Information about the chemical structure of petroleum resins and asphaltenes is important for both clarifying the aspects of petroleum genesis and development and improvement of processing technologies as applied to the residual fractions of heavy oils, in which a total concentration of resin–asphaltene compounds (RAC) can exceed 35 wt %.

To get information about the structure of hydrocarbon and heteroorganic structural moieties in the molecules of resins and asphaltenes, their thermolysis for several hours in an inert gas atmosphere or in the presence of water at relatively low (300–370°C) temperatures is widely practiced [1–21]. Parallel and sequential experiments in a wider temperature range of thermolysis (160–650°C) [22–25] offer an opportunity to determine the composition of resin and asphaltene components, which occur as occluded impurities or structural units bound in RAC molecules by labile chemical bonds. The products of flash pyrolysis of the samples under study differ in the relative amount of the “unresolvable complex mixture” of unidentified compounds; the chemical group and molecular composition; and the relative amount of identified types of compounds, such as normal and isoprenoid alkanes, α-olefins, cyclohexanes, cheilanthanes and hopanes, hopenes, pregnanes and steranes, alkylbenzenes, naphthalenes, phenanthrenes and anthracenes, and benzol- and dibenzothiophenes.

One of the ways to reduce the probability of formation of secondary products during analytical pyrolysis of petroleum resins and asphaltenes is a combination of flash pyrolysis with analysis of volatile products of thermal degradation by gas chromatography/mass spectrometry (GC–MS) in the on-line mode. The capabilities of this method as applied to the analysis of structure of asphaltenes, and benzene- and ethanol—benzene resins of natural high-sulfur asphaltite from the Ivanovskoe deposit in Orenburg oblast were demonstrated in [26, 27]. It was shown that the volatile products of flash pyrolysis of these samples are dominated by unidentified components of the unresolvable complex mixture (UCM) manifested as the “hump” in the total ion current (TIC) chromatogram. It was established [26, 27] that for all the initial samples, the volatile products of flash pyrolysis at 650°C are characterized by the same set of identified compounds that includes normal and isoprenoid alkanes; α-olefins; cyclohexanes; steranes; pregnanes; cheilanthanes; hopanes; hopenes; pregnanes and steranes, alkylbenzenes, naphthalenes, phenanthrenes and anthracenes, and benzo- and dibenzothiophenes. This finding confirms the presence of most of the aforementioned compounds as structural units of RAC molecules of the natural asphaltite examined. Some differences in the relative amount of these types of
The objects of study were the asphaltene and resin fractions of heavy, high-resin, high-sulfur crude oil of the Usa field, which were isolated from the oil using the standard procedure [28]. The asphaltene fractions were obtained by their fractional precipitation from solutions containing chloroform and hexane in different ratios, and the resin fractions were isolated by elution from a silica gel-packed chromatographic column filled with solvents of varying polarity. The fractionation procedures are detailed in [29].

The mode of flash pyrolysis of resin and asphaltene fractions was selected on the basis of the results of their Rock-Eval pyrolysis analysis [30]. The pyrolysis and related operations were carried out with a Source Rock Analyzer™ (Humble Instruments & Services, Inc.) using the temperature rise program comprising isothermal (150°C) heating for 3 min followed by linear heating at a rate of 25°C/min to 650°C and holding at this temperature for 1 min.

The flash pyrolysis of all the samples was conducted at 650°C for 20 s. According to the Rock-Eval analysis data, this temperature corresponds to the completion of thermal degradation of the sample. The samples of resin or asphaltene fractions were placed into a quartz tube of 2 mm in diameter wrapped in a platinum wire coil. The pyrolysis cell (CDS 1500, Valved interface) was directly connected to the gas chromatograph injector, an arrangement that allowed for the on-line analysis of volatile products. The GC–MS analysis conditions are detailed in [26, 27]. Data acquisition and processing were performed in the SCAN mode using the software ChemStation. The relative amount of different types of compounds in the volatile products of flash pyrolysis was determined by measuring the total area of identified peaks of different types of compounds in their mass chromatograms.

**RESULTS AND DISCUSSION**

As follows from the data in Table 1, the chromatographic fractions of resins (R1–R2) differ in the molecular weight (MW), which increases with an increase in polarity of the fraction. The nitrogen, sulfur, and oxygen contents change nonmonotonically, exhibiting a few extrema and reaching the maximal values in the most polar fractions. An increase in the polarity of the fraction is accompanied by an increase in its aromaticity. This is evidenced by a reduction in the (H/C)at ratio from 1.49 to 1.26.

In the A1–A4 series, the molecular weight of the asphaltene fractions and the oxygen content decrease and the nitrogen content increases (Table 1). A difference in the sulfur content is less than for the resin fractions. An increase in (H/C)at from 0.95 to 1.14 in the A1–A4 series suggest a reduction in the aromaticity of the fractions.

It is believed [30] that at temperatures up to 300°C, organic compounds that are present in the sample in the free, adsorbed or labile-bonded state, are released (peak S1). Above 300°C, the cracking of the organic matter of the sample takes place, with the maximal rate of its degradation being reached at a temperature corresponding to peak S2. The Rock-Eval pyrograms of the test samples (Fig. 1) show that the maximum of peak S1 lies in the temperature range of 150–250°C. This means that the aforementioned organic compounds have a relatively low molecular weight.

From Table 2 it follows that the proportion of these low-molecular-weight organic compounds in the test resin and asphaltene samples is 2.3–15.3%. The main contribution to the yield of volatile pyrolysis products is made by the high-temperature step (see the values of the S1/(S1 + S2) parameter in Table 2). As the mole-