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Note

Gas chromatographic analysis of the vapours and gases discharged from the thermal fields of Kamchatka

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Studies into the composition of vapours and gases discharged during solfataric and fumarolic activity of volcanoes are of great interest not only for solving the problems of the geology, volcanology and utilization of thermal springs, but also for elucidating the abiogenic synthesis of various organic compounds.

Volcanic gaseous products contain hydrogen, water vapour, carbon monoxide, carbon dioxide, nitrogen, hydrogen cyanide, ammonia, hydrocarbons¹⁻⁵, and other components that can, under certain conditions, yield more complex substances as a result of reactions⁶⁻⁸.

Reliable determination of the chemical composition of gases is complicated by a number of factors, the effect of which on the analysis results is difficult to assess. These include (1) difficulties in sampling, arising from elevated temperatures, dilution of the gases with air, etc., (2) variations in the composition of the sample during its storage and preparation for analysis and (3) changes in the composition of gas samples taken from a particular hydrothermal system in the course of time.

Although the analysis of volcanic gases by various methods has been widely covered in the literature, including tables summarizing worldwide data^{9,10}, the interpretation of most measurement results is difficult for the above reasons. This is particularly true for gases discharged by active volcanoes during eruption. The lack of satisfactory data concerning the composition of such volcanic gases has been mentioned elsewhere^{6,11}.

However, recent work published by Tazieff's group¹² shows the possibility of determining the chemical composition of volcanic gases at the eruption site with the aid of a field chromatograph. The analysis of gases *in situ* considerably enhances the reliability of measurements and allows the actual ratio of the components of mixtures to be determined at a particular point in time.

To solve these problems and to determine chromatographically the composition of gases at the point of sampling, a field chromatograph has been developed.

EXPERIMENTAL

Laboratory and field tests on the self-contained portable gas chromatograph have shown that its sensitivity threshold, in the case of calibration with air, is about

10^{-5} g, the current through the bridge of the thermal conductivity cell (Gow-Mac, Madison, NJ, U.S.A.) being 150 mA. Calibration graphs were derived from peak areas. The samples were separated on stainless-steel columns (1.5 m \times 2 mm I.D.) packed with Porapak Q (100–120 mesh) (Waters Assoc., Milford, MA, U.S.A.). The detector and columns were housed in a common thermostat which is essentially a steam-jacket. The measurements were carried out isothermally at ambient temperature and at the boiling point of the heat-transfer medium.

The total weight of the field chromatograph is 5.5 kg, including the bottle of carrier gas. The power supply to the instrument consists of 12-V silver–zinc batteries. The instrument was designed for 8 h of continuous operation. The electronic part of the instrument was illustrated and its applications described in an earlier paper¹³.

The sampling of gases with a high water vapour content were carried out using procedures described elsewhere^{1,14}, without using any solutions absorbing individual components.

The gas samples from the Nizhne–Koshelevsky thermal field were taken in 1979 in 150–200 cm³ glass ampoules that had been washed and evacuated in advance, which were immediately sealed. In 1980 gas samples were also taken in evacuated glass ampoules provided with an air-tight injector having a silicone-rubber septum. However, such ampoules were later found to be permeable to air when samples are stored for a long time in an evacuated state. The samples were analysed on Varian Aerograph 1800 and Pye 104 chromatographs equipped with CDS-101 and Kent Chromalog 2 integrators, then identified using an LKB-9000 gas chromatograph–mass spectrometer. The separations were carried out with 2 m \times 2 mm I.D. glass columns packed with Porapak Q (60–80 mesh) and molecular sieve 5A (50–80 mesh) (Alltech, Arlington Heights, IL, U.S.A.) and 1 m \times 2 mm I.D. columns packed with Tenax GC (30–60 mesh) (Applied Science Labs., State College, PA, U.S.A.).

RESULTS AND DISCUSSION

The results of field analyses showed that the major component in the vapours and gases discharged from the thermal fields after water vapour, is carbon dioxide (Table I). The concentration of methane does not exceed 1.5% by weight. The chro-

TABLE I
COMPOSITION OF GAS SAMPLES (WEIGHT-%)

Field analysis: August 1979.

<i>Point of sampling (thermal fields)</i>	<i>T(°C)</i>	<i>O₂ + Ar + N₂</i>	<i>CO₂</i>	<i>H₂S</i>	<i>CH₄</i>
Vostochnaya Pauzhetka well	97	40.9	57.1	N.D.*	2.0
Severo–Kambalny range 1st group, lower point	95	24.4	74.6	N.D.	1.0
Severo–Kambalny range, 1st group, upper point, vapour–gas spray	95	17.2	81.8	N.D.	1.0

* N.D. = Not detected.

matogram is shown in Fig. 1. Increasing the temperature to 100°C did not provide any additional information about the composition of the gases.

Our field experience has shown that the use of a portable self-contained chromatograph offers the advantages of statistical reliability of the results and the possibility of monitoring the sampling procedure, in view of the fact that the atmospheric oxygen contaminating the volcanic gas during sampling often results in changes to the chemical composition.

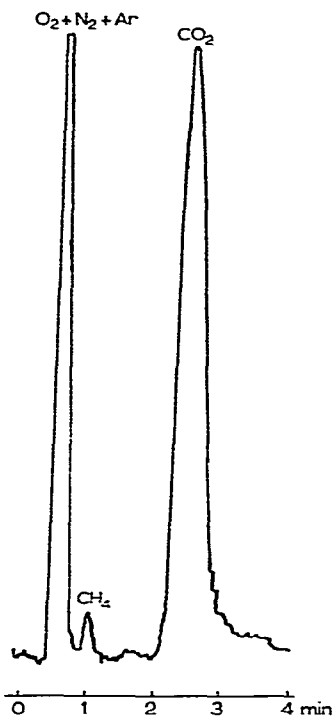


Fig. 1. Gas sample from Vostochnaya Pauzhetka well. Field chromatograph. Sorbent, Porapak Q; column, 1.5 m \times 2 mm I.D.; sample volume, 300 μ l; temperature of column and detector, 25°C; carrier gas, helium (30 cm³/min).

However, an instrument designed for field application cannot incorporate many of the advances in gas chromatography. The concentrations of some gases are insignificant and lie below the sensitivity range of a field chromatograph. The separation of helium and hydrogen and of argon and oxygen requires low temperatures and adequately conditioned columns. This is why field work should preferably be complemented by laboratory analysis.

The use of a flame-ionization detector has made it possible to determine the concentration of light hydrocarbons (C₁-C₆). The results (Tables II and III) are presented with due account for the correction factors taken from Dietz's work¹⁵. The methane peak was selected as a reference as it is quantitatively present in all chromatograms. The gas taken from well 9 is characterized by a high content of nitrogen and methane with almost no water vapour. The argon to nitrogen ratio is almost twice as

TABLE II
COMPOSITION OF GAS SAMPLES (WEIGHT-%)

Laboratory analysis: August 1979.

Point of sampling (thermal fields)	T(°C)	O ₂ + Ar	N ₂	CO ₂	H ₂ S	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₃ H ₈	ΣC ₄ H ₁₀	ΣC ₅ H ₁₂	ΣC ₆ H ₁₄
Severo-Kambalny range, 1st group, lower point, spontaneous gas	15	1.24	5.76	92.64	N.D.*	0.34	5.0 · 10 ⁻³	2.8 · 10 ⁻³	N.D.	N.D.	N.D.	N.D.
Vernine-Koshelevsky, vapour-gas spray	95	5.45	18.08	76.36	N.D.	0.11	3.0 · 10 ⁻³	5.0 · 10 ⁻⁴	N.D.	N.D.	N.D.	N.D.
Nizhne-Koshelevsky well 9, depth 600 m	20	0.89	10.37	72.64	N.D.	14.63	1.13	0.48	0.20	0.05	0.20	0.20

* N.D. = not detected.

TABLE III
COMPOSITION OF GAS SAMPLES (WEIGHT-%)

Laboratory analysis: August 1980.

Point of sampling (thermal fields)	T(°C)	Ar	O ₂	N ₂	CO ₂	H ₂ S	CH ₄	C ₂ H ₆	C ₃ H ₈	ΣC ₄ H ₁₀	ΣC ₅ H ₁₂	ΣC ₆ H ₁₄
Nizhne-Koshelevsky field: well 9, depth 600 m	12	0.41	1.94	14.00	66.64	N.D.*	15.95	0.73	0.24	6.0 · 10 ⁻²	< 10 ⁻²	N.D.
		0.49	2.12	14.96	64.80	N.D.	16.63	0.74	0.20	5.0 · 10 ⁻²	< 10 ⁻²	N.D.
		0.54	1.54	13.12	68.50	N.D.	15.18	0.77	0.23	6.0 · 10 ⁻²	2.0 · 10 ⁻²	N.D.
		0.35	1.37	11.62	67.84	N.D.	17.85	0.74	0.20	3.0 · 10 ⁻²	< 10 ⁻²	N.D.
well 10, sample 1020	12	0.21	1.60	6.31	86.37	1.34	3.93	0.14	4.0 · 10 ⁻²	1.0 · 10 ⁻²	1.0 · 10 ⁻²	1.0 · 10 ⁻²

* N.D. = Not detected.

high as that in air. It has also been established that the condensates of the samples taken in the Koshelevsky thermal fields contain C₉–C₁₄ hydrocarbons, aromatic hydrocarbons, aldehydes, etc.⁴. The results (Tables II and III) and published data^{5,16} suggest that the chemical composition of the gases from the Nizhne–Koshelevsky thermal field has remained stable over several decades. The gas from well 10 was sampled during drilling and provides no additional data except for having a unique composition.

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REFERENCES

- 1 L. A. Basharina, *Byull. Vulkanol. Stn. Akad. Nauk SSSR*, 24 (1956) 21.
- 2 A. M. Chirkov, L. N. Barabanov, L. A. Basharina and K. K. Zelenov, *Byull. Vulkanol. Stn. Akad. Nauk SSSR*, 48 (1972) 33.
- 3 S. I. Naboko (Editor), *Volcanism, Hydrothermal processes and Ore-Bearing*, Nedra, Moscow, 1974, p. 209.
- 4 L. M. Mukhin, V. B. Bondarev and E. N. Safonova, *Mod. Geol.*, 6 (1978) 119.
- 5 V. V. Ivanov, *Tr. Lab. Vulkanol. Akad. Nauk SSSR*, 12 (1956) 197.
- 6 S. W. Fox and K. Dose, *Molecular Evolution and the Origin of Life*, Freeman, San Francisco, 1972.
- 7 V. B. Bondarev and N. V. Porshnev, *Dokl. Akad. Nauk SSSR*, 252 (1980) 455.
- 8 J. Oro and J. Han, *J. Gas Chromatogr.*, 9 (1967) 480.
- 9 D. E. White and G. A. Waring, in M. Fleischer (Editor), *Data of Geochemistry*, 6th ed., U.S. Geol. Surv. Prof. Pap., No. 440-K, 1963, p. 1.
- 10 G. E. Sigvaldason, in *Phys. Volcanol.*, Amsterdam, 1974, p. 215.
- 11 V. N. Sharapov, I. B. Simbirev, G. A. Tretyakov, L. B. Milova and A. I. Vasileva, *Magmatism and Hydrothermal Systems of the Volcano Mutnovsky, Kamchatka*, Nauka, Novosibirsk, 1979, p. 100.
- 12 Le Guern, P. Bicocchi, A. Nohl and H. Tazieff, *C.R. Acad. Sci.*, 288 (1979) 867.
- 13 D. F. Nenarokov, S. S. Karavaev, V. V. Brazhnikov and K. I. Sakodynskii, *Chromatographia*, 4 (1971) 106.
- 14 A. M. Pozhkov, R. V. Guseva and A. A. Ponomarev, in *Hydrothermal Processes in Regions of Contemporaneous Magmatism Activity*, Nauka, Moscow, 1977, p. 198.
- 15 W. A. Dietz, *J. Gas Chromatogr.*, 5 (1967) 68.
- 16 N. S. Beskrovny and V. A. Lobkov, in *Hydrothermal Processes in Regions of Contemporaneous Magmatism Activity*, Nauka, Moscow, 1977, p. 110.