Triton Analytics Corp.
16840 Barker Springs #302
Houston, TX 77084
ph 281-578-2289
fax 281-578-2295
http://www.TritonAnalytics.com
e-mail Dan.Villalanti@TritonAnalytics.com

Hydrocarbon Type Analysis by Gas Chromatography-Mass Spectrometry (NOISE™)

Frequently Asked Questions

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Questions:

1. Why do I need type analyses?

Knowing the chemical composition of a feed or product can provide crucial information when optimizing processes or deciding where to direct streams for maximum profitability. Type analysis answers questions like what are the concentrations of n-paraffins, isoparaffins, cycloparaffins, and aromatics and what are their carbon number distributions. Thus you can find out if the hydrotreater is reducing the concentration of polynuclear aromatics or if the catalytic reformer is isomerizing the n-paraffins and not making too many aromatics. Other applications of type analyses include identifying oil spills, evaluating unit performance for maintenance scheduling, and making the most of a new crude.

2. What kinds of hydrocarbon samples can you type?

The analysis quantitatively classifies complex low olefinic hydrocarbon mixtures by their chemical composition, or type of hydrocarbon that boil between 150F and 1000F. This includes paraffins, cycloparaffins, and aromatics from C5 to C41. It is designed for the analysis of crude oil, isolated crude oil fractions in the boiling ranges from SR Light Naphtha through heavy gas oils, and refinery process streams.

3. What is the precision and accuracy?

Multiple analyses of the same sample show a relative standard error of less than 5% for concentrations greater than 10% volume. Absolute accuracy is about 10% based upon comparison with NMR data (*Anal. Chem.* 64, 2227, 1992).

4. What reports will I get and what will they tell me?

Results are reported in a series of tables and graphs in units of liquid volume percentage or weight percentage. The basic report is a table giving the fractional percentage of total paraffins, cycloparaffins, mono-, di-, tri-, and tetra-aromatics, together with the average carbon number of the normal paraffins, estimates of isoparaffins, concentrations of benzothiophenes (Z-6) and dibenzothiophenes (Z-12), and an estimate of the empirical formula for the sample. The concentrations of the normal paraffins are determined from C5 through C40 and presented graphically.

A second table gives the carbon number distribution from C5 to C40+ for each Z number. This table is also presented graphically as an area chart to help you visualize the distributions. The distributions are usually normalized to percentage of total sample, but can be normalized to 100 percent within a fraction.

5. Can you provide custom reports?

Yes, you can get different normalizations and print out formats and data on diskette or by e-mail as Excel or Lotus® files. Tell us your requirements.

6. How long does it take to get reports?

Standard reports for single samples normally have a two day turn around.

7. How much sample do you need and where do I send it?

One milliliter in an autosampler vial is plenty. Send it to Triton, attention NOISE. Please attach information about to whom to report results.

8. What is a hydrocarbon type?

Petroleum samples are generally complex, containing hundreds or thousands of compounds. Individualy, however, the compounds have relatively simple structures allowing one to group them into homologous series or types. The "Z number" classification system is a convenient method of grouping hydrocarbons that has been in use for more than 50 years. It serves to classify hydrocarbon types by their chemical functionality with the only variable being the number of carbon atoms making up the molecule.

In the formula C_nH_{2n+Z}, n refers to the number of carbon atoms and Z is called the hydrogen deficiency of the organic molecule. This Z number for hydrocarbons can be either positive or negative. The convention defines the chemical composition of the molecule. Some examples illustrate this classification scheme.

A paraffin compound such as methane, is defined as $C_1H_{2\times1+2}$ or CH_4, (mw 16). Methane is the smallest of the paraffin series of hydrocarbons, all having Z=+2. Ethane, C_2H_6, (mw 30) the next heavier compound in the paraffin series, differs from methane simply by a CH_2 (methylene,

14 amu) group. This series continues with sequential addition of methylene units. Benzene C_6H_6 (mw 78) becomes $C_6H_{2\times6-6}$. In this example, n equals 6 and Z equals -6. The family of alkyl benzenes all have the same Z number and differ only in the number of carbons, n. Table 1 shows more examples of hydrocarbon types by Z number. Note that higher Z numbers (i.e. larger negative) describe more than one type of hydrocarbon. Fortunately, the combination of gas chromatography and mass spectrometry often allows one to distinguish them.

Z number	Hydrocarbon examples
+2	paraffins (alkanes)
0	cycloparaffins (cyclanes)
-2	dicycloparaffins
-4	tricycloparaffins
-6	monoaromatics (benzenes), tetracycloparaffins
-8	dicyclobenzenes (indans, tetralins)
-10	tricyclobenzenes
-12	diaromatics (naphthalenes), tetracyclobenzenes
-14	tricyclonaphthalenes, biphenyls
-16	tetracyclonaphthalenes
-18	triaromatics (phenanthrenes, anthracenes)
-20	tetracyclophenanthrenes
-22	pyrenes
-24	tetraaromatics

Table 1: Examples of hydrocarbon types by Z number

9. What is unique about this particular GC-MS procedure?

The use of gas chromatography-mass spectrometry (GC-MS) for hydrocarbon type analysis was advanced by the development of a fundamentally new method only recently available to organizations other than those in a large research organization, specifically, Shell Oil Company. Known within Shell as Townsend discharge chemical ionization (CI) by nitric oxide (TDCINO) , the technique was developed and proven as a viable analytical method in the early 1980's at the Shell Development Co. Westhollow Research Center (WRC) in Houston, Texas. A technical paper describing the technique appears in the journal of Analytical Chemistry (*Anal. Chem.* 64, 2227, 1992). Triton, who refers to the technique as nitric oxide ionization spectrometry evaluation (NOISE™), is the only commercial laboratory providing this analytical service.

The complexity of mixtures of hydrocarbons precludes the identification and quantification of individual hydrocarbons except for certain specific isolated compounds. This is because the number of isomers for each type of hydrocarbon increases geometrically with carbon number. Because of the simplified mass spectra that nitric oxide chemical ionization yields we can, however, classify the various hydrocarbon types using the equation C_nH_{2n+Z}.