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Determination of hydrocarbon types and benzene content in light petroleum distillates and products - Multidimensional gas chromatography method

轻质石油馏分和产品中烃族组成和苯含量的测定 多维气相色谱法

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0 Warning notice

A warning printed before Clause 1 states that the people who use the document should have practical experience of regular laboratory work; that its use may involve hazardous materials, equipment and operations and that it does not point out all the possible safety problems; and that the user is responsible for adopting suitable safety and health measures and for ensuring compliance with the conditions laid down by national regulations.

1 Scope

The document describes a test method that uses multidimensional gas chromatography to determine hydrocarbon types such as olefins and aromatics, and the benzene content, in light petroleum distillates and products.

It applies to the determination of olefins, aromatics and benzene in light petroleum

distillates and products with a final boiling point not higher than 215 °C, such as gasoline, gasoline blending components and solvent oils. The measurable concentration ranges are: olefins from 0.5 % to 70 % by volume, corresponding to 0.4 % to 64 % by mass; aromatics from 1 % to 80 % by volume, corresponding to 1.2 % to 92 % by mass; and benzene from 0.2 % to 10 % by volume, corresponding to 0.2 % to 12 % by mass. For samples whose content falls outside those ranges the precision has not been established.

It also applies to gasoline products obtained from unconventional crudes such as shale or oil sands, and to hydrocarbon fuels synthesised from non-petroleum mineral fuels such as Fischer-Tropsch oils, but for these the precision has likewise not been established.

Motor gasoline often contains ether or alcohol oxygenate components, and several oxygenates may be present together. Ethers in the sample elute together with the olefin components and alcohols elute together with the C7 plus aromatic components. For gasoline samples containing oxygenates, the type and content of the oxygenates are determined by another test method, such as NB/SH/T 0663, and the hydrocarbon type results are corrected as necessary following the procedure of Annex A.

The document does not apply to the determination of the content of individual components within the hydrocarbon types, benzene excepted.

3 Terms and definitions

3.1 Saturates, or saturated hydrocarbons: the collective name for the paraffin and naphthene components with carbon numbers from 4 to 12.

3.2 Olefins, or olefin hydrocarbons: chain olefins and cyclic olefins with carbon numbers from 4 to 12. A note excludes cyclic dienes with rings larger than six-membered.

3.3 C7 plus aromatics: the aromatic components in a light petroleum distillate or product other than benzene. A note includes single-ring substituted aromatics, aryl olefins, and cyclic dienes with rings larger than six-membered.

3.4 Olefins trap: the chromatographic column in the analysis system that selectively retains the olefin components out of a mixture of saturates and olefins. A note states that at a given temperature the column traps and releases the olefin components reversibly, which meets the need for repeated use; that at a set temperature it retains the olefin components selectively out of the mixture and lets the saturate components through; and that when the temperature is raised the retained olefin components are released completely.

4 Summary of the method

A measured amount of sample is injected directly into the gas chromatograph. After separation, the hydrocarbon type components enter a flame ionisation detector one after another and are detected, giving the chromatographic peak area of each hydrocarbon type.

The retention time of each hydrocarbon type is fixed by means of a reference sample, quantification is by the corrected area normalisation method, and the volume fraction or mass fraction of each hydrocarbon type in the test portion is calculated. The principle of the analysis is shown in Figure 1 and the gas chromatograph with its separation system in Figure 2.

For some light solvent oil products the olefin content need not be determined; in that case the sample does not have to pass through the olefins trap after injection.

5 Interfering substances

5.1 High boiling, high carbon number aliphatic hydrocarbons in the sample, of carbon number 13 and above, may not separate completely from benzene on the column of N,N-bis(alpha-cyanoethyl)formamide, which affects the detection of benzene and of the aromatic components; the final boiling point of the sample should therefore not exceed 215 °C.

5.2 Ethers in a gasoline sample, such as methyl tert-butyl ether, are retained in the olefins trap and elute together with the olefin components, so that the olefin area fraction obtained from the chromatogram includes the share of the ethers. Alcohols such as ethanol and methanol elute within the retention time range of the C7 plus aromatics, so that the C7 plus aromatic area fraction obtained includes the contribution of the alcohols. The content of the ethers or alcohols in the gasoline is determined by a related method such as NB/SH/T 0663 and the result is corrected according to Annex A.

5.3 Small amounts of sulfur and nitrogen compounds in the sample may be irreversibly adsorbed in the olefins trap, which may in the end lower the capacity of the trap and so shorten its service life. Experiments on several kinds of sample have shown no effect on the determination results.

5.4 No effect on the analysis results has been found from antioxidants, detergents, antistatic additives, lead antiknock additives or manganese antiknock additives in the sample.

5.5 A small amount of dissolved water in the sample does not interfere with the determination; free water, if present, can be removed with anhydrous sodium sulfate or by filtration through filter paper.

6 Apparatus

6.1 Gas chromatograph: the instrument includes at least an injector, a vaporising chamber, a column oven, a flame ionisation detector and a chromatography workstation. Stable control of the carrier gas and detector gas flow rates matters for accurate, reliable and repeatable results, and a system with electronic flow control should be used. The flame ionisation detector meets or betters the requirements of Table 1. Further hardware is

needed to carry out the method, including the chromatographic column, the olefins trap, the balancing column, the switching valves and the corresponding temperature control devices.

6.2 Olefins trap: at a given temperature, when the aliphatic hydrocarbons separated by the polar column, that is the mixture of saturates and olefins, pass through it, the trap retains the olefin components completely and lets the saturate components through. The trapping temperature is usually 120 °C to 135 °C. When the temperature is raised the trap releases all the retained olefin components completely; the release temperature is usually 190 °C to 210 °C. The actual temperature setting is fixed according to the particular trap. The performance of the trap can be verified with the system verification sample or the quality control sample. If olefins are found to escape from the trap, the operating conditions should be adjusted, and the trap replaced if that is not enough.

6.3 Balancing column: it neither retains nor adsorbs the hydrocarbon type components and serves only to balance the pressure, so that the baseline stays steady when the valves are switched.

6.4 Switching valves: to operate as the document prescribes, the analysis system includes two two-position six-port valves. The valves may be switched manually or automatically; automatic switching should be used so that the switching time is accurate.

6.5 Temperature control of the system components: the polar separation column, the olefins trap and the switching valves each have an independent temperature control system, and every part in contact with the sample is held at a temperature that prevents the sample from condensing. Table 2 lists typical control temperature ranges for some components. Some components call for isothermal operation, others for a repeatable temperature programme. The temperatures listed in Table 2 are only a typical operating range and may be adjusted to suit the particular polar column or olefins trap; any means of temperature control that meets the requirements of the analysis system may be used.

6.6 Valve switching drive system: where the valves are driven pneumatically, the air pressure supplied to the pneumatic system meets the drive requirement, so that the valves switch quickly.

6.7 Carrier gas purification device: to protect the service life of the olefins trap, besides the molecular sieve and activated carbon purifiers usual in gas chromatography, which remove water and hydrocarbon impurities from the carrier gas, a dedicated deoxygenating purifier is fitted, so that the oxygen in the carrier gas stays below 1 microlitre per litre by volume.

6.8 Chromatographic column, the polar separation column: any column may be used that separates benzene completely from n-dodecane or 1-undecene among the aliphatic hydrocarbons and separates benzene completely from toluene, while leaving a suitable valve switching time. To ensure the separation, the ratio of the retention time of benzene to that of 1-undecene is required to be greater than 1.5 with a resolution greater than 2.0, and the ratio of the retention time of toluene to that of benzene greater than 1.25 with a