

Geochemical studies of rocks

- Group composition determination of bitumoids
- Isotope composition analysis of bitumoid carbon ($\delta^{13}\text{C}/^{12}\text{C}$) and its separate fractions
- Chromatography-mass-spectrometric studies of molecular composition and distribution of biomarker hydrocarbons in the fractions of the bitumoid
- Identification of content C, H, N, S, O in core samples
- Isotope composition analysis of hydrogen ($\delta^2\text{H}/^1\text{H}$), nitrogen ($\delta^{15}\text{N}/^{14}\text{N}$), sulfur ($\delta^{34}\text{S}/^{32}\text{S}$), oxygen ($\delta^{18}\text{O}/^{16}\text{O}$)
- Pyrolytic studies
- Flash pyrolysis GC/MS
- Kinetic studies

Complex of the accelerated extraction of soluble organic matter (bitumoid) of rocks for the full cycle of geochemical studies

Extraction of bitumoid from core samples with preservation of extract and quantitative content determination

Dionex ASE 350 Accelerated Solvent Extractor (Thermo Fisher Scientific, the USA)



Function: release of organic extracts from various powdery objects (core material, rocks, soils, ground deposits, ecological and food objects) in the automatic mode, with a possibility of consecutive extraction by different solvents, with receiving separate fractions and groups of substances, receiving powder samples after extraction and also selective isolation of groups of substances using various adsorbents.

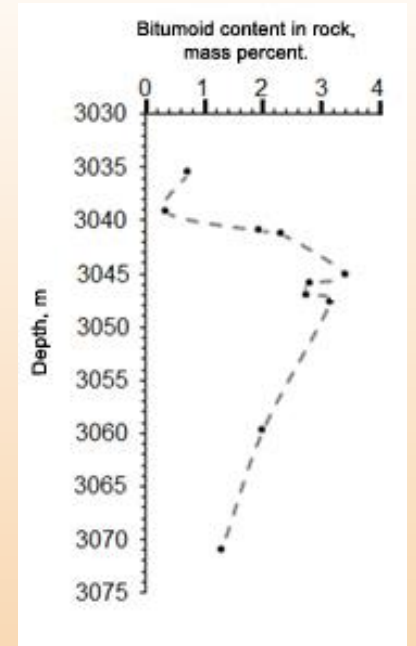
The system allows to place up to 24 samples with a possibility of adjustment of temperature, the used solvent, quantities of extraction cycles, is equipped with convenient collecting extracts in the adapted viols for the subsequent concentration using Rocket Evaporator Vacuum Centrifugal Evaporator. ASE method application for sample preparation for study in the field of oil and gas geochemistry allows to reduce repeatedly extraction time in comparison with traditionally used Soxhlet Extractor.

Rocket Evaporator Vacuum Centrifugal Evaporator (SP Scientific, USA)



Function: concentration (evaporation) of liquid extracts with capability of direct automated collection of concentrate into special vials for subsequent types of studies. It is equipped with a carousel for viols and flasks of various volumes that allows to carry out simultaneous individual concentration up to 6 samples of extracts and up to 300 ml and 18 extracts in viols of 60 ml.

Example of analysis results of bitumoid content distribution on a well log



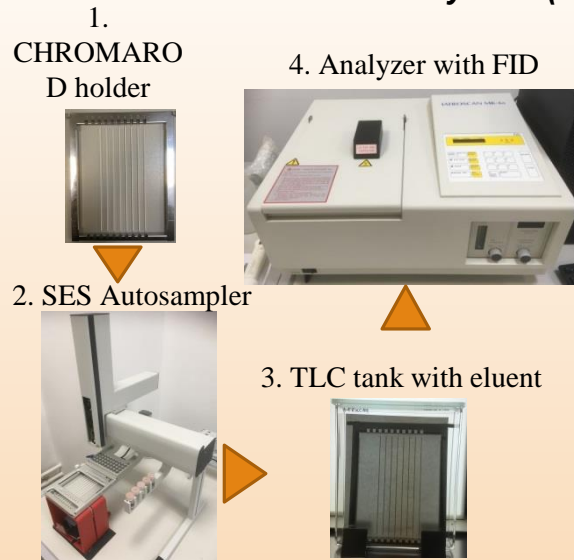
The received extracts remain for the subsequent types of studies (analysis of group, component and isotope composition)

Determination of bitumoid group composition

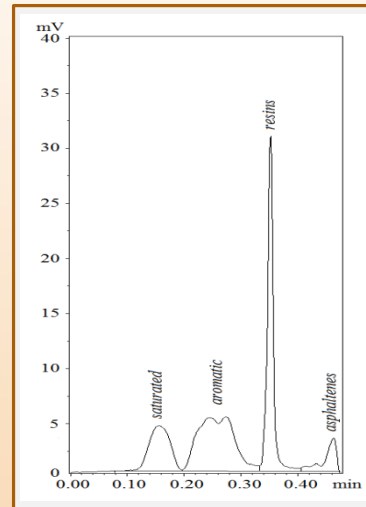
(core sampling for detailed geochemical studies on the basis of the preliminary pyrolytic analysis)

Group analysis of extracts using method of thin layer chromatography with flame ionization detection (TLC-FID)

Iatroscan MK-6s System (SES Analytical, Germany)



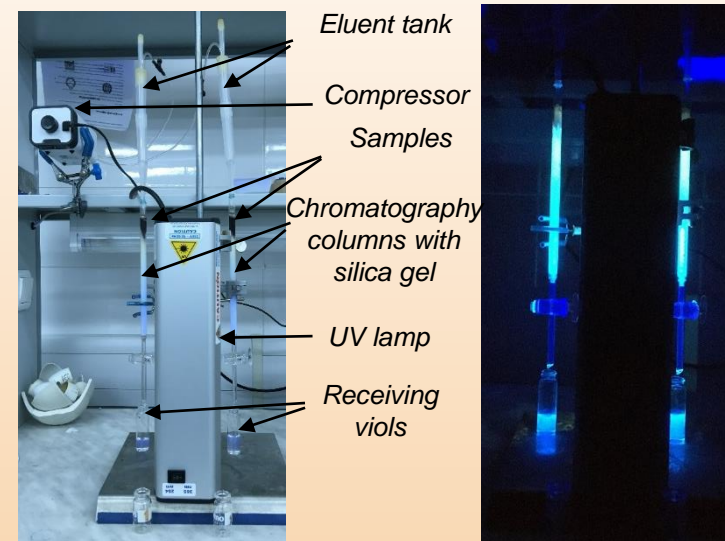
Example of chromatogram:



The system is applied for the quantitative analysis of content in organic extracts of rocks and oil stripped fractions (boiling point > 300 °C) 4 groups of components (saturated hydrocarbons – Saturated; aromatic hydrocarbons – Aromatic; polar N,S, O-components soluble in the low-boiling N-alkanes – Resins; polar components insoluble in the low-boiling N-alkanes – Asphaltenes) using group analysis method “SARA”, in accordance with IP 469/01 standard “Determination of Saturated, Aromatic and polar compounds in petroleum products by thin layer chromatography and flame ionization detection” (Institute of Energy, Great Britain).

Separation of extracts by method of column liquid adsorption chromatography on silica gel (with quantitative determination of mass fractions of the extracted fractions)

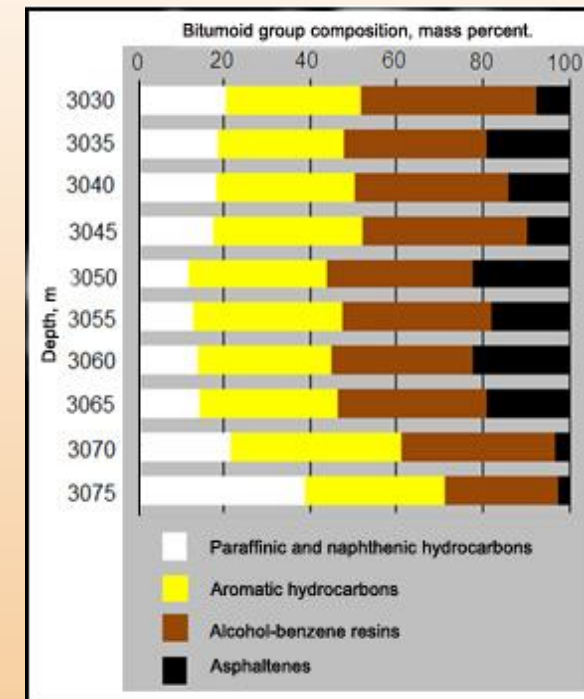
Interface of elution fractions is visible under UV light ($\lambda=365$ nanometer)



The separated fractions are gathered in pre-weighed viols and kept for the subsequent analysis of component and isotope composition



Example of group analysis results of bitumoid composition (distribution of fractions in bitumoid content on a well log)



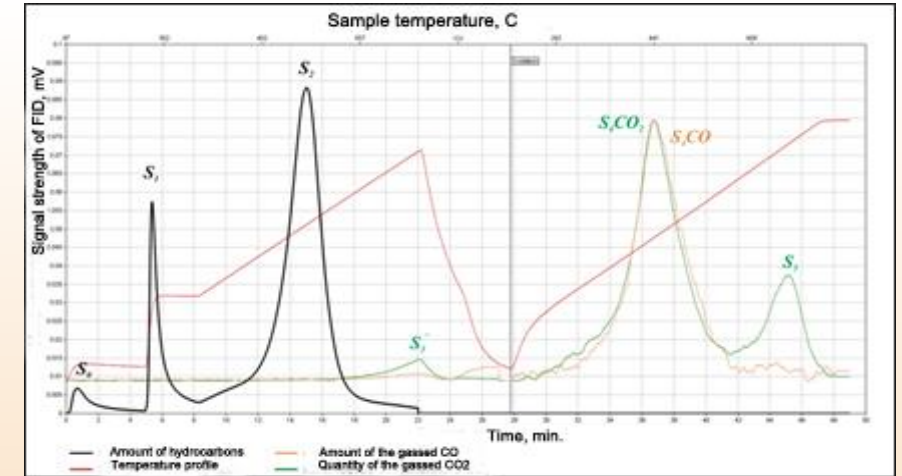
Pyrolytic studies



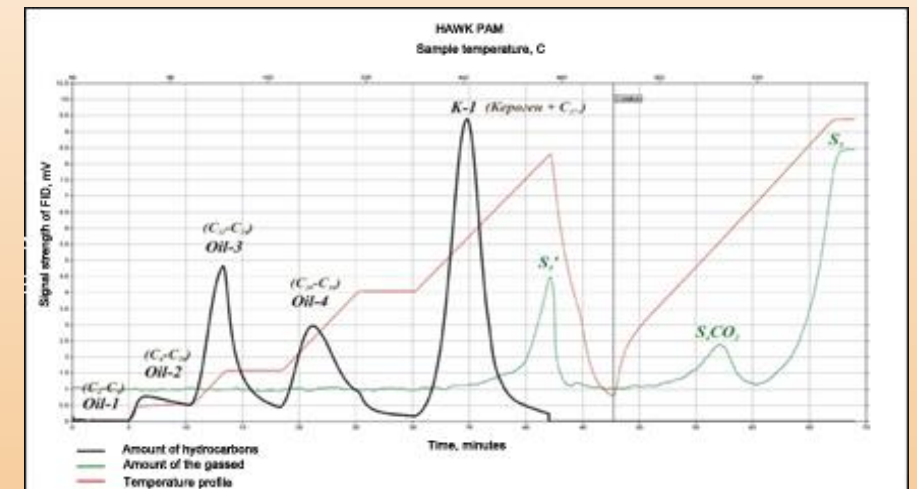
HAWK Resource Workstation for Pyrolysis
(Hydrocarbon Analyzer With Kinetics, Wildcat Technologies, USA)

Function: assessment of generating potential, maturity degree, type and conditions of organic matter formation

S ₀	S ₁	S ₂	T _{max}	PI	TOC	GOC
Thermally liberated gaseous hydrocarbons	Thermally liberated light hydrocarbons	Residual generating potential	Temperature at S ₂ peak	Productivity index	Total organic carbon	Generative organic carbon
(mg HC/g rock)	(mg HC/g rock)	(mg HC/g rock)	°C		(wt. %)	(wt. %)
NGOC	S3	HI	OI	CC	OSI	
Non-generative organic carbon	CO ₂ formed from carbonates at pyrolysis	Hydrogen index	Oxygen index	Carbonate carbon	Oil saturation index	
(wt. %)	(mg CO ₂ /g rock)	(mg HC/g rock)	(mg CO ₂ /g rock)	(wt. %)	(mg HC/g rock TOC)	
Peak	Oil-1	Oil-2	Oil-3	Oil-4	K-1	
Temperature	Heating from 25°C to 65°C	Heating from 60°C to 90°C, at 25°C per minute, hold for 5 minutes at T=90°C	Heating from 90°C to 180°C, at 25°C per minute, hold for 5 minutes at T=180°C	Heating from 180°C to 350°C, at 25°C per minute, hold for 5 minutes at T=350°C	Heating from 350°C to 650°C, at 25°C per minute, hold for 5 minutes at T=650°C	
Hydrocarbon fractions	C1-C5	C6-C10	C11-C19	C20-C40	kerogen	
Fraction structure	Fixed gases	Fixed light hydrocarbons		resins	asphaltenes; probably resins, bitumens	
	alkanes and arenas					



Pictogram of the sample and the temperature program in the Bulk method



Pictogram of the sample and the temperature program at the PAM method

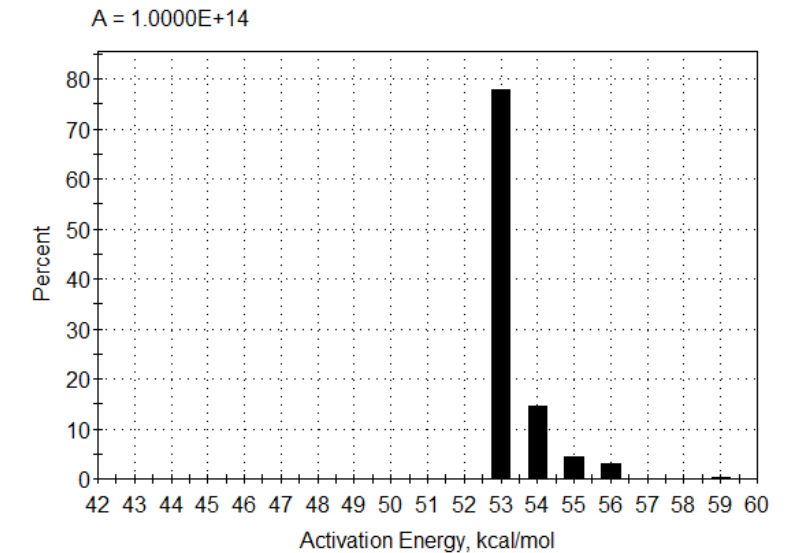
Kinetic studies

Analytical studies of kinetics of organic matter decomposition using specialized equipment HAWK and software “Kinetics2015” are based on the kinetic model Tissot and Espitalie which allows to predict the content of the hydrocarbons gassed at primary cracking of kerogen at temperature increasing over time.

Decomposition of kerogen and formation of hydrocarbons is described by a series of parallel chemical reactions. The mathematical model of decomposition of kerogen and formation of hydrocarbons is provided by Arrhenius equation, where the speed reaction constant depends on the activation energy, the preexponential factor and the heating temperature.

The distribution of generating potential realization according to activation energy and also the preexponential factor (A) are determined in laboratory setting. The essence of the kinetic method consists in heating of the series from 3 weighed quantities of the same sample with different speeds of pyrolysis temperature increase in inert environment. The received results of pyrolysis are processed using special software. The outcome is kinetic spectra of hydrocarbon formation from kerogen.

During the studies of catagenically transformed deposits the histogram of energy activation distribution of thermal decomposition of organic matter reflects only residual values which can be mathematically restored to the initial ones.



Kinetic spectra of hydrocarbon formation from kerogen

Pyrolytic analysis of core samples

Quantity of migrational HC (S0+S1) and kerogen (S2)

Oil and gas source potential (S0+S1+S2)

CQuantity (TOS) and quality (HI, OI) organic matter

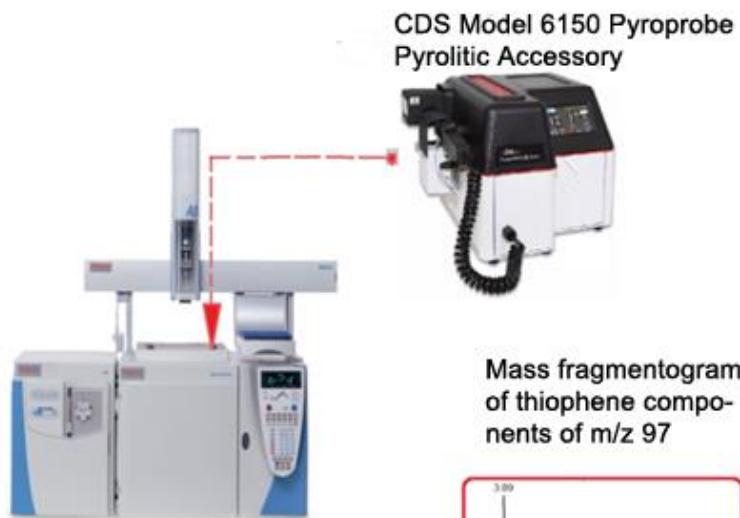
Maturity degree (Tmax, PI, HI) organic matter

Kinetic parameters of kerogen (activation energy spectra)

- Determination of oil saturated intervals and its power
- Geochemical characteristics of oil and gas source rocks
- Evaluation of conditions of organic matter formation
- Calculation of the generated HC quantity and assessment of transformation degree of organic matter

- **Evaluation of oil and gas reservoirs**
- **Calculation of HC reserves**
- **Clarification of oil recovery ways at thermal methods of formation stimulation**
- **Basin modeling**

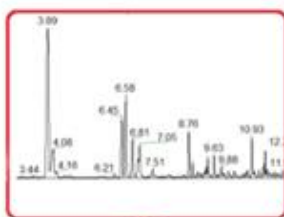
The analysis of core samples and the nonvolatile high-molecular-weight organic components (resins and asphaltine fractions of bitumoid, insoluble residue of organic matter of rock (kerogen) by method of pyrolytic chromatography-mass spectrometry (flash pyrolysis GC/MS)



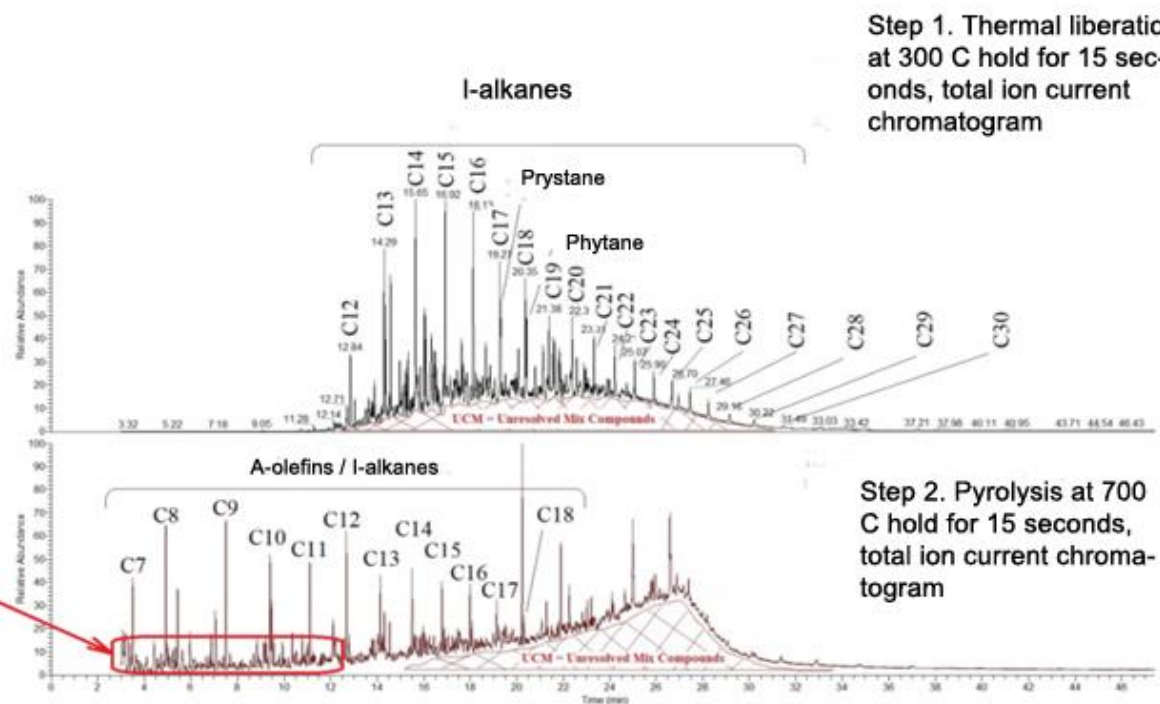
Trace 1310/TSQ 8000 EVO Chromatography-Mass-Spectrometer (Thermo Fisher Scientific, USA)

CDS Model 6150 Pyroprobe Pyrolytic Accessory

Mass fragmentogram of thiophene components of m/z 97



Mass chromatogram example of consecutive flash pyrolysis products of Bazhenov formation rock:



Step 1. Thermal liberation at 300 C hold for 15 seconds, total ion current chromatogram

Step 2. Pyrolysis at 700 C hold for 15 seconds, total ion current chromatogram

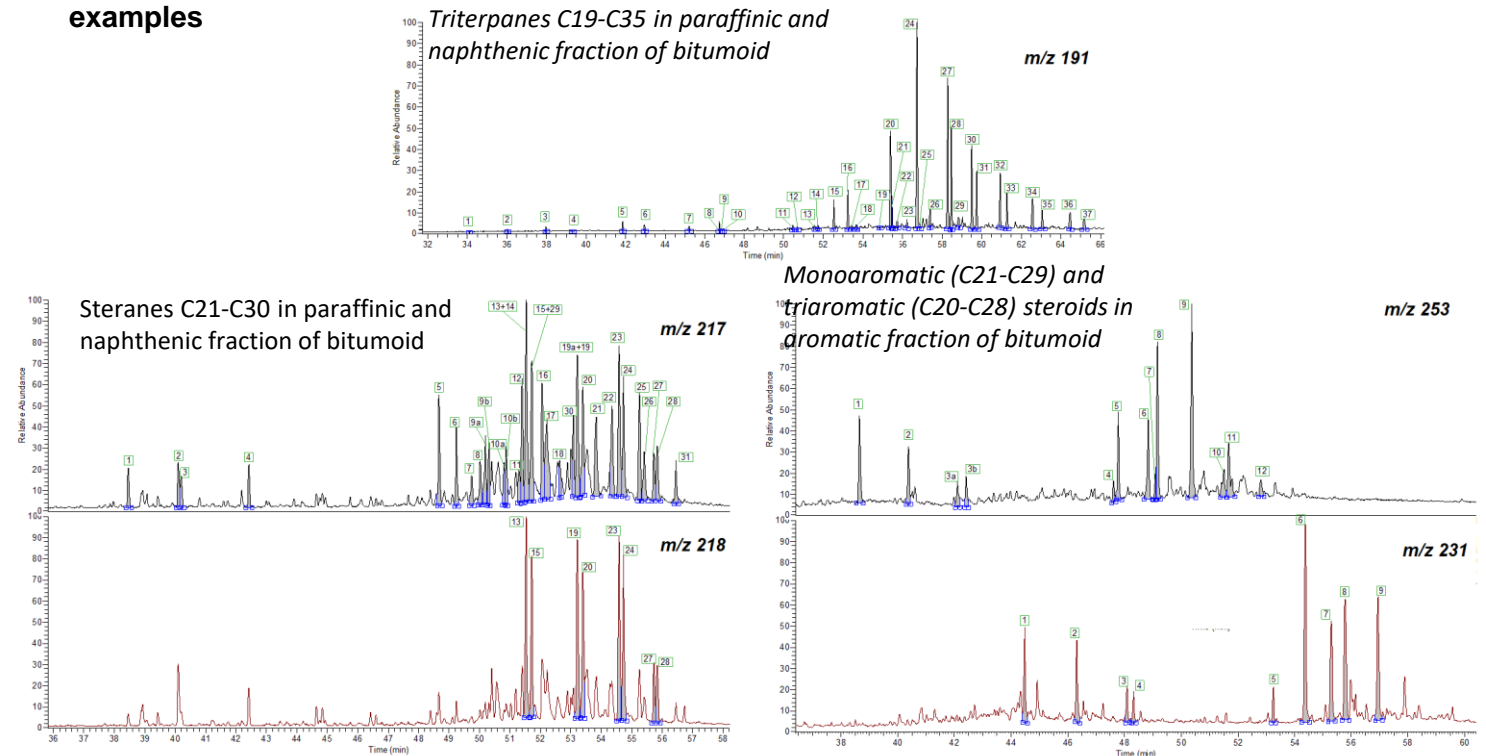
Chromatography-mass-spectrometric studies of molecular composition and distribution of biomarker hydrocarbons in paraffinic and naphthenic and aromatic fractions of the bitumoid

The analysis of biomarker hydrocarbons is made using Trace 1310/TSQ 8000 EVO Chromatography-Mass-Spectrometer (Thermo Fisher Scientific, USA)

About 160 individual HC compounds for each sample are identified, a number of molecular biomarker parameters for characteristic of genesis of initial organic matter of rocks, lithologic and facies conditions of its transformation and also degree of catagenetic transformation made on the basis of this identification.



Mass fragmentogram examples



Element composition determination of rock using CHNS-O Analyzer

Thermo Flash 2000 Analyzer is intended for determination of carbon, hydrogen, nitrogen, sulfur and oxygen. The analyzer consists of three main units: the reactor, the dividing system, the detector and it also works by the principle of “dynamic flash”



ISOTOPE RATIO MASS SPECTROMETRY OF LIGHT ELEMENTS (IRMS)



Structure of the complex:

1. Delta V Advantage Isotope Mass Spectrometer
2. ConFlo IV Universal System of Gas Distribution
3. EA Isolink CNSOH Flash IRMS Element Analyzer + Ramped GC Oven (option for the isotope analysis of sulfur)
4. GasBench II + GC PAL Autosampler System of sample preparation for the study of carbonates and water samples
5. Gas TRACE GC ULTRA Chromatograph + Tri Plus RHS Autosampler
6. The GC IsoLink interface for flaring and transferring of the components under chromatograph analysis to CO₂ and H₂
7. ISQ 7000 Quadrupole Mass Spectrometer

[blocks 1+4] Ratio measurement ¹³C/¹²C and ¹⁸O/¹⁶O in carbonate material of core samples

Example of differentiation of ¹³C/¹²C and ¹⁸O/¹⁶O values for carbonate material of core samples of different formations of the cross section. "Lightening" of isotope composition of oxygen is clearly demonstrated with depth, reflecting differences in environmental conditions at carbonate material sedimentation

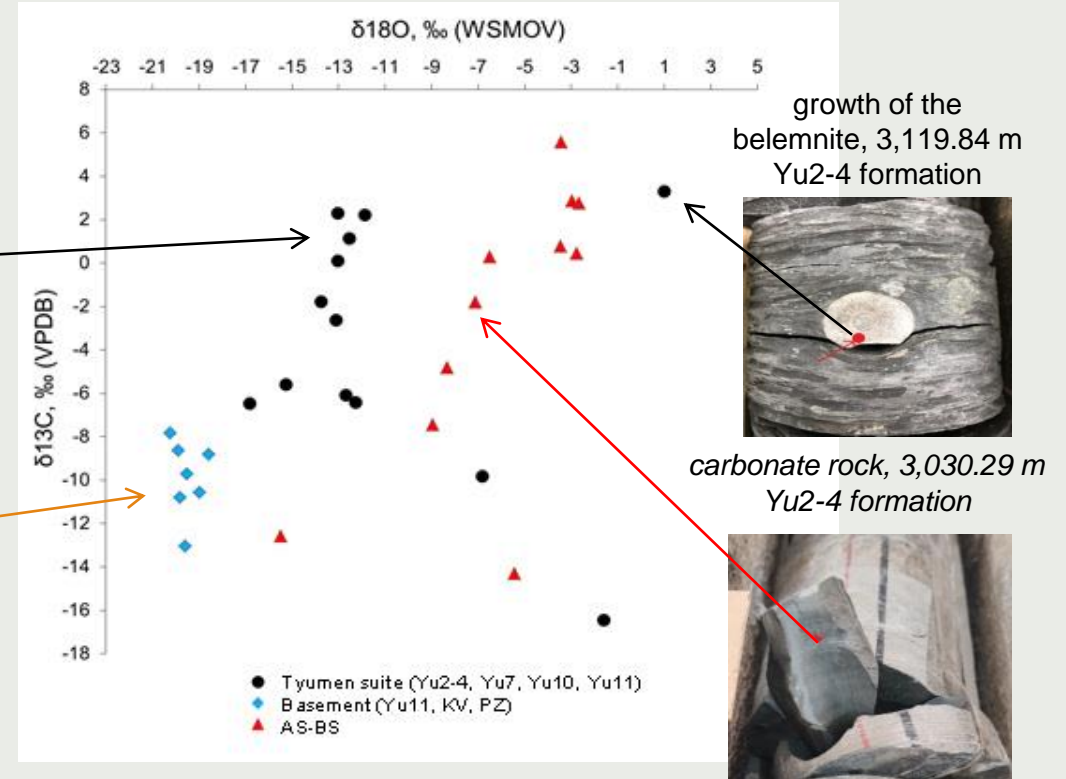
APPLICATION:

- origin characteristic of carbonate material of rocks;
- assessment of environmental conditions at carbonate material sedimentation (paleotemperature reconstruction)
- carbonatization stage assessment

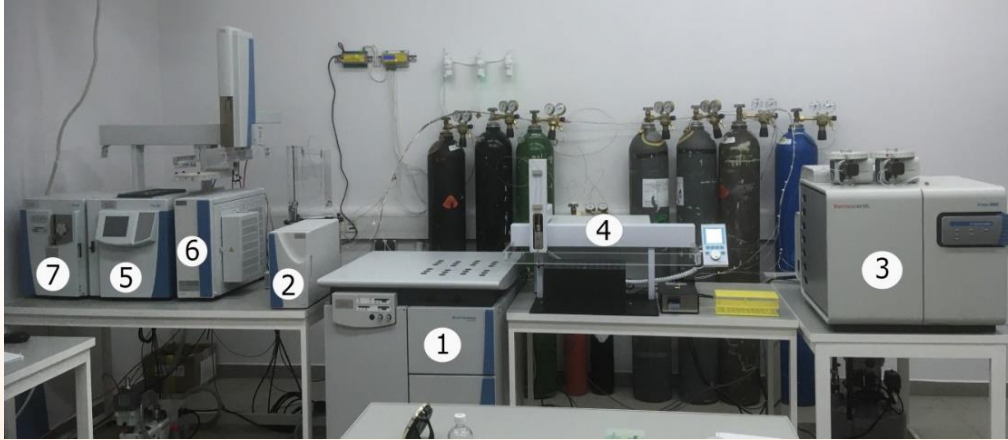
sideritic layer,
3,387.09 m Yu11
formation



carbonate streak,
3,689.5 m PZ
formation



ISOTOPE RATIO MASS SPECTROMETRY OF LIGHT ELEMENTS (IRMS)



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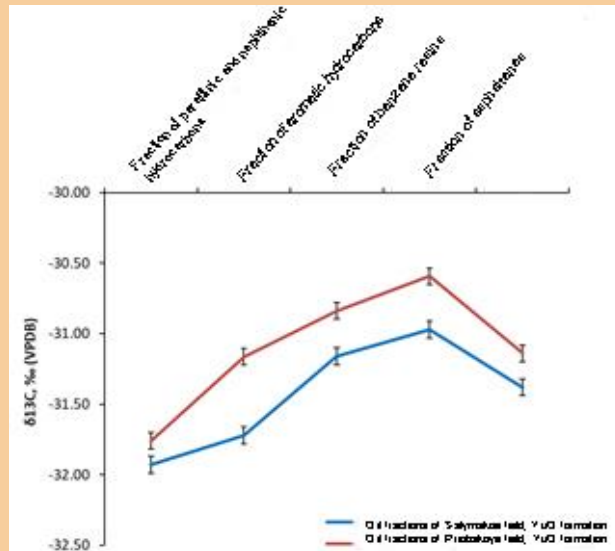
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blocks [1+2+3] Ratio measurement ¹³C/¹²C and D/H in oil and organic extracts of rocks (bitumoids); in separate chromatographic fractions preparative isolated from oil and bitumoids (paraffinic and naphthenic, aromatic, benzene resins, alcohol-benzene resins, asphaltenes)

APPLICATION:

- assessment of genesis of oil and bitumoid initial organic matter of rocks,
- characteristics of lithologic and facies conditions of the accumulation and transformation at diagenesis and katagenesis,
- correlation relationship establishment of potentially oil and gas source rocks with genetically related hydrocarbon fluids of areas under study and also correlations and differences between fluids

Example of differences in distribution of δ¹³C values of oil chromatographic fractions of the same formation but different fields within the same oil and gas area



[blocks 1+2+5+6+7] Ratio measurement ¹³C/¹²C и D/H of methane and HC C₂-C₅ in wellhead gas tests; in individual N-alkanes of paraffinic fraction of oil / bitumoid

Application:

- assessment of methane, CO₂, HC (C₂-C₅) (biogenous or oil) genesis
- assessment of degree of catagenetic transformation of the oil and gas generating rocks

Example of differences in distribution of δ¹³C values in wellhead gas of oil fields within the central part of KhMAO

