Physical Chemistry

Study of Polycyclic Aromatic Hydrocarbons of Norio Oil by GC-MS Method

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ABSTRACT: Polycyclic aromatic hydrocarbons from vacuum gas oil fraction of Norio oil (Georgia) with boiling point 340–590°C was studied by GC-MS method. As a result of using multistage separation method, over one thousand samples of crude oil were collected: 876 samples from petroleum ether eluates, 78 samples from benzene extracts, 90 crystal samples. Petroleum ether eluate #56 and the components obtained from its crystallization were studied. Gas-chromatographic (GC) separation of the samples concentrate was carried out of capillary columns (15 m and 30 m) by dimethyl-polysiloxane in programmed temperature conditions. For analysis of the obtained data an automated system of mass deconvolution and identification (AMDIS) was used. In the eluate under investigation the following structures were identified: indenes, tetralines, dinaphtilbenzenes, naphthalenes, fluorenes, phenantrenes, antracenes, mono- and polyalkyl derivatives of naphtofluorene and phenantrene, and terpeniles. In crystal samples of the eluate the banzantracene, chrizene, their methyl-, dimethyl and trymethyl-analoges, phenentrene derivatives, antracenes and pyrenes were identified. The results of the present work show that the complex analysis of gas chromatography retention indices and mass-spectral data was successfully used for the structure elucidation of the components of this particular complex mixture. © *2017 Bull. Georg. Natl. Acad. Sci.*

Key words: crude oil, polycyclic aromatic hydrocarbons, GC retention indices, AMDIS system

Norio oil deposit located to the north-east of Tbilisi at the distance of 30-35 km (Fig. 1), and in the north-east plane of Martkopi-Norio anticline was put into operation in 1939 and is effective up to this very day. The important for exploitation Norio oil was related to Middle Miocene, lower and middle Sarmatian substages sediments. Oil and gas horizons are studied only at the depth of 700 m. Relatively deep horizons situated at the depth of 1000-2000 m are not studied and are considered prospective for oil and gas exploration objects [1]. North plane of Norio-Satskhenisi anticline is composed of the middle and upper Miocene and Maikopian deposits.

Systematic research of Norio oil began in the 1950-ies at the Petre Melikishvili Institute of Physical and Organic chemistry under the guidance of the Georgian Academy

Members Leonide Melikadze [2] and Christophore Areshidze [3], and continues up to day [4-6].

It was found that Norio oil is of napthen-aromatic type with the average density of 0.845 g/cm³; the output of light fractions is at a level of 67%, the content of asphalthenes is 0.33%, petroleum resins – 2.5%; paraffins – 0.9%; sulfur – 0.32%.

Investigation of high boiling fractions of Georgian oils testify that the Norio oil is rich with aromatic hydrocarbons and is characterized by intensive luminescence due to the presence of highly condensed aromatic hydrocarbons. Therefore, identification and separation of polycyclic aromatic compounds from crude oil by modern methods of investigation is a sphere of interest for many researchers using various separation methods and mass spectrometry tools (fundamental GC-MS and interfaces are described in [7], list of references is given in [8] and other modern books). Traditional GC-MS still remains one of the most reliable methods for structure elucidation, the use of automated deconvolution software [9] expands the limits of GC-MS application, and the use of reliable mass spectral and GC retention index libraries remains highly relevant in oil research.

The aim of our research was to study the content of polycyclic aromatic hydrocarbons in Norio oil using GC-MS and taking into consideration our recent results [5-6].

Experimental

A vacuum gas oil fraction with boiling point 340-590°C is about 28% of Norio crude oil. For the extraction of aromatic hydrocarbons from this fraction, the following separation techniques were applied:

• atmospheric and vacuum distillation of fractions with b.p. 340°C

• vacuum distillation of fractions with b.p. 340-590°C

• aniline extraction of aromatic hydrocarbons from the 340-590°C fractions followed by removal of the solvent (distillation, diluted HCl, water)

• vacuum distillation, yielding eight portions of the gas oil concentrates

• further separation of these fractions on a 300 cm x 5 cm silica gel chromatography column with the use of petroleum ether as an eluent under nitrogen gas pressure followed by extraction of remaining organic compounds with hot benzene

• Crystallization.

As a result, 876 petroleum ether and 78 benzene eluates were obtained, accounting for 7.08% of the initial crude oil mass. The GC-MS experiments were performed on a GC-MS magnetic sector mass spectrometer operated at standard experimental conditions. The GC separation was achieved on the Dimethyl-polysiloxane-containing capillary columns (15 m and 30 m), with the use of the following temperature parameters: from 100°C to 240°C at 2°C/min, and from 240°C to 270°C at 5°C/min (14 min). Automated mass deconvolution and identification system (AMDIS) was used for data analysis. In addition, manual extraction of spectra was applied to insufficiently separated components.
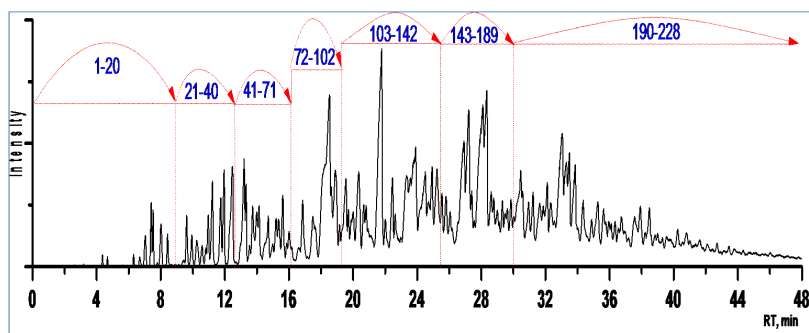

Fig. 1. GC of a Petroleum ether concentrate # 56

Results and Discussion

Fig. 1 depicts a chromatogram of typical analysis of the Norio petroleum ether eluates. The absence of the raised baseline hump does indicate that the above described pretreatments led to successful extraction of aromatic components from the crude oil. This chromatogram corresponds to sample # 56 out of 876 petroleum ether concentrates, and its major components

are phenanthrenes, anthracenes, fluorenes, naphthalenes and biphenyls (Table 1).

The mass spectra of isomeric aromatic hydrocarbons are found to be quite similar, and in some cases only peak ratios can be used for structure elucidation of regio-isomers as seen in Figs. 2 and 3 for isomeric methylindenes and dimethylnaphthalenes.

The chromatograms become "cleaner" for the

Table 1. Polycyclic aromatic hydrocarbons of a Petroleum ether concentrate # 56

| Fraction	Compounds
1 – 20	Methylindenes, Naphthalene, Biphenyl, Acenaphthene, Methylnapthalenes, Dimethylnaphthalenes, Dimethylindenes, Diphenylmethane and Methylbiphenyls
21 – 40	Dimethyl- and Methyl-ethylnaphthalenes, Methylbiphenyls and Fluorene
41 – 71	Di- and Trimethylbiphenyls, 1H-Phenalene, Methyl- and Dimethylacenaphthe-nes, Dimethylfluorenes, Tetramethyl-, Ethyl-Trimethyl-, Diethyl-, Methylpropyl- and Butylnaphthalenes, Methylacenaphthenes, Methylfluorenes
72 – 102	Tetramethyl-, Methyl-Diethyl-, Ethyl-Propyl-, Iso- and n.-Pentyl- and Pentamethyl-naphthalenes , 1,4-Diphenylbutane, Dimethyldihydrofluorene, Trimethyl- , Methyl-Ethyl and n-Propyl-biphenyls, Methyl-, Dimethyl- and Ethylfluorenes, Dihydroanthracenes
103 – 142	Di- and Tetrahydroanthracenes, Dimethyl-, Tetramethyl-, Methyl-Ethyl- and Diethyl-Fluorenes, Trimethyl- and Methyl ethylacenaphthenes, Ethyl-Propyl-, and Iso-hexylnaphthalenes, Phenanthrene, Anthracene
143 – 189	Methyl- and Dimethylanthracenes, Di- and Tetrahydro-ethylanthracenes, Methyl Ethylphenanthrenes, Dimethyl- and Ethyldihydroanthracenes, Dihydro- and Octahydro-cyclopentaphenanthrenes, Butylfluorene
190 – 228	Methyl-, Dimethyl- and Methyl-Ethyl-anthracenes, Dihydrobenzanthracene, Dihydropyrene, Dimethyl-phenylnaphthalenes, Terphenyls
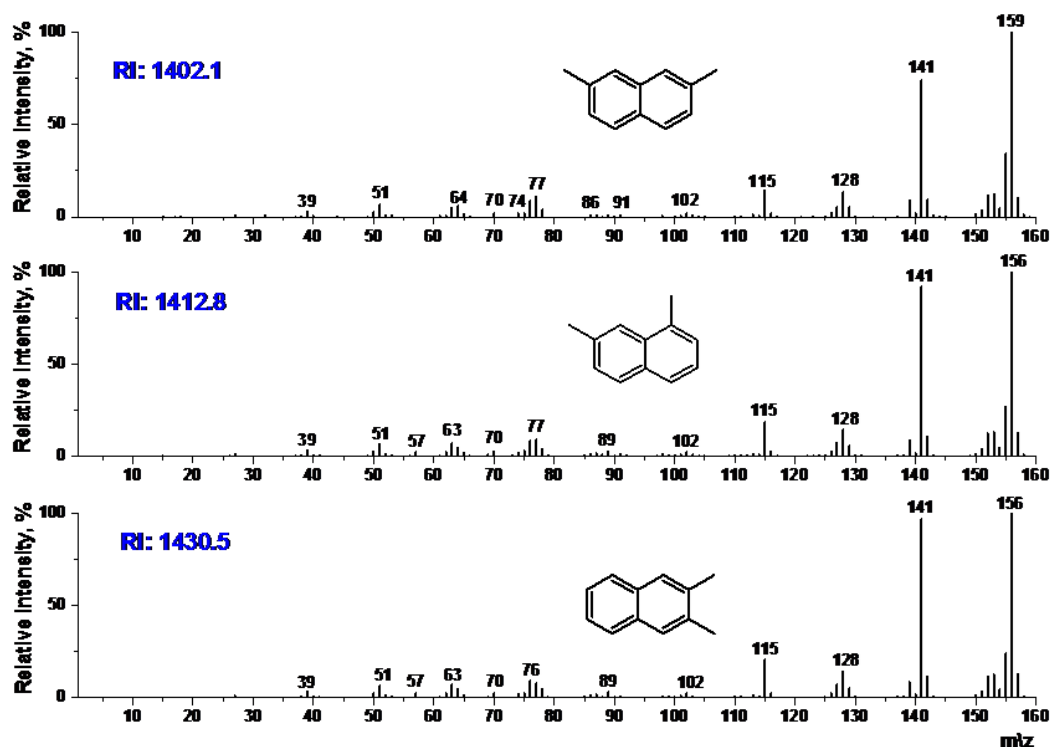
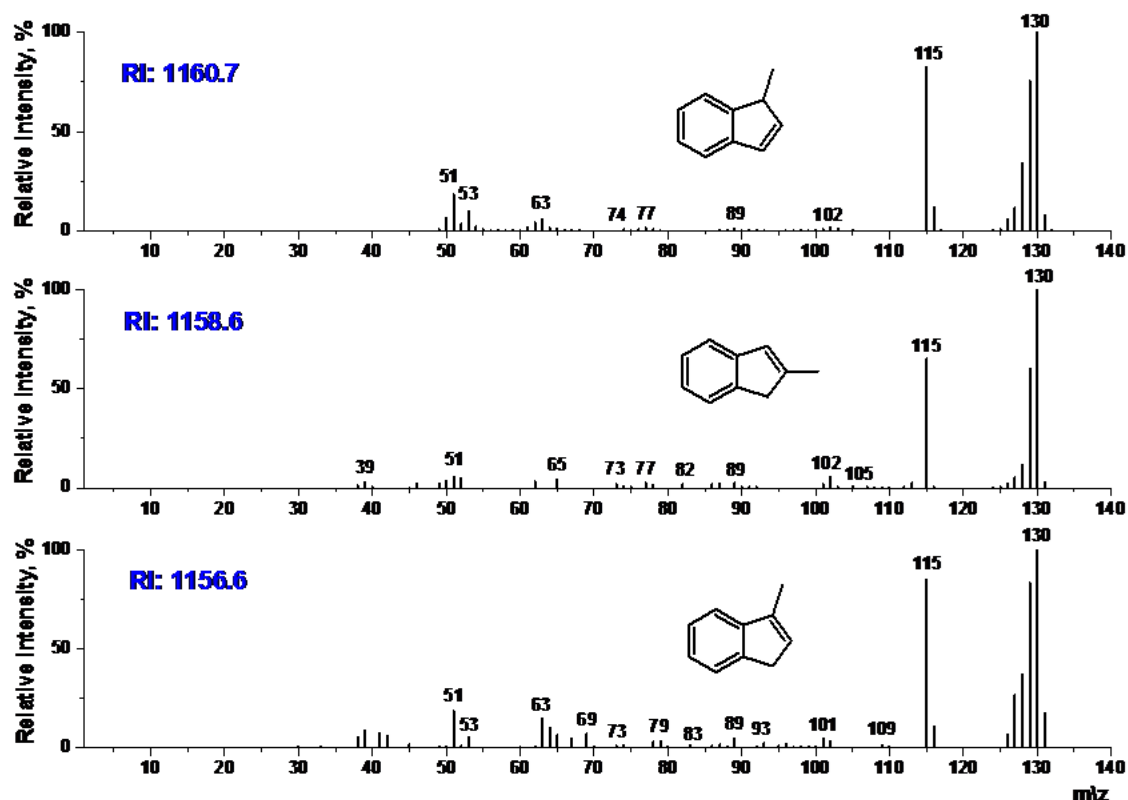**Fig. 2.** Mass spectra of isomeric 1-, 2- and 3-Methylindenes

Fig. 3. Mass spectra of isomeric 2, 7-, 1, 7- and 2, 3-Dimethylnaphthalenes
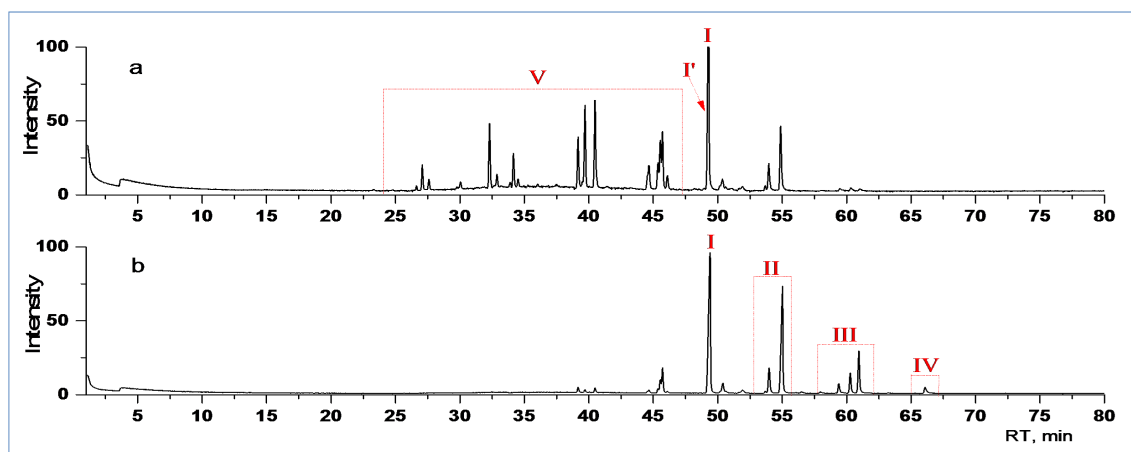

Fig. 4. GC of "natural precipitation" (a) and recrystallization (b) products obtained from Sample # 56 (Figure 3): Major components: I, I' - Benz[a]anthracene and Chrysene, their II - methyl-, III - dimethyl- and IV - trimethyl-(III) derivatives, V – substituted phenanthrenes, anthracenes, pyrenes

crystals formed from sample #56 and maintained at temperature 3-5⁰C (Fig. 4a), and for the recrystallization products (Fig. 4b).

The GC peak separations on a 15 m column are sufficient for the preliminary analysis; complete separation of isobaric structures can be achieved on a longer GC columns. At this point, structures on a molecular level were easily determined for homologous phenanthrene - 4-Methyl-, 3,6-Dimethyl-, 2,3,5-Trimethyl- and 3,4,5,6-Tetramethyl-phenanthrenes, as well as for other aromatic compounds for Chrysene - 1-Methylpyrene and its Dimethyl-, Trimethyl- and

Tetramethyl-analogs and Benz[a]anthracene and its Methyl-, Dimethyl- and Trimethyl-analogs. GC retention index values for these compounds are not presently available.

In addition, identification of overlapping peaks is not always an easy task; this problem was ameliorated by making use of AMDIS and by manual data extraction as needed. The results of the present work show that the complex analysis of gas chromatography retention indexes and mass spectral data was successfully used for the structure elucidation of the components of this particular complex mixture.

Conclusion

A method for the preliminary extraction of aromatic hydrocarbons from crude oils including distillation, the use of aniline as a solvent, and pressure column chromatography was shown to be sufficient for the successful determination of these hydrocarbons at a molecular level by traditional GC-MS. National Institute of Standards and Technology is going to use several compounds extracted from the Norio oil as reference samples.

ფიზიკური ქიმია

ნორიოს ნავთობის პოლიციკლური არომატული ნახშირწყალბადების შესწავლა GC-MS მეთოდით

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*ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, პეტრე მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, თბილისი, საქართველო
**აკადემიის წევრი, საქართველოს მეცნიერებათა ეროვნული აკადემია; ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი,პეტრე მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, თბილისი, საქართველო
§ სტანდარტების და ტექნოლოგიების ეროვნული ინსტიტუტი, კაიზერბურგი, აშშ

შესწავლილი იყო ნორიოს ნავთობის (საქართველო) 340-590⁰C კაკუშ ფრაქციაში მაღალმოლეკულური არომატული ნახშირწყალბადები ქრომატო-მასსპექტრომეტრული (GC-MS) მეთოდით. ნედლი ნავთობიდან არომატული ნაერთების კონცენტრატის მისაღებად გამოყენებული იყო დაფოფის მრავალსაფეხურიანი მეთოდიკა: ატმოსფერული და კაკუშ დისტილაცია, კაკუშ ფრაქციიდან ანილინით არომატიკის კონცენტრატის ექსტრაპირება, მისი დაფოფა რ�a ნაწილად კაკუშ დისტილაციით სარექტიფიკაციო სვეტზე, შემდეგ ხდება დისტილატების დაფოფა ქრომატოგრაფიულ სვეტზე სილიკაგელით - პეტროლეინის ეთერით ელუირება აზოტის წნევის ქვეშ, ნარჩენ ორგანიკის კი, ცხელი ბენზოლით ექსტრაპირება და კრისტალიზაცია/რეკრისტალიზაცია. შედგად/ შედგად მიღებული იყო 900-მდე პეტროლეინის ელუატი, 78 ბენზოლის ექსტრაქტი, 90 კრისტალური ნაერთი. შესწავლილია პეტროლეინის ეთირ ელუატი #56 და მისი კრისტალიზაციით მიღებული კომპონენტები. კონცენტრატის ნიმუშების აირ-ქრომატოგრაფიული (GC) დაფოფა ჩატარდა კაპილარულ სვეტებზე (15 მ და 30 მ) დიმეთილ-პოლისილოქსანით, პროგრა-

მირებული ტემპერატურის პირობებში. ექსტრაქტის ქრომატოგრამაზე ნედლ ნავთობთან შედარებით ნულოვანი ხაზი მკვეთრად დადაბლებულია, რაც მიუთითებს არომატული ნახშირწყალბადების კონცენტრატის წარმატებით გამოყოფაზე, რაც გადამწყვეტ ფაქტორს წარმოადგენს GC-MS მეთოდით სტრუქტურების დასადგენად. GC-MS ექსპერიმენტი ჩატარდა ხელსაწყოს მაგნიტურ სექტორში სტანდარტულ პირობებში, მონაცემთა ფაილების ანალიზი შესრულდა ავტომატური MS დეკონვოლუციისა და იდენტიფიცირების სისტემის (AMDIS) გამოყენებით. ელექტრონული იონიზაციით ფრაგმენტაციისა და GC შეკავების ინდექსების ანალიზის საფუძველზე საკვლევ ელუატში იდენტიფიცირებულია პოლიციკლური არომატული სტრუქტურების: ინდენების, ტეტრალინების, დინაფთილბენზოლების, ნაფტალინების, აცენაფტილენების, ფლუორენების, ფენანტრენების, ანთრაცენების, ნაფთოფლუორენებისა და ფენანტრენების მონო- და პოლიალ-კილწარმოებულები, აგრეთვე ტერპანილები; ხოლო ელუატის კრისტალურ ნიმუშებში იდენტი-ფიცირებულია: ბენზანტრაცენი, ქრიზენი, მათი მეთილ-, დიმეთილ- და ტრიმეთილ- ანალოგები, ფენანტრენის წარმოებულები, ანტრაცენები და პირენები. ნორიოს ნავთობის მაღალმდუღარე ფრაქციის დაყოფის მრავალსაფეხურიანი მეთოდიკის გამოფენებით შესაძლებელი გახდა პოლიციკლური არომატული სპექტრების დადგენა მოლეკულურ დონეზე ტრადიციული GC-MS მეთოდის საშუალებით.

REFERENCES

1. *Vakhania E., Papava D.* (1996) Life-giving gusher. Tbilisi, 150 p.
2. *Melikadze L.D., Eliava T.A., Usharauli E.A.* (1958) To the knowledge of the nature of the fluorescent components of oil. Tbilisi, 26 p.
3. *Areshidze Ch.I.* (1980) Researches in Petroleum Chemistry. Tbilisi, 235 p.
4. *Topuria E.N., Lekveishvili E.U., Khetsuriani N.T., Edilashvili I.L.* (2007) Issledovanie uglevodorodnogo sostava srednykh i visokokipyashchikh frakcii gruzinskikh neftei metodami mass- i khromatomass-spektrometrii. J. Mass-spektrometria, **4**, 3: 197-226, M. (in Russian).
5. *Khetsuriani N.T., Usharauli E.A., Topuria E.N., Mchedlishvili I.D.* (2011) Materiali IX Mezhdunarodnoi mass-spectrometricheskoi konferencii po neftekhimii, ekologii i pishchevoi khimii "PETROMASS-2011", pp. 128-133, M. (in Russian).
6. *Khetsuriani N.T., Topuria E.N., Murray J.A., Todua N.G., Gonzalez C.A., Mikaia A.I.* (2014) Proceedings of the X International Mass Spectrometry Conference on Petrochemistry and Environment, "Petromass 2014", Tbilisi, p. 41-42.
7. *Pyle S.M. et.al.* (1997) J. Amer. Soc. Mass Spectrom. **7**: 183-190.
8. *Alford J.B., Peterson M.S., Green Ch.C.* (2014) Impacts of Oil Spill Disasters on Marine Habitats and Fisheries in North America. CRC Press, 340 p.
9. *Rodgers R.P. et.al.* (2011) Anal. Chemistry. **83**: 4665-4687.