

IDENTIFICATION OF DISSOLVED ORGANIC SUBSTANCE OF DAGESTAN THERMAL WATER'S DEPOSITS

A.G. Kaymarazov, R.B. Apandiev

Institute for Geothermal Problems Dagestan Scientific Center, RAS
Makhachkala, Dagestan, 367030, Russia

ABSTRACT

The components of dissolved organic substance (DOS) of thermal salt waters related to Mesozoic aquifers of Dagestan have been analysed by GC/MS. The homologs of mono (C_2 - C_8 , C_{10} - C_{16})-, dicarboxylic aliphatic (C_5 - C_{15}) acids, mono (C_7 - C_{10})-, di (C_8 - C_9)-, tricarboxylic aromatic acids, phthalic (C_8 - C_9) and naphthalic (C_6 - C_8) acids; carboxylic acids (C_6 - C_8), aliphatic alcohols (C_7 - C_{10}); hydrocarbons (C_{11} - C_{32}) - among them the chemofossilic substances - have been established in the DOS. Together with mentioned homologous series of organic compounds have been identified halogen derivatives with the similar structure to the algae's metabolites.

INTRODUCTION

The development of hydrothermal resources as one of perspective renewable sources of energy and valuable hydromineral raw materials can be realized on the basis of the complex approach in the decision a number of problems, among which ecological aspects are the most significant.

Thermal salt water of the majority of Dagestan deposits are characterized by the rather high contents of organic substances making in recalculation on organic carbon up to and more than 1 g/dm^3 . However the contents of dissolved organic substance in thermal waters of region is investigated nowadays not enough. Meanwhile the information on composition of DOS is necessary, on the one hand, for deeper understanding of genesis of organic substance of underground waters and for the study of a role of DOS in formation of chemical structure of underground waters, on the other hand, for the decision of questions of defence biosphere, in connection with prospect of wide development of geothermal resources of the region.

With this aim in view the research DOS of various types of Dagestan thermal water's deposits: edge waters of Yuzhnosuhokumsk group of oil deposits, geothermal water of Makhachkala-Ternair deposit and self-effusive thermal water of Berikey thermoanomaly, - related to Mesozoic and Cenozoic aquifers is carried out.

The known technique of fractional division of

organic substances of natural and industrial waste waters into the groups various acidity: acidic DOS, carboxylic and other weak acids, neutral DOS, basic DOS and amphoteric DOS, combining extraction and sorption methods was used for separation of the DOS ingredients.

The analysis of components of mentioned above fractions DOS was carried out by gas chromatography/mass spectrometry (GC/MS, by electron impact EI), as the method which has received a wide circulation in organic geochemistry. The identification of substances was carried out by comparison of the most abundant peaks in the mass spectra of analyzed components with literary [Cornu A., Massot R., 1975] and measured mass spectra of standard compounds and on the basis of the common characteristic paths of dissociative ionization of their molecules [Budsikiewicz H., et al, 1967; Vulfson N.S., et al, 1986]. The components of acidic and basic fractions was studied in the form of methyl esters acids and trimethylsilyl ethers alcohols, after its preliminary chemical modification [Zaikin V.G., Mikaya A.I., 1987]. The principles of group identification of organic compounds on spectra ionic series and numbers of homologous groups of major peaks of mass spectra [Zenkewich I.G., Ioffe B.V., 1986] were used for interpretation of mass spectra some components of the amphoteric and basic fractions DOS.

RESULTS AND DISCUSSION

A number of the homologous series of aliphatic compounds: monocarboxylic acids, including higher fatty acids, dicarboxylic acids, monohydric alcohols and n-alkanes - are established in the composition of acidic, basic and neutral fractions DOS of mentioned above water's deposits. The aromatic components DOS are submitted by alkylbenzoic acids, phthalic acids, tricarboxylic acids, naphthalic acids, and carboxylic acids. The components DOS cycloparaffinic series are submitted by naphthenic acids. Also unitary halogen derivatives of carboxylic acids and alkanes was identified.

Aliphatic Monocarboxylic Acids

The study of group composition of acidic fractions DOS have carried by GC/MS of free acids and their methylated analogues. Small peaks of M^+ -ions are contained both in mass spectra of the free carboxylic acids, and in the ones their methyl esters (or they at all are absent). However, the peaks of fragment ions $[M-CH_3O]^+$ observed in all of the spectra allows rather simply to identify analyzed components as the corresponding members of homologous series of methyl esters monocarboxylic aliphatic acids. Furthermore, the abundant peaks of rearrangement ions the following composition: $(R)HC=C(OCH_3)-OH^+$; $R = H$ m/z 74; $R = CH_3$ m/z 88 and $(R)HC=C(R_1)-C(OCH_3)=OH^+$; $R = R_1 = H$ m/z 87; $R = H, R_1 = CH_3$; $R = CH_3, R_1 = H$ m/z 101 - allows to distinguish homologs with the linear or branched structures. More intensive peaks of the fragment ion $[M-CH_3O]^+$ in the spectra of methylated isomeric acids in comparison with linear analogues also indicate on the presence of alkyl substituent in the molecular structure.

Thus, the homologous series of monocarboxylic aliphatic acids of linear structure from acetic acid up to caprylic acid, including isomeric acids: isobutyric, 2-, 3-methylbutyric acids were established in the acidic fractions DOS of mentioned above thermal waters.

The higher fatty acids including lauric, myristic, palmitic and stearic acids are established in content of the fraction weak acids of edge water of Yuzhnosuhokumsk' deposits. Mass spectra of methylated components 1 - 4 of this fraction exhibit peaks for $[(CH_2)_nCOOCH_3]^+$ -ion series, together with the peaks of M and $[M-CH_3O]^+$ ions (see Table I).

Table I. The major ions in the EI mass spectra of methyl esters analyzed higher fatty acids: $CH_3(CH_2)_nCOOCH_3$, $n = 10, 12, 14, 16$.

Component		1	2	3	4
n		10	12	14	16
Ion	m/z	relative intensity, %			
$CH_2=C(OH)OCH_3^+$	74	100	100	100	100
$(CH_2)_2COOCH_3^+$	87	58	78	68	58
$(CH_2)_3COOCH_3^+$	101	20	9	37	15
$(CH_2)_4COOCH_3^+$	115	17	6	18	14
$(CH_2)_5COOCH_3^+$	129	17	25	32	13
$(CH_2)_6COOCH_3^+$	143	27	28	68	20
$(CH_2)_7COOCH_3^+$	157	4	9	8	6
$(CH_2)_8COOCH_3^+$	171	10	9	16	3
$(CH_2)_9COOCH_3^+$	185	30	3	21	4
$(CH_2)_{10}COOCH_3^+$	199	-	14	16	6
$(CH_2)_{11}COOCH_3^+$	213			6	3
$(CH_2)_{12}COOCH_3^+$	227			26	1
$(CH_2)_{13}COOCH_3^+$	241			5	2
$(CH_2)_{14}COOCH_3^+$	255				5
$[M-CH_3O]^+$		8	9	18	3
M^+		7	18	40	8

Three ions of considerable higher intensity at m/z 87, 143, 199 have the periodicity four CH_2 -links. The methylated component 4 and methylstearate show very similar mass spectra [Oldham G., Stenhagen E. 19721.

Dicarboxylic Aliphatic Acids

Dicarboxylic aliphatic acids is the most numerous of homologous series of acidic substances, established in the edge water of Yuzhnosuhokumsk' deposits.

It is possible, the origin some of them is connected to destruction of the unsaturated fatty acids. So, destruction of higher of unsaturated fatty acids involved the proximal fragment of them molecules can proceed in forming the dicarboxylic acids with the number C-atoms 7, 8, 10, 11, 13 [Barton D., Ollis W.D., 19791.

A number of researches [Harison A.G., 1988; Howe J., Williams D.H., 1968; Schwarz H., 1975] is devoted to study of behaviour various alkyl esters of dicarboxylic aliphatic acids in conditions of electron impact. The presence at structure their molecules two methoxycarbonyl groups causes more complex fragmentation pathways of M^+ -ions in comparison with destruction the esters monocarboxylic acids. One or another important pathway for the decomposition of M^+ -ions of methylated dicarboxylic acids is defined also the amount CH_2 -links in a molecule. The major ions in the mass spectra of analyzed components and probable structures for some of the ions are presented in Table II.

This is allowed to establish a series dicarboxylic acids from glutaric acid up to pentadecanedioic acid: $(CH_2)_n(COOH)_2$, $n = 3-13$, mainly of linear structure and the larger quantitative contributions for the components with even number C-atoms in a molecule.

The mass spectra of components 2 and 8 are considered as examples of the ones acid with branched structure. The component 2 was identified as 3-methylglutaric acid. The mass spectra of methylated component 2 and dimethyladipate contain abundant peaks at m/z 101, correspond to $[M-CH_3O-CH_2CO]^+$ ion, in contrast to the spectrum of dimethyl ester of 2-methylglutaric acid. On the other hand, the spectrum of dimethyladipate exhibits intensive peak at m/z 111, correspond to $[M-CH_3O-CH_3OH]^+$ ion, which absents in the spectrum of methylated component 2 [Howe J., Williams D.H., 19681. The more intensive peak of rearrangement ion with m/z 88 in the mass spectrum of methylated component 8 in comparison with the peaks of ions at m/z 74 and 87 indicates that at least one of methoxycarbonyl groups contains a CH_3 -substituent in α -position. This is allowed to determine the component 8 as 2-methylundecanedioic acid.

Table II. The major ions in the EI mass spectra of dimethyl esters analyzed aliphatic dicarboxylic acids: $(CH_2)_n(COOCH_3)_2$, $n = 3-11$.

Component		1	2	3	4	5	6	7	8	9	10
n		3	4	5	6	7	8	9	9	10	11
ion	m/z	relative intensity, %									
[M-MeO] ⁺		87	82	52	56	57	27	41	5	22	29
[M-MeOH] ⁺		60	36	14	9	11	4	6	-	2	5
[M-MeO-CO] ⁺		100	55	12	6	4	2	-	7	-	-
[M-MeOH-CO] ⁺		62	100	28	13	7	2	2	-	3	-
[M-MeO-MeOH] ⁺		14	-	32	23	16	4	3	3	2	-
[M-2 MeOH] ⁺		-	-	20	84	100	19	7	-	4	7
[M-MeO-CH ₂ CO] ⁺		43	87	100	100	66	24	30	10	21	28
[M-MeOH-CH ₂ CO] ⁺		-	-	14	9	7	2	2	-	2	2
[M-MeO-MeOH-CO] ⁺		43	38	26	27	23	11	6	3	3	5
[M-2MeOH-CO] ⁺		8	12	8	18	25	31	21	8	6	6
[M-MeO-CO-CH ₂ CO] ⁺		100	80	37	11	6	-	3	8	1	-
[M-123] ⁺		-	-	-	-	4	4	10	7	12	15
	115	16	2	12	8	6	5	4	7	5	11
	101	100	87	16	12	17	8	9	16	7	11
	88	46	57	9	8	10	5	7	87	6	9
	74	36	59	70	93	71	85	82	43	84	71
	73	28	80	31	8	10	10	7	13	10	13
	59	100	90	42	43	39	44	44	46	51	40
	55	68	91	64	56	71	100	100	100	100	100

Naphthenic Acids

Series of cycloalkanoic acids (C₆-C₈) was established in content of the acidic fraction DOS of Makhachkala-Temair water's deposit.

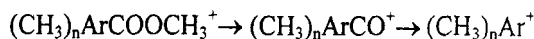
Mass spectra their methyl esters together with abundant peaks of molecular ions (m/z 128, 142, 156, respectively) are contained the peaks of [M-CH₃O]⁺, [M-CH₃OH]⁺, [M-COOCH₃]⁺, [M-HCOOCH₃]⁺, COOCH₃⁺ ions and [Alk]⁺ ions (at m/z 69, 83, 97, respectively), which allow to indicate the presence of methoxycarbonyl and cycloalkyl molecular fragments. It has allowed to identify the following acids: cyclopentanoic, cyclohexanoic, methylcyclohexanoic and cyclohexylacetic acids.

As single homolog of this series - 2-methylcyclopropanoic acid - was found in the composition of acidic fraction DOS of edge water of Yuzhnosuhokumsk' deposits. In the mass spectrum its methyl ester in addition to the peaks of M⁺ ion (m/z 114) and fragment ions: [M-CH₃O]⁺, [M-CH₃OH]⁺ (m/z 83, 82), COOCH₃⁺ is contained the peak at m/z 39, correspond to C₃H₃⁺-ions, which indicates on presence cyclopropyl fragment in a molecule of substrate. The mass spectrum of this methylated component quantitatively tallies with the literary spectrum of methyl ester 2-methylcyclopropanoic acid [Chizhov O.S., et al, 1979].

Alkylbenzoic Acids

The acids are found out by this homologous series of carboxylic acids was found in acidic fractions of DOS of all mentioned above water's deposits.

Specific fragmentation pathway for M⁺-ions methyl esters alkylbenzoic acids:



n=0	m/z 136	m/z 105	m/z 77
n=1	m/z 150	m/z 119	m/z 91
n=2	m/z 164	m/z 133	m/z 105
n=3	m/z 178	m/z 147	m/z 119

has allowed to identify benzoic acid, methylbenzoic, dimethylbenzoic and trimethylbenzoic acids.

The absence in the mass spectra of methylbenzoic acids the peaks of [M-CH₃OH]⁺ ions gives evidence that any of the established acids does not contain CH₃-group in a ortho-position to carboxylic group.

On the basis of the comparative analysis the measured and reference spectra [Cornu A., Massot R., 1975] is made the conclusion about the probable presence m-tolyl (M⁺; m/z 150) and mesitylic (M⁺; m/z 164) acids in the composition of the studied fractions.

Also with use the EI mass spectra of methylated derivatives naphthoic and methylnaphthoic acids:

(M^+ , m/z 186, 200; $[M-CH_3O]^+$, m/z 155, 169; $[M-COOCH_3]^+$, m/z 127, 141, respectively) are established.

Phthalic and Hydroxybenzoic Acids

The members of these homologous series of organic substances are found in acidic fractions of DOS of all mentioned above water's deposits.

The analysis of mass spectrum of methyl ester of the lightest component these acidic groups (M^+ , m/z 166) unequivocally specifies the presence of hydroxybenzoic acid.

The difficulty of identification the heavier homologs with the use mass spectra of methylated acids is explained on the one hand by similar decomposition pathways their M^+ -ions, on the other hand by the same values of mass numbers of molecular ions both the methylated hydroxybenzoic and methylated phthalic acids from homolog with empirical formula: $C_{10}H_{10}O_4$ (M^+ ; m/z 194).

Therefore together with spectra usual methyl esters analyzed substances the ones of deuterated analogues containing CD_3 -label only on carboxyl groups were measured. The observable 6-a.m.u. shifts for peaks of M^+ -ions (m/z 194 \rightarrow m/z 200, m/z 208 \rightarrow 214, respectively) and 3-a.m.u. shifts for peaks $[M-CH_3O]^+$ -ions unequivocally specifies the presence of phthalic acids with empirical formula: $C_6H_4(COOH)_2$ and $C_7H_6(COOH)_2$.

On the basis of the comparative analysis of the measured and reference spectra [Cornu A., Massot R., 1975] $C_6H_4(COOH)_2$ isomers were identified as phthalic and terephthalic acids.

Tricarboxylic acid also is established in the edge water of Yuzhnosuhokumsk' deposits. Mass spectrum its permethylated derivative (M^+ , m/z 252) is demonstrated the fragmentation pathway: $[M-CH_3O]^+$, m/z 221; $[M-COOCH_3]^+$, m/z 193 - similar to destruction of M^+ -ions methyl esters benzoic and phthalic acids.

Carbolic Acids

Series of carbolic acids (C_6 - C_8) was established in content of the fraction weak acids of Makhachkala-Ternair water's deposit. The analysis of mass spectra free phenols and their methylated derivative has confirmed the presence phenol (M^+ , m/z 94 and 108, respectively), ortho- and para - crezylic acids (M^+ , m/z 108 and 122, respectively), 2,3- and 3,4-dimethyl phenols (M^+ , m/z 122 and 136, respectively), which formerly were established in these waters by our colleagues [Ramazanov A.Sh., 1992].

Monohydric Alcohols

This homologous series was established in

composition of the basic fraction DOS of edge waters Yuzhnosuhokumsk' deposits.

The modification of the component this fraction with the mixture of hexamethylsilazane and trimethylchlorosilane (2:1) was preceded by CG/MS analysis.

All the mass spectra of O-trimethylsilyl (TMS) derivatives exhibit the peaks correspond to $[M-CH_3]^+$ (or $[M-Me]^+$), $[M-(CH_3)_3SiOH]^+$ (or $[M-Me_3SiOH]^+$) ions, which easily allow to define molecular weight of the alcohol. In addition to they contain the peaks correspond to $[Me_3Si-O=CHR]^+$ ions $R = CH_3 \cdot C_4H_9$. These ions are produced by cleavage $C_\alpha - C_\beta$ - linkages to O-atom, thereby allowing to determine the position OH- groups in a molecule [Dube G., Krigsmann H., 1968; Ubik., et al, 1975].

Thus it was established the homologous series of monohydric alcohols (C_7 - C_{10}) (see Table III) for which the higher contribution the components with even number C-atoms in a molecule is marked.

The components 1 and 4 are identified respectively, as heptanol-4 and nonanol-5 - secondary symmetric alcohols. The destruction their M^+ -ions is accompanied by formation $[M-Me_3Si]^+$ -ions with m/z 115, 143 and character fragments: $Me_3Si-O=CHR^+$ with m/z 145, 159, respectively.

The representative of aliphatic diols - butanediol-1,2 - was found together with monohydric alcohols. Mass spectrum its bis (TMS) ether contains the peaks of fragment ions, allowing to determine the position of both OH- groups in a molecule substrate: $Me_3Si-O=CHC_2H_5^+$ at m/z 131 (100%), $Me_3Si-O=CH_2^+$ at m/z 103 (28%) and $Me_3SiOCH_2-CH=OSiMe_3^+$ at m/z 205 (8%)

Hydrocarbons

The compositions of the neutral fractions DOS of waters all mentioned above deposits mainly are submitted with hydrocarbons.

The mass spectra of components of these fractions was useful to establish following homologous series of alkanes: C_{11} - C_{32} for Yuzhnosuhokumsk' waters, C_{14} - C_{30} for Makhachkala-Ternair waters, C_{19} - C_{29} for Berikej's waters. The observable gradual reduction the intensities of peaks $[C_nH_{2n+1}]^+$ ions together with increasing n value, from $C_4H_9^+$ ion allows to make a conclusion about mainly representation of n-alkanes in the contents of all investigated fractions.

Halogen Derivatives

The halogen derivatives with the similar structure to the algae's metabolites was found in self-effusive thermal water Berikej thermoanomaly.

Among them the representatives of halogenacetic acids and halogenalkanes were identified on mass numbers of characteristic ions:

Table III. The major ions in the EI mass spectra of trimethylsilyl ethers analyzed aliphatic alcohols:
 $CH_3(CH_2)_nOTMS$, $n = 6-9$

Component		1	2	3	4	5	6	7	8	9
n		6	7	7	8	8	9	9	9	9
ion	m/z	relative intensity, %								
M^+		7	6	5	14	10	2	2	4	1
$[M-Me]^+$		57	18	65	-	9	36	42	100	31
$[M-Me_3SiOH]^+$		23	8	12	10	1	6	23	23	21
$[M-Me_3SiOH_2]^+$		8	5	-	9	-	4	25	26	26
$[M-Me_3Si]^+$		100	6	2	27	8	3	2	3	1
$TMS-O=CH_2^+$	103	17	57	100	56	64	63	62	51	76
$TMS-O=CHCH_3^+$	117	16	5	6	10	11	5	8	5	6
$TMS-O=CHC_2H_5^+$	131	9	4	3	20	7	4	20	13	6
$TMS-O=CHC_3H_7^+$	145	87	7	2	18	14	3	4	5	3
$TMS-O=CHC_4H_9^+$	159	17	-	-	36	18	2	3	-	7
$Me_2SiOCHCH_2^+$	101	16	4	1	18	16	10	8	7	7
$Me_2SiOCHCHCH_3^+$	115	100	4	2	34	20	17	7	5	3
$Me_2SiOCHCHC_2H_5^+$	129	25	6	2	12	4	15	6	4	3
$Me_2SiOCHCHC_3H_7^+$	143	34	12	3	17	8	3	7	4	4
Me_3Si^+	73	87	93	67	100	100	72	92	66	72
$Me_2Si=OH^+$	75	93	100	54	69	73	66	63	57	43
$C_3H_5^+$	41	49	41	11	60	49	32	36	22	28
$C_3H_7^+$	43	67	86	10	66	87	43	43	31	41
$C_4H_7^+$	55	23	16	8	40	92	57	65	67	100
$C_4H_9^+$	57	14	16	22	82	50	51	75	58	74
$C_5H_9^+$	69	17	22	13	62	82	63	100	77	93
$C_3H_{11}^+$	71	6	5	2	20	31	21	27	19	23
$C_6H_{11}^+$	83	25	13	10	57	46	100	93	45	65
$C_6H_{13}^+$	85	5	16	2	28	14	15	11	21	11
$C_7H_{13}^+$	97	8	3	2	12	34	48	63	42	61

a) methyl ester dichloroacetic acid: $CHCl_2CO^+$ at m/z 111, 113; $CHCl_2^+$ at m/z 83, 85; b) methyl ester trichloroacetic acid: M^+ at m/z 176, 178; CCl_3^+ at m/z 117, 119, 121; c) hexachlorethane: $C_2Cl_5^+$ at m/z 119, 58%, m/z 201, 100%, m/z 203, 63%, m/z 205, 16%; CCl_3^+ at m/z 117, 100%, m/z 119, 97%, m/z 121, 34%; d) heptachlorethane: $HC_2Cl_4^+$ at m/z 165, 76%, m/z 167, 100%, m/z 169, 46%, m/z 171, 10%; CCl_3^+ at m/z 117, 100%, m/z 119, 94%, m/z 121, 21%) - having similar structure to secondary metabolites of red algae, which capable as known to develop halogenated polyketides.

The detection not probable prior Br-, J-derivatives, but Cl-substituted substrates is likely to result from the interaction between the OS of sedimentary mantle and chloride brine by high temperatures and pressures.

EXPERIMENTAL

The EI mass spectra were obtained by use of a liquid probe inlet with VARIAN MAT 311A mass spectrometer at 70 eV equipped with capillary column (25 m, SE-30, carrier gas - helium, 1 ml/c).

Spectra were recorded at ion source temperature 150 °C. The temperature in the site of evaporation was 270 °C.

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