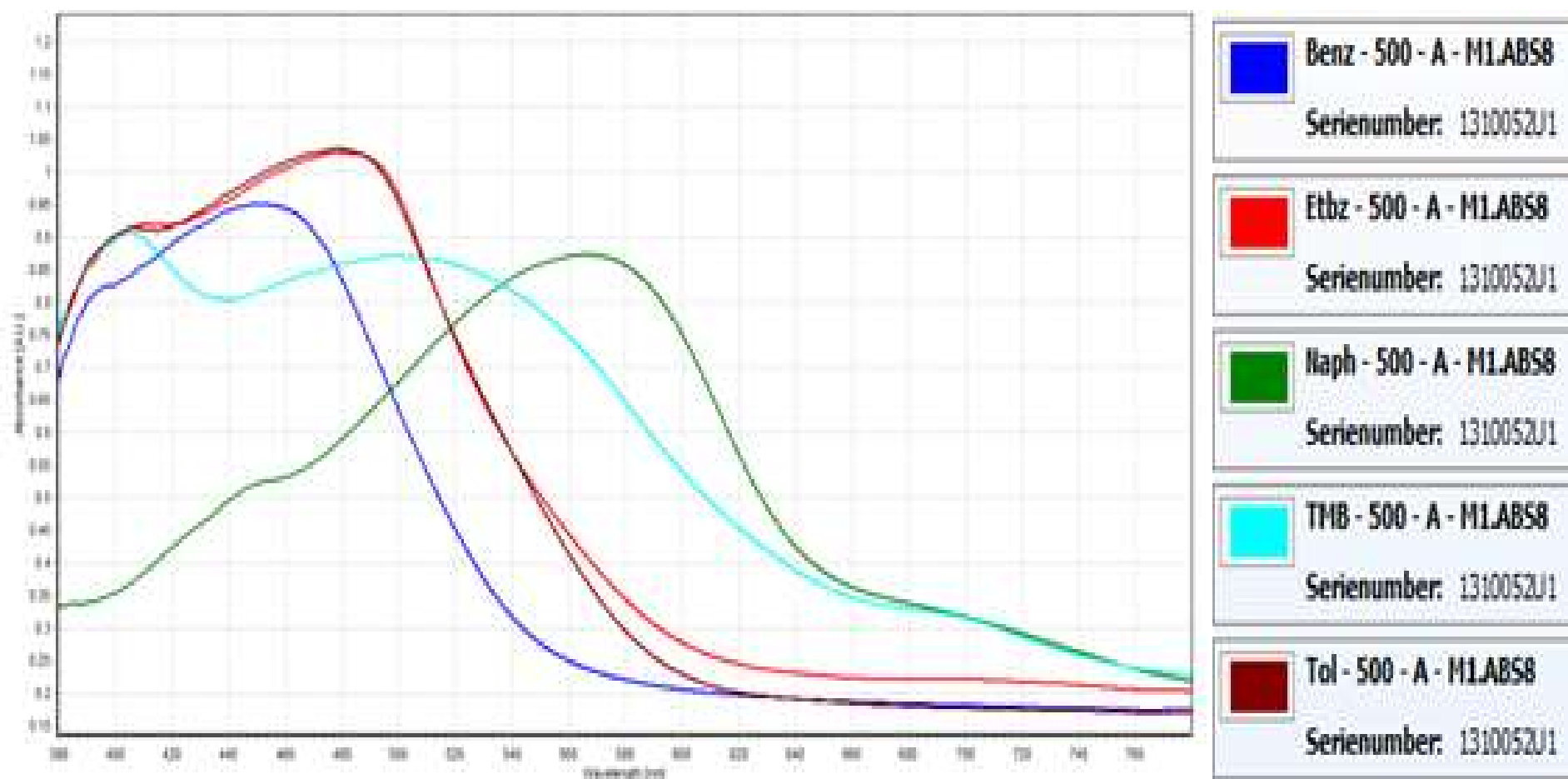
References

1. Ganz, H.H., Le Varlet, X., Van der Veen, F.M., Keen, M.A. and Van den Bos, G.A.: Reservoir Geochemistry of Oil Fields in The Netherlands," *Proc. 18th*

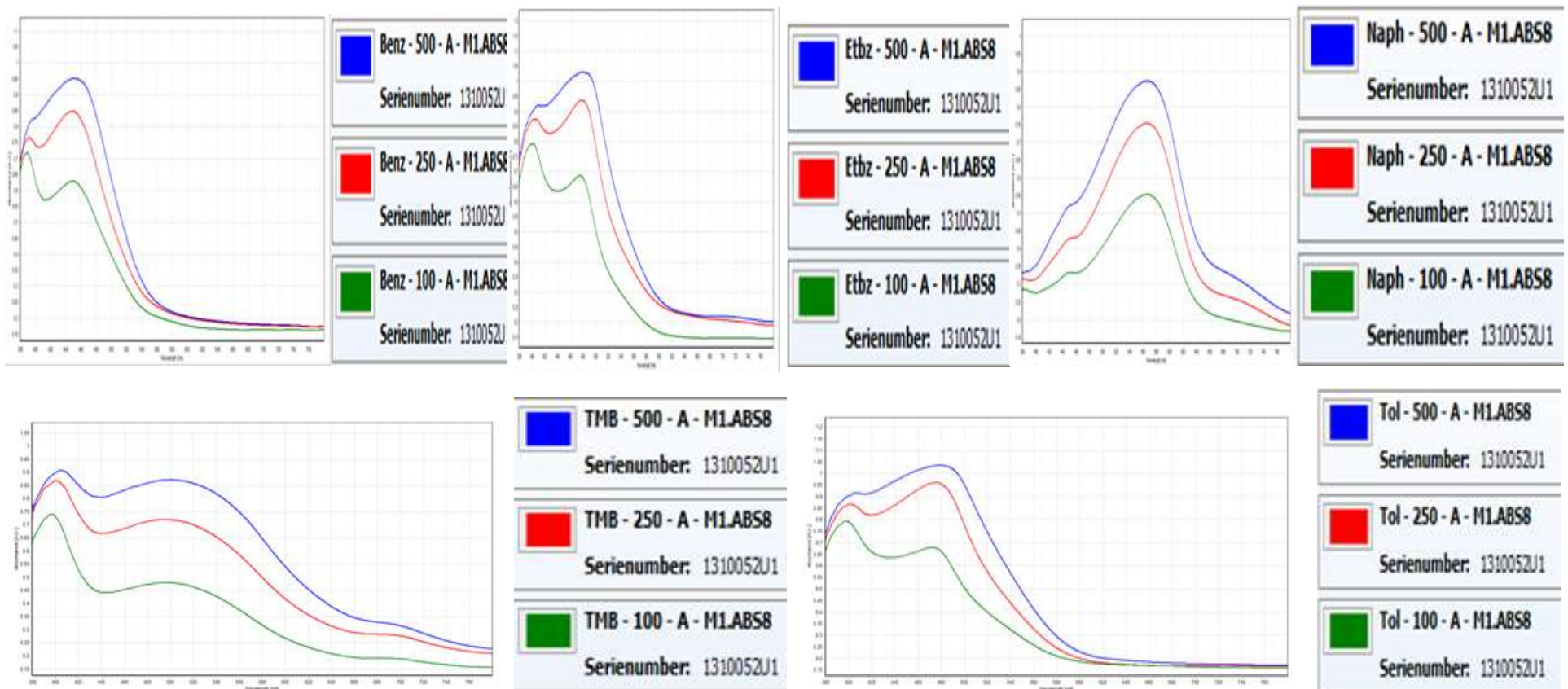
- International Meeting on Organic Geochemistry, Maastricht/The Netherlands (1997), 1, 109.*
2. Ganz, H.H., Hempton, M., Knowles, W., Van der Veen, F., and Kreulen, R., *Integrated Reservoir Geochemistry: Finding Oil by Reconstructing Migration Pathways and Paleo Oil-Water-Contacts, Society of Petroleum Engineers, Paper SPE 56896.*
3. Nederlof, P.J.R., Gijzen, M.A., and Doyle, M.A.: "Application of Reservoir Geochemistry to Field Appraisal," *Proc., Middle East Geoscience Conf., Bahrain (1994) 2, 709.*
4. Nederlof, P.J.R., Van der Veen, F.M. and Van den Bos, G.A.: "Application of Reservoir Geochemistry in Oman," *Proc., 17th International Meeting on Organic Geochemistry, Spain (1995), 329.*
5. Shell Bulletin Number 4.

For more information on oil theft, see the LegalOil.com website at <http://www.legaloil.com>.

Aromatics – Qualitative Fingerprint Identification – By Spectral Curve

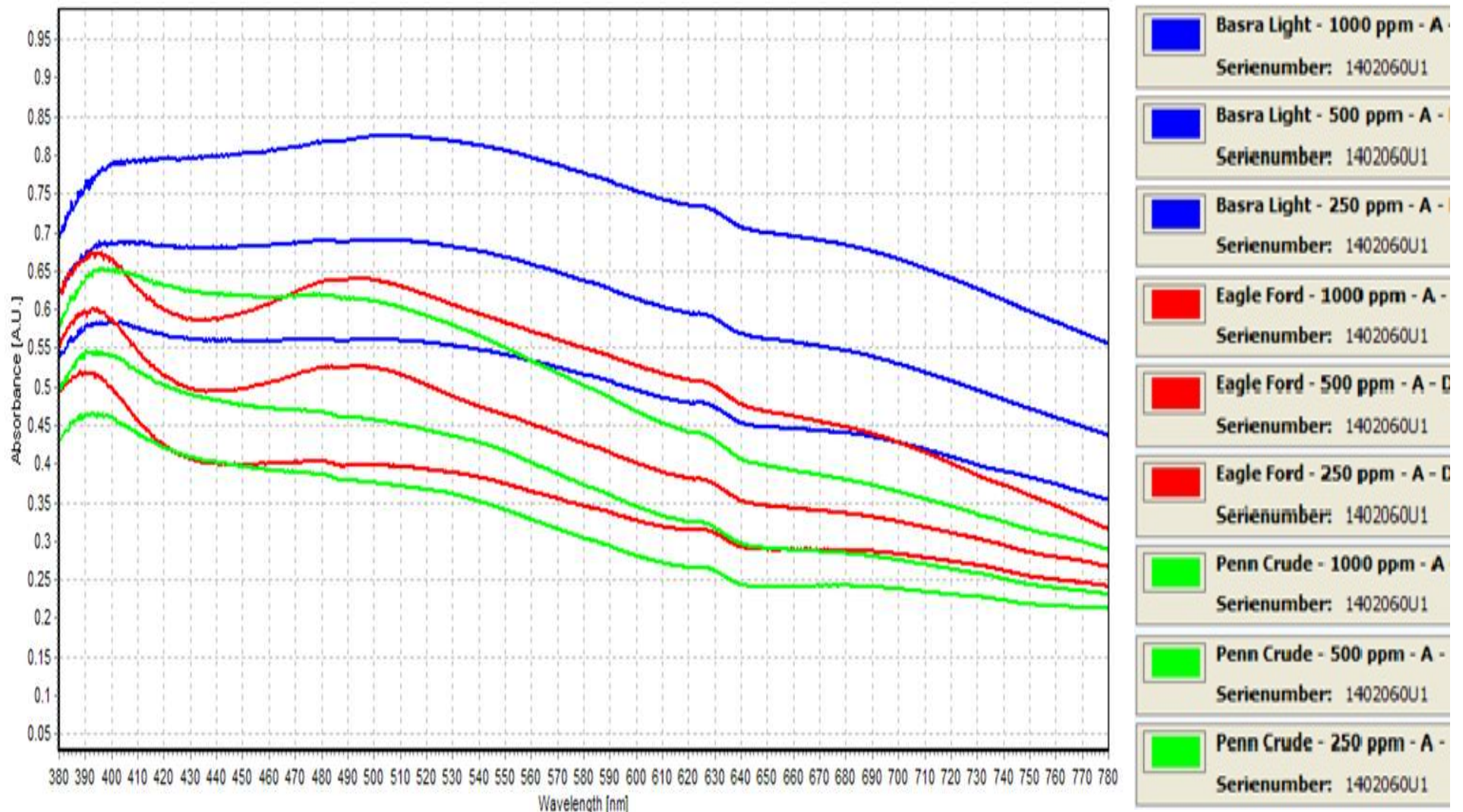


Aromatics – Quantitative Concentration – By Area Under Curve

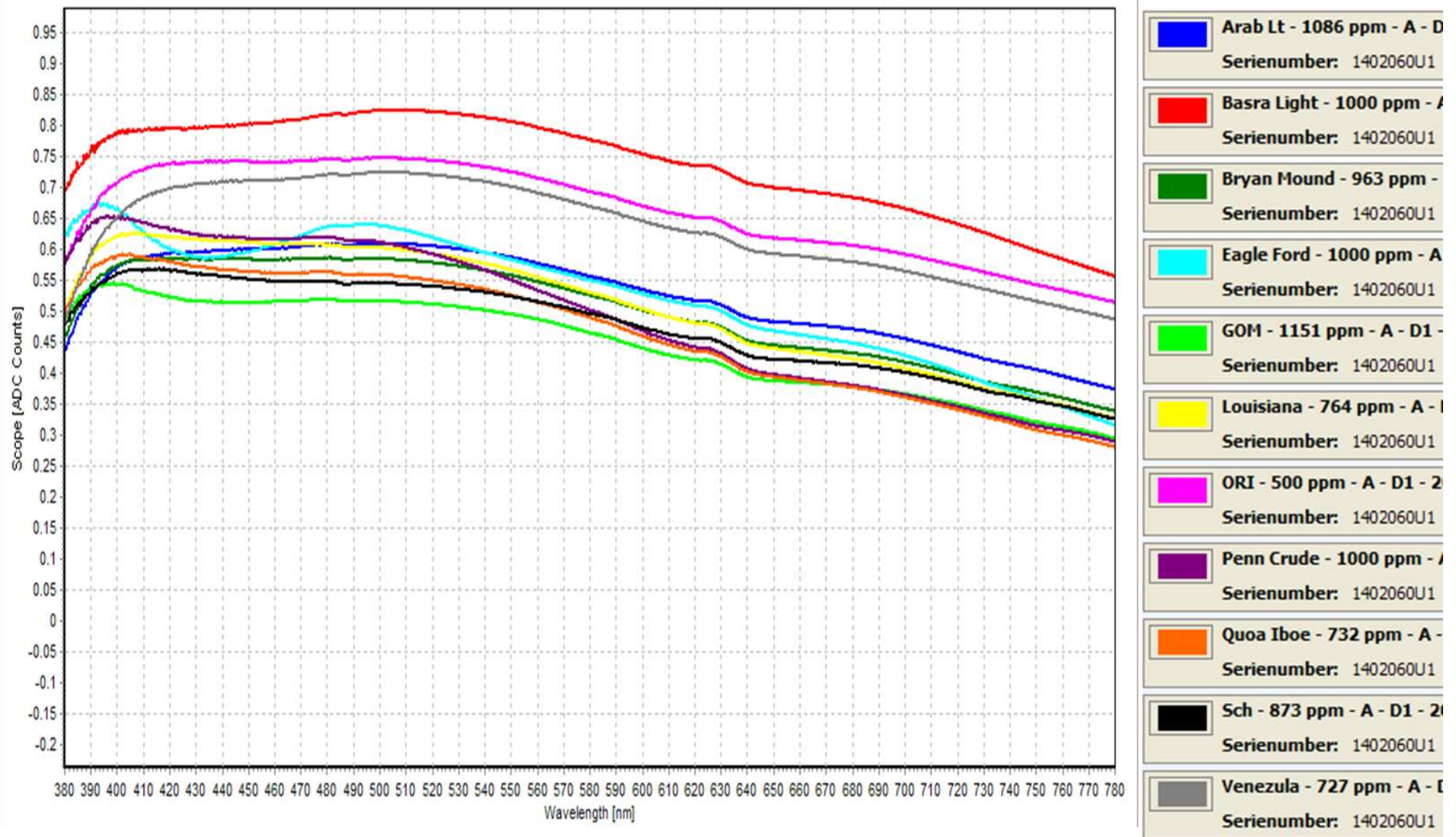


Three Crude Oils Comparison

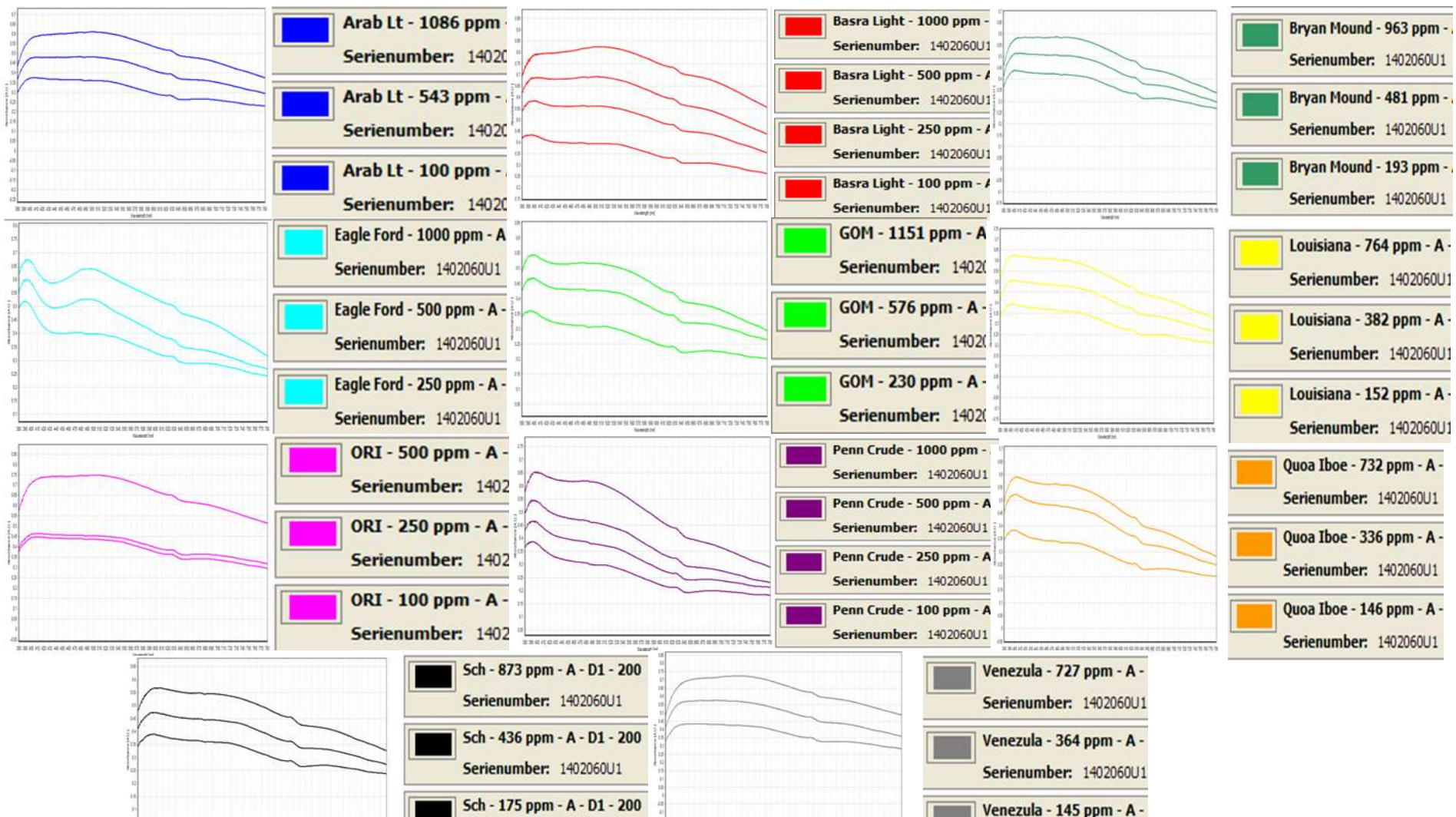
Three Concentration Levels



Eleven Crude Oils Comparison



Sample Eleven Crude at Multiple Concentration Levels



Identification of Spectrograms according to Amount (mg) of Analyte

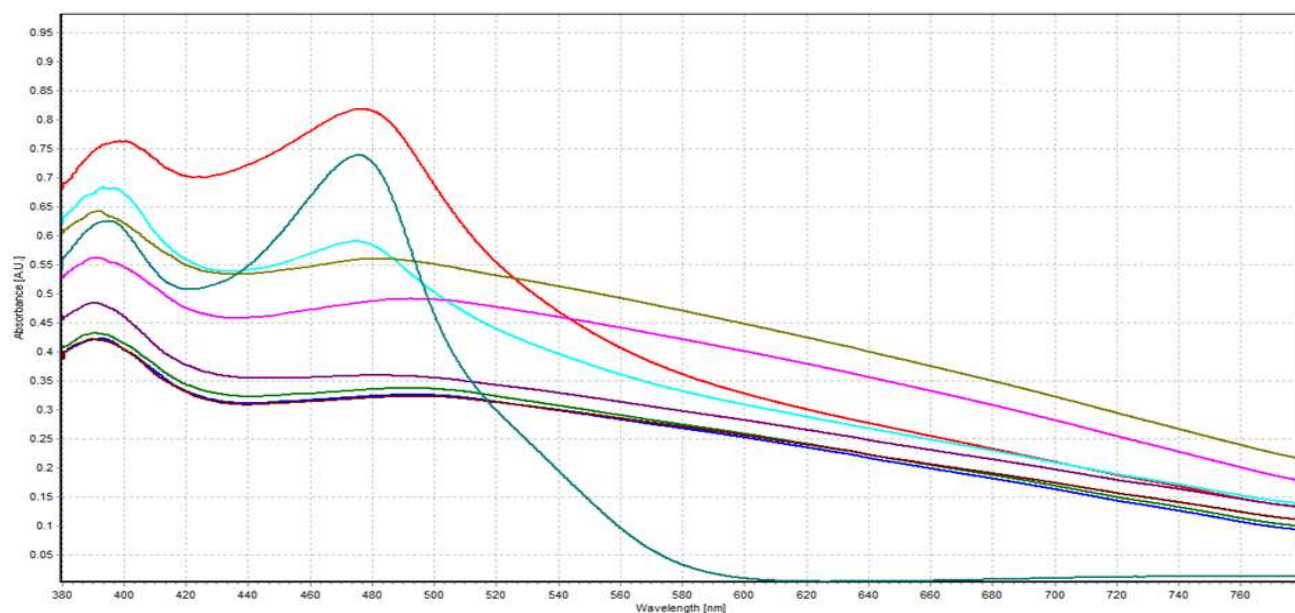
These are spectrograms taken, using the Hanby CRS method, of two analytes (Eagle Ford Oil and Toluene). The legend on the right side indicates the substances and spectrogram (from top to bottom, 1-9). The number of the spectrogram (1-9) is referenced at 500 nm (top to bottom) in Table 1. Table 2 indicates amounts of substances used in the preparation for the CRS procedure.

Table 1

<u>Spectrogram Number</u>	<u>Spectrogram Color</u>	<u>Analytes</u>
2	Red	EF & Tol
8	Camo Green	EF
4	Cyan Green	EF & Tol
7	Magenta	EF & Tol
9	Medium Green	Tol
6	Purple	EF & Tol

Table 2 (mg of Analyte)

<u>Eagle Ford</u>	<u>Toluene</u>	Note: Spectrograms 1, 3, & 5 are
0.25	0.147	repeats of samples of 0.25 mg of
0.5	0.010	Eagle Ford oil with no added
0.25	0.05	Toluene
0.50	0	
0	0.0735	
0.25	0.005	



█	EF - Green - 250 ppm - A - M1.ABS8 Serienumber: 1310052U1
█	EF - Green - 250 ppm - .2 ml of Serienumber: 1310052U1
█	EF - Green - 250 ppm - A - M1 - Serienumber: 1310052U1
█	EF - Green - 250 ppm - .2 ml of Tol Serienumber: 1310052U1
█	EF - Green - 250 ppm - A - M1 - Serienumber: 1310052U1
█	EF - Green - 250 ppm - .2 ml of Tol Serienumber: 1310052U1
█	EF - Green - 500 ppm - A - M1.ABS8 Serienumber: 1310052U1
█	EF - Green - 500 ppm - .4 ml of Tol Serienumber: 1310052U1
█	Tol - .1 ml of .0735 in 1 ml - A - Serienumber: 1310052U1

Some Identified Technology Applications

- **Development of A Hydrocarbon Smart Grid**
 - A Library or Database of Crude Oil Standards by **CRS** Fingerprinting by extraction from Core / Rock and Crude Oil Fluids provides the reference points to validate origin
 - Quick Analysis and Validation closes the opportunity for Undocumented Crude Oil Assets to enter the transportation process, thereby shutting down the Terrorist Organization Funding Vehicles

Some Identified Technology Applications

- **Source Validation and Asset Security**
 - Testing at each transfer logistics point, allows for a means of documenting the source origin
 - Assures no blending or mixing of undocumented and/or asset change during transportation process
 - Terrorist Organizations are funded by the selling of undocumented crude oil assets by blending or mixing with documented.

Some Identified Technology Applications

- **Laboratory Quality Data**
 - Real-time Analysis of Samples in Field
 - Knowing Progress without Delay
- **Fingerprinting – DNA Analysis**
 - Each Well of Same Crude Type Has Distinct Identification
 - Documentation of Contamination to Source

Some Identified Technology Applications

- **Responsible Party - Liability**
 - Environmental Spills
 - Remediation Responsibility
 - Monitoring and Progress
- **Water Table / Production Water**
 - Baseline for Liability Protection
 - Real-time Analysis of Cleaning

Some Identified Technology Applications

- **Preventing Refinery Shutdowns - \$10MM/day**
 - Level of Condensate in Crude on Way Into
 - Identifying Responsible Party
 - Document Refined Going Out
- **Preventing Blowouts at Well Sites**
 - Mud Weight – Condensate Level
 - Real-time Adjustments
 - Saves Time, Money \$\$\$ and **Lives (invaluable)**

What's Been Said of HANBY'S

Chemical Reaction Spectrophotometry

- “This is The Holy Grail for Exploration and Production and Asset Security Documentation”

What's Been Said of HANBY'S

Chemical Reaction Spectrophotometry

- “Disruptive Technology”
- “Lab in the Field”

What's Been Said of HANBY'S

Chemical Reaction Spectrophotometry

- “Game Changing”
- “A Paradigm Shift for
Environmental Protection”

This Concludes The Presentation

- We **“Thank You”** for Your Time and Interest.
- We Have An Exhibitor Table For You To Come By For Additional Details.
- info@HanbyPetroAnalysis.com and info@HanbyEnvironmental.com
www.HanbyPetroAnalysis.com and www.HanbyEnvironmental.com