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Miniaturization of Gas-Chromatographic Instruments

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Abstract—The current state trends in the development of portable gas chromatographs were considered. A classification of portable chromatographs was proposed (compact devices, field devices, on-chip micro chromatographs, and special micro chromatographs). Performance and analytical characteristics of domestically produced and foreign portable chromatographs were presented. Portable gas chromatographs for space exploration, high-flow-rate gas chromatography, and new applications of portable chromatographs were considered.

The interest in the miniaturization of gas-chromatographic instruments (the development of portable, transportable, and handheld chromatographs) was shown for four decades. This interest has increased in the past decade because of the development of so-called field analytical chemistry. It takes often days or sometimes weeks to perform a conventional analysis, where specimens are sampled, transported, kept, and only then analyzed. In contrast, field analyses are performed at the place where a test sample is located. On-site rapid analyses are required in many cases, because the results may be important for human and animal safety and environmental protection, or a delay in the results of analysis can lead to considerable financial losses. For field applications of analytical chemistry, test methods, test tools, and components for rapid on-site tests are developed [1].

In addition, for the last five years, leading chromatographic companies (Perkin-Elmer, Hewlett-Packard, and Varian) have absorbed smaller companies that produced portable chromatographs (Photovac, Microsensor Technology, and Chrompack, respectively) and started investing in these fields.

There are several basic fields of application for portable chromatographs. These include the analysis of production-area air, living-area air, and mine air; the analysis of the atmosphere of enclosed spaces and compartments (car passenger, spaceship, and submarine compartments and cabs); the investigation of atmospheres of other planets; the analysis of surface waters and contaminated soils; on-the-fly monitoring of wastes and emissions; the analysis of exhausts; the determination of toxicants and their metabolites in the environment; the analyses of emergency situations (explosions, accidents, conflagrations, etc.); rapid forensic analysis; the detection of explosives in airports; the geological survey of gas and oil basins; the determination of leaks in gas pipelines; determination of blood alcohol levels in drivers; the rapid control of foods; and many other applications.

Main directions in miniaturizing chromatographs. Table 1 presents a classification of portable chromatographs. Compact chromatographs were primarily designed for mobile laboratories, though they can be used at stationary ones. Basic performance characteristics of portable chromatographs are similar to those of usual laboratory devices. Among them are the Tsvet-KhPM-5, the Kristall-5000, the HP 6850, and other chromatographs. This direction is rather promising because the present-day technologies permit a significant decrease in chromatograph size without sacrificing its technical and performance characteristics. The benefits are obvious: savings of power, materials, and laboratory place.

A second promising direction in the miniaturizing of chromatographs is the development of portable gas chromatographs (transportable or handheld) for on-site analysis [2]. Such instruments are gas or power operated. They are light, reliable, easy to operate, and provide rapid analyses. Their performance characteristics are significantly worse than those of the previous-type instruments. These instruments can be used in laboratories for simple analysis. This is why many chromatographs of this type are adaptive.

Field chromatographs can give results immediately. However, they cannot completely replace laboratory instruments. Field chromatographs can confirm whether the composition of a sample changes or not during its transportation (i.e., between sampling and analysis). However, in some cases field chromatographs can give more reliable results than laboratory instruments, e.g., in determining volatile compounds that cannot occur in a sample for a long time.

A third direction is the development of super-miniaturized chip-based chromatographs. Microsensor Technology (USA) pioneered in the development of miniaturized gas chromatographs. In 1975 at Stanford University, researchers of this company developed a prototype micro chromatograph based on silicon technology. This chromatograph was equipped with a

Table 1. Classification of portable chromatographs

Туре	Purpose	Advantages, capabilities			
Compact	For mobile and stationary laboratories	Saving of costs, power, materials, and space with analytical characteristics similar to those of stationary chromatographs, weight 10–25 kg			
Portable, transportable, field	For on-site analysis	Small weight, rapid analysis, gas and power self-supporting, weight 5–15 kg			
Chip-based chromatographs (silicon micromachining technology), handheld, personal, pocket	For on-site analysis, handheld	For the fast resolution of relatively simple analytical problems, fully self-supporting, restricted analytical capabilities, weight 0.2–3 kg			
Specially designed chromatographs, micro chromatographs	For space investigations	Automated analysis, small weight, resistant to impact and shaking			

katharometer. It was intended for air analysis in space-crafts [3–5].

Chromatographs of the fourth type are portable instruments for space investigations [6–8]. Stringent requirements are imposed upon these chromatographs. In addition to light weight and low power consumption, these chromatographs should possess extreme reliability under diverse conditions (at atmospheric pressure, in vacuum, at high pressures and temperatures), high stability and to vibrations resistance to impact, quick warm-up, minimum data-transfer time, and long-term stability of characteristics (up to ten years and longer).

ENGINEERING AND DESIGN FEATURES AND PERFORMANCE CHARACTERISTICS OF DOMESTICALLY PRODUCED PORTABLE GAS CHROMATOGRAPHS

Table 2 presents basic analytical properties of the most popular domestically produced portable gas chromatographs.

Below we consider the main applications of these chromatographs.

Domestically produced portable chromatographs

KhPM-1 and KhPM-2 portable compact chromatographs were designed for the determination of single substances or total organic substances in gas mixtures. They can be used for detecting gas leakages in gas networks, city or plant pipelines, in oil and gas exploration, and as mobile instruments for performing various analyses. The instruments can operate in the self-supporting field mode for up to eight hours. The instruments are equipped with built-in microprocessors. These models were developed in 1977.

KhPM-4 handheld gas chromatograph has the same capabilities as the KhPM-2 chromatograph. Moreover, it can be used for atmospheric-air analysis. This chromatograph is more versatile because, in addi-

tion to a flame ionization detector, it is equipped with an extracompact, power-saving, modulated-flow thermal conductivity detector.

Sampling and injection are performed with a micro syringe, a valve, and a micro compressor. Data is processed with a built-in microcomputer. There is a port for a chart recorder [10].

Tsvet P-182 chromatograph is equipped with a photoionization detector for determining pollutants in the atmosphere, especially polynuclear aromatic hydrocarbons. Compared to FID, this detector is more sensitive to PAHs by a factor of 20.

A gas (helium) is fed with a built-in cylinder (0.4 L) or with an external source. A built-in control and data processing unit automatically acquires and stores parameters of peak (heights, areas, and retention times) and calculates the required concentrations.

MKh series chromatographs are light weight (3 kg). These are the MKh-1 chromatograph with a thermal conductivity detector, the MKh-2 chromatograph with flame-ionization and photoionization detectors, and the MKh-3 chromatograph with a thermionic detector. The micro chromatographs are fully gas and power operated. A microprocessor control unit based on a single-crystal microcomputer requires low power (only 6 W). A built-in small battery provides long-time operation without recharging. A solid-state compact (matchbox size) hydrogen generator produces compressed gas at a flow rate of 10 mL/min. Hydrogen as a carrier gas is very suitable for flame ionization, thermal conductivity, thermionic, and photoionization detectors. Capillary columns are used with adsorbed or immobilized liquid phases on the inner surface. Such columns are highly efficient. Moreover, they are characterized by low-flow resistances and extremely low consumption of the carrier gas. The gas injector was made using silicon-based technology. The columns are placed in specially designed removable cassettes that are thermostatically controlled either in an isothermal

Table 2. Technical characteristics of domestically produced portable chromatographs

		Technical characteristics						
Model	Company	detectors	injection	thermostat	columns	power, w	weight, kg	operating voltage, v
KhPM-1	OAO Tsvet	FID	Pump	Isothermal	Packed	1.5–40	10	12
KhPM-2	OAO Tsvet	FID	Valve, sy- ringe	Isothermal 50–200°C	Packed 1–3 m	1.5–40	16	220 VAC, 12 VDC
KhPM-4	"	FID, TCD	"	50-200°C	_	20	11	"
Tsvet P-182	"	FID	"	50–200°C	Capillary 0.5–3 m	40	12	"
Tsvet-MKh	"	FID, PID, TID, TCD		50–200°C		6	3	12
EkhO-M	OOO Sib- ertekh	ECD	Syringe; Preconcentrator	40–175°C	Polycapil- lary	40	11	12 VDC
EkhO-EW	"	PID, ECD, AID	Valve, sy- ringe	50–180°C	Polycapil- lary	25, 60	12.9	"
PGMKh	Khromdet	FID	"	50–100°C			10	"
FGKh-1	NPP Khim- pribor	FID	"		Capillary 20–25 m		10	"
FGKh-2	"	PID (TCD, TID)		50–250°C, programmed with 10°/min	"		10	"
AKhG-002	Ekonoks	TCD	Valve	_	_	70	16.5	"
MKhK	NIIKhROM	TCD	Valve	50–150°C	1, 2, 4, 8 m	60, 400	6–8	220
MKhP	"	PID	Syringe				"	
MKhF	"	FID					"	

Note: Detectors: FID is flame-ionization detector, TCD is thermal conductivity detector, PID is photoionization detector, ECD is electron-capture detector, TID is thermionic ionization detector, and AID is argon ionization detector.

mode (from 50 to 200°C) or in a temperature-programmed mode (at a rate of 1 to 10°C/min). For heating, an extra power supply unit is connected to the thermostat heaters. To provide hydrogen burning, oxygen is supplied from a hydrogen generator. A microcomputer provides storing as many as ten chromatograms, each including up to ten peaks. The data are displayed on a liquid-crystal screen, which allows the sequential control of retention times, peak heights and widths, and component concentrations (after calibration). The chromatograph can be hooked up to a more powerful computer.

EkhO-M portable chromatographs were designed for the rapid detection of explosives in airports. These chromatographs can also be used for the field analysis of toxic organic compounds.

The chromatographs are equipped with fast polycapillary columns (efficiency up to 5000 theoretical plates), highly sensitive electron capture detectors (minimum detectable level 5×10^{-13} g of an analyte in a sample), an injector for remote sampling, and a display. The instrument can be connected to a chart recorder or a notebook, and the data can be processed

using internal or external databases. A preconcentrator provides preconcentration with a factor of 1000. One determination takes 20–200 s. During tests in the United States, the ECD of this chromatograph was found to be one of the most reliable ones [2].

EkhO-EW portable chromatograph designed for the field analysis of substances of different classes. These chromatographs are manufactured by the joint Russia-American Sibertekh Company. The chromatographs are equipped with three changeable detectors: a photoionization detector, an argon-ionization detector, and an electron capture detector. They are also equipped with three changeable injector systems: a syringe injector, an automated loop injector, and an injector with a remote preconcentrator. The instruments can operate with straight polycapillary columns with the following liquid phases: SE-30, SE-54, and OV-17 polysiloxanes and Carbowax 20M polyethylene glycol. Chromatographs of this series are suited for routine analyses in industry; field water, soil, and air analyses; the rapid analyses of natural gases and mineral oils at places of exploration, production, and processing sites [11]; and for other purposes.

Handheld Compact Gas Chromatograph with a photoionization detector (Khromdet) was first designed for air monitoring in industrial and living areas, especially for the determination of such toxic and dangerous compounds as benzene, toluene, xylene, acetone, cyclohexane, chlorobenzene, and others at the MAC level. Among the characteristic features of this instrument is the temperature control capability of the whole analytical unit, including the injector, and the presence of a firmware for metrological data processing, which provides calibration and the elimination of memory effects due to the backflush of the injection port.

FGKh-1 and FGKh-2 Portable Gas Chromatographs are recommended for mobile analytical laboratories, sanitation inspection teams, and rescue parties for rapidly controlling the atmosphere of production premises and sanitary zones. They are also suited for on-site field analysis. The FGKh-1 chromatograph is equipped with a built-in integrator. The FGKh-2 instrument comes with a notebook.

AkhG002 Compact Gas Chromatograph was designed for technological control in heat-and-power engineering and in the electric machine industry. It provides the determination of hydrogen, methane, oxygen, nitrogen, carbon oxide, and carbon dioxide.

Compact Chromatographs of the MKh series were designed for determining alcohols (C₁–C₅ in the form of alkyl nitrites) in forensic examinations and toxicological analysis (by the procedure accepted by the Ministry of Health, Model MKhK), for the analysis of natural gases and the determination of burning gases in the air (according to *GOST [State Standard]* 23 781, Model MKhG), for the detection of alcohol substitutes in biological samples (by the procedure accepted by the Ministry of Health), for the quality control of strong drinks (Model MKhP), and for the determination of aromatic and other organic compounds in the environment (Model MKhF). The instruments can be equipped with as many as eight types of analytical columns.

TECHNICAL AND ANALYTICAL CAPABILITIES OF FOREIGN PORTABLE GAS CHROMATOGRAPHS

Table 3 presents technical characteristics of the most well-known gas chromatographs manufactured abroad. The first portable gas chromatographs were manufactured in 1968–1969. Among them is following:

The chromatograph manufactured by Carle Instrument Inc. (weight 8.8 kg) with a flame ionization detector, a katharometer, and two parallel columns. The chromatograph operates in an isothermal mode (to 200°C) and requires (115 V AC) a power supply [12];

The Gow-Mac. Instruments chromatograph (8 kg) has flame ionization and thermal conductivity detec-

tors, an isothermal mode to 300°C, 20 V DC and 115 V AC power supply [13];

The chromatograph manufactured by Analytical Instruments Development (8.8 kg) has flame ionization and thermal conductivity detectors, an isothermal mode to 250°C, 10 V DC power supply [14];

The instrument by Unico Environmental Instruments (15.2 kg) has two parallel columns, flame ionization and thermal conductivity detectors based on thermistors, without temperature control [15].

In its analytical capabilities, the Model 311D Portable Gas Chromatograph ranks together with laboratory chromatographs. The thermostat can operate isothermally up to 200°C. It is the heaviest portable chromatograph (25 kg) enclosed in a metal container with handles for carrying. The Model 311 D Portable Gas Chromatograph can be simultaneously equipped with two from three available detectors: a photoionization detector, an electron capture detector, and a far-UV absorbance detector ($\lambda = 120$ nm). The injector allows manual syringe injections of liquid samples into capillary or packed columns. The built-in sample pump permits air sampling. A 10-port valve was designed for gas sampling. The installation of a precolumn and a backflush mode is possible. A cylinder of an aluminum alloy provides carrier gas for 8-10 hours of operation (equipped with a refill adapter). A built-in microprocessor can record chromatograms and print the results; a built-in chart recorder is also provided.

All units are easily accessible. The instrument is highly reliable and easy to maintain. An explosion-proof model of the instrument is available by a special order.

Snapshot is a held-hand chromatograph (4 kg). It is fully gas and power operated. It is equipped with readily interchangeable application modules (seven units). Each module is preprogrammed for detecting target chemicals. SnapShot is used for the determination of light aromatic hydrocarbons in the air. The determination of benzene takes 4 min. The analysis of a mixture of benzene, toluene, ethylbenzene, and o- and p-xylenes takes 10 min. The minimum detectable concentrations are 1×10^{-5} vol. % for benzene and 1 ppm for toluene and C₈ aromatic compounds. The total concentration range covers 0.1 to 1000 ppm. The instrument is equipped with a metal capillary column $(10 \text{ m} \times 0.53 \text{ mm})$ a CP-Wax (polyethylene glycol) nonpolar stationary phase. Carbon dioxide is used as a carrier gas. It is supplied from special small cylinders filled with liquefied CO₂; the column is supplied with the chromatograph. A sample is injected using a valve. Separations are performed at 45°C. A photoionization detector (a 10.6 eV lamp) is used. Chromatograms are not displayed but stored. If necessary, the chromatograms can be printed or translated to a computer via an RS-232 port (up to 500 analysis data can be stored, memory 30 Kb). The instrument is easy to operate. In 1994, successful field tests were performed the

Table 3. Technical characteristics of foreign portable chromatographs

		Technical characteristics							
Model	Company	detectors	injection	thermostat	columns	operating voltage, V	weight, kg		
311DGC	HNU Systems	FID, ECD, PID, FPD, and TCD		50–200°C, programmed with 1–15°/min	CC or PC	110, 115, 230	25		
Model 4100	Electronic Sensor Technology	Surface acoustic wave resonator	Cryofocus- ing mode	50–200°C, programmed	CC	120, 12	15. 9		
MSI-301	Microsensor Systems	Surface acoustic wave resonator	Injection pump	5–40°C	CC or PC	120, 12	5.4		
P200 P200H	MTI Analytical Instruments	TCD	Micro-ma- chined injec- tor	50–180°C	_	12	10.4		
FM-2000	O.I. Analytical	FID, PID, FPD, and FID/PID	Valve, pre- concentrator	_	CC	110	8.1		
Snapshot	PE Photovac	PID	Valve	45°C	Large-diam- eter CC	12	4.4		
Voyager	PE Photovac	PID, ECD	Syringe, valve	55–80°C	Large-diameter CC, micro pump	12	6.8		
Scentoscreen	Sentex Systems	ECD, PID, TCD, micro argon-ioniza- tion detector		To 180°C, programmed	CC 30 m, PC 3.6 m	110/220	14		
Scentograph Plus II	Sentex Systems	ECD, PID, TCD, micro argon-ioniza- tion detector	Syringe, valve, pre- concentrator	To 180°C, programmed	CC to 105 m	12	21.8		
Micro GC CP-2002	Chrompack Varian	TCD	Valve	30–180°C, isothermal	PC 3.6 m; two PC and CC columns	110, 12	6.7		

Note: Detectors: FID is flame-ionization detector, ECD is electron-capture detector, PID is photoionization detector, FPD is flame photometric detector, TCD is thermal conductivity detector, PFPD is pulse flame photometric detector; columns: CC is capillary columns, PC is packed columns, and PMC is packed micro columns.

results obtained agreed well with those obtained using a HP 5890 GC laboratory stationary chromatograph [16].

PE Photovac Voyager is a compact (6.8 kg) battery-operated chromatograph. It can be carried conveniently by its handle or in a specially designed harness leaving both hands free. The instruments come with several application assays and are capable of operating in various modes: (1) fast scanning of total volatile substances in industrial reservoirs before their filling; (2) collection of data on the concentration of compounds while servicing manufacturing equipment; and (3) development of procedures for the specialized determination of pollutants in air. Additional compounds can be added to the assays. The instrument is very simple to use. Running an assay and collecting data is as simple as press and go. The instruments are very convenient for the determination of toxic volatile

organic compounds in working areas and in soils in emergency situations. After running an analysis, a list of detected components and their concentrations (in ppm or ppb) are displayed on a screen.

HP Micro GC is a portable gas micro chromatograph. Hewlett-Packard guarantees that this chromatograph provides field results of quality close to that of laboratory instruments. The chromatograph is suited for rapid analyses of petroleum sites on the open sea, vent gases and vapors, and volatile emissions from wastes. The instrument can be used for analyses in shops and reactors.

Four chromatographic modules are arranged in a chromatograph case (brief case-size). Miniaturized injectors and detectors permit the use of short capillary columns of small diameter providing highly efficient and rapid separation. A precision micro injector is char-

Company	Bruker Instr.	Inficon	Viking Inst.
Model	EM640, EM640S	Hapsite	Spectra Trak 572
Thermostat	50–300°C isothermal mode and three programming rates	-	50–325°C isothermal and programmed
Columns	30 m × 0.2 mm	$30 \text{ m} \times 0.32 \text{ mm}$	60 m × 0.32 mm
Carrier gas	N ₂ , He	N_2	He, N_2, H_2
Injection	Capillary split or splitless injector	_	Capillary split or splitless injector
Mass range	1–640	1–300	1.6–700
Maximum mass-scanning rate	2000 a.m.u./s	1000 a.m.u./s	1800 a.m.u./s
Ionization	Electron impact	Electron impact, 70 eV	Electron impact, 70 eV
Vacuum system	Getter pump	Getter pump	Turbomolecular pump
Sensitivity	1 ng/s (S/N 10 : 1)	100 pg for hexachlorobenzene	
Dynamic range	10^{9}	_	10^{6}
Weight, kg	60	16	34
Dimensions $(h \times w \times d)$	$55 \times 45 \times 35$	$18 \times 43 \times 46$	$46 \times 61 \times 29$

Table 4. Technical characteristics of portable GC mass spectrometers

acterized by high reliability. A sensitive katharometer is micro-machined in silicon. An analysis of natural-gas samples (C_1 – C_{10}) takes 160 s. Analyses of mixtures of inorganic gases with sulfur-containing compounds take 30 s. Mixtures of other volatile compounds can be analyzed within 50 s. The instrument provides backflush capability for analyzing mixtures of heavy components. The shortening of the analysis time by a factor of ten allows one to resolve industrial problems rapidly.

The P series micro chromatograph is a portable and self-supporting device for field analysis. It is equipped with a built-in gas container providing operation for 40 hours and a battery providing operation for 8 hours.

Quad chromatographs were designed for rapid complex analyses.

Varian Micro GC. Model CP-2002P is a portable one- or two-channel gas chromatograph. Micro injectors (without moving parts) and katharometers (volume only 200 nL) are based on silicon micro-machining technology. The use of capillary columns allows mixtures like natural gas to be analyzed rapidly (up to 650 analyses per day). The precision and reproducibility of the instrument satisfy the ISO 6976 Standard. The instrument is used in field analyses and for gas monitoring near industrial plants. In 2000, the Varian-Chrompack Company manufactured the CP-2003 portable gas chromatograph with a micro electronic gas control, backflush, and micro-gasifier capabilities for the analysis of liquefied gases. This instrument can be equipped with four independent modules for solving complex analytical problems. Analytical capabilities of the CP-2003 are better than those of the other micro chromatographs.

Portable gas chromatograph—mass spectrometers (Table 4 [2]) provide both quantitative and qualita-

tive field analyses. These instruments can be mounted on vehicles. All instruments are based on microprocessors providing self-contained operation. The instruments can operate with more powerful external computers. These instruments are indispensable for the detection of dangerous pollutants in unknown mixtures (in explosions and accidents, for analyzing poisongases or explosives, etc.)

Chip-based chromatographs Based on the dielectric properties of pure silicon, a special technology was developed. Using this technology, one can fabricate miniature microelectronic devices [17]. Fabrication includes several steps: polishing of a silicon plate, oxidation to SiO₂, deposition of a photoresist, photolithography, etching of silicon oxide, the removal of the photoresist, etching in the silicon microstructure, and others. This technology can be used to create any threedimensional item in silicon. The technology seems to be most promising for manufacturing miniaturized gas chromatographs, in particular, micro injectors, capillary columns, and thermal conductivity detectors. All these devices can be arranged on a round plate 5 cm in diameter. At first, such silicon gas chromatographs operated at room temperature and were used for the analysis of gases and volatiles compounds. In [18, 19], a 15-component mixture was separated for 10 s at 28°C using a capillary column (200 cm \times 0.135 mm) and a DB 1701 film liquid phase.

Reviews [20, 21] were devoted to miniaturized chromatographs.

A more perfect micro chromatograph based on micro-machining technology was described in [22]. The dimensions of the device are 23 cm² with a height of 2.5 mm. A spiral capillary column (0.9 mm in

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Purpose	Detectors	Columns	Temperature mode	Carrier gas	Weight, kg	Power, W	Develop- ment year
Analysis of gases, water, hydrocarbons, and organic acids (Moon project)	Three dis- charge detec- tors	Three paral- lel packed columns	Isothermal, 105°C	Не	5.6	72	1962–1963
Analysis of products of the Mars soil pyrolysis	Mass spec- trometer	Micro packed col- umn	Isothermal	Не	7 (GC + MS) 0.1 (GC)	10	1966
Analysis of the Mars atmospheric composition	Micro katha- rometer	Two micro packed col- umns	Isothermal	Не	1.2	1	1966
Spacecraft air analysis (permanent gases, water, hydrocarbons, etc.)	Ionization cross-sec- tion detector	Three parallel columns	Isothermal, 65°C	Не	-	-	1966
Analysis of gases and vola- tile compounds in the Mars atmosphere	Micro katha- rometer	Two col- umns packed with Pora- pack Q and R		Не	-	_	1968
Analysis of the Mars atmosphere composition (minia-		Micro packed col-	Isothermal, 23°C, pro-	H_2	0.07–0.15 (without elec-	2.5–5	1970

grammed

Table 5. Portable gas chromatographs for space research

length) was coated with copper phthalocyanine as a stationary phase (film thickness $0.2 \mu m$).

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turized gas chromatograph)

Applications of chip-based gas chromatographs for analyzing volatile pollutants were described in [23–27].

PORTABLE GAS CHROMATOGRAPHS IN SPACE RESEARCH

Portable gas chromatographs for space research (analysis of the atmospheric and ground of planets and spacecraft air) have been developed since 1962. Relevant reviews were published [6–8]. Special requirements for gas chromatographs for space research were discussed in detail in [6–8, 28–30]. These requirements govern the design of the automated setups for sample preparation (adjusting sample pressure to the column pressure, compression or decompression, etc.) and sample injection. They also determine the applications of capillary or micro-packed columns with very small gas-carrier flows and very stable sorbents, applications of temperature-programmed conditions, automatic switching to different columns, and others.

In 1962–1970, several gas chromatographs for space research were developed (see Table 5 presenting the basic technical characteristics of these instruments).

Since 1982, the USSR and the USA have launched spacecrafts to Venus and Mars. These spacecrafts were equipped with scientific instrumentation, including portable gas chromatographs. For the first time, the determination of the atmospheric composition of these planets was performed using gas chromatographs and GC mass spectrometers [31–35]. In the USSR, the

research was performed within the context of the Venera 11-14 and Vega projects. In the USA, the research was performed in the context of the Viking and Pioneer–Venus projects.

tronic unit)

Table 6 contains the basic technical characteristics of gas chromatographs used in these investigations. In addition to the properties mentioned above, the instruments are characterized by high vibrostability and resistance to impacts. It was necessary for these characteristics to be stable within ten years (estimated flight time to some planets).

A miniaturized gas chromatograph used in the Viking project had the dimensions $9 \times 9 \times 6$ cm. It was connected with an injection system and a carrier-gas (He) supplier. The instrument was equipped with two columns and a katharometer. The injector consisted of five miniaturized solenoid valves. It provided the injection of sample volumes of up to 0.1 mL. Identical columns (one column was reference) (7.6 m \times 1.1 mm) were made of stainless steel and packed with Porapack Q (particle size 100-120 mesh). An analysis was performed at 24° C at the carrier-gas rate of 13.5 mL/min. A mixture of H_2 , N_2 , O_2 , CH_4 , Kr, and CO_2 was separated completely; Ar and CO were separated partially.

These instruments determined for the first time the atmospheric composition of the planets. The sensitivity of the determination was as high as 0.1 nmol. Miniaturized automated gas chromatographs operated successfully and fulfilled the requirements of the program.

In addition to the analysis of the atmosphere, the GC Mass Spectrometer (Viking project) had to detect organic impurities in the Mars soil after its pyrolysis [36].

Purpose	Project	Detectors	Columns	Thermostat	Carrier gas	Injection
Analysis of Mars' atmosphere and soil	Viking, 1975– 1976, (USA)	TCD, MS	7.6 m \times 1.1 mm packed with Porapack Q, 2 m \times 0.75 mm packed with Tenax	24°C	He, 13.5 mL/min	Valves
Analysis of Venus' atmosphere	Venera 11–14 Projects, Sig- ma GC 1978– 1982	Neon-ion- ization detector	Three columns packed with Polisorb, zeolite, and magnesium oxide, 2 m, 2.5 m	70°C	Ne	Valves
Analysis of Venus' atmosphere and Halley's comet's atmosphere	Vega 1984– 1985, Sigma-3 GC	Helium- ionization TCD, two ECDs	Three columns with Porapack QS, N, and E	70°C	Ne, H ₂	Valves
Analysis of Venus' atmosphere	"Pioneer–Ve- nus" 1978	TCD	$15.85 \text{ m} \times 1.1 \text{ mm}$ packed with Porapak N, $2.1 \text{ m} \times 1.1 \text{ mm}$ with poly-DBV	18°C	He, 35 mL/min	Valves
Analysis of Titan's (the Saturn's moon) atmosphere	"Cassini–Huy- gens" 1997–2004	MS	Three parallel columns with pora PLOTQ, PLOT Al ₂ O ₃ , and zeolite	Pro- grammed	_	_

Table 6. Technical characteristics of portable gas chromatographs designed for space research

In other words, it had to detect signs of life on the planet.

The whole complex consisted of an injector, a device for pyrolysis, columns, a carrier-gas supplier, and a mass spectrometer.

At the step of sampling, CO, CO₂, and H₂O were preliminarily eliminated to improve the detection limits of permanent atmospheric gases. CO and CO₂ were absorbed with lithium hydroxide and silver oxide; H₂O was absorbed with magnesium perchlorate. A soil sample was powdered and sieved to obtain particle size smaller than 300 μm. Next, the sample was injected into a pyrolysis oven and heated to 50–500°C.

A column (2 m \times 0.75 mm) made of stainless steel was packed with 2,6-diphenyl-p-phenylene oxide (Tenax GC) coated with poly-p-phenoxylene (Poly-MPE). At the beginning of the analysis, the column temperature was 50°C for 10 min. Next, the column was heated at a rate 8°/min to 200°C. The column temperature was maintained at this level for one hour. The carrier-gas flow rate was 2 mL/min. The mass spectrometer was based on electron-impact ionization and operated in the mass range from 12 to 215. Before an ion trap, hydrogen was absorbed in a palladium separator.

The result of these examinations was the determination of the composition of the Mars atmosphere (CO₂, 95.3%; N₂, 2.7%; 40 Ar, 1.6%; O₂, 0.13%; CO, 0.08–0.27%; and H₂O, 0 < 0.3%). The presence of Ne (2.5 ppm), 36 Ar (0.5 ppm), Kr (0.3 ppm), Xe (0.08 ppm), and O₃ (0.003 ppm) was detected.

Venera 11, 12 Projects. A Sigma analytical instrument consisted of a gas chromatograph and a mass

spectrometer [33, 34]. The gas chromatograph was equipped with three columns and three detectors. The first column (2 m in length) was packed with Polisorb-1 for the separation of H_2S , COS, SO_2 , H_2O , and CO_2 . The second column (2.5 m) packed with molecular sieves was designed for the separation of permanent and noble gases $(H_2, O_2, N_2, CO, He, Ar, Kr, and CH_4)$. Argon was determined using the third column packed with manganese oxide. The column temperature was 70°C. Neon was used as the carrier gas. The chromatograph was equipped with a neon-ionization detector with a source of beta rays. The minimum detectable level was lower than 1 ppm (sample volume of 1 mL). Gas chromatographs worked in the Venus atmosphere for 4 hours. Eight samplings were performed. The last sample was taken at the surface in very severe conditions (pressure 90 atm., temperature 730 K).

Sigma-2 chromatographs were used in the Venera 13 and Venera 14 projects. Their basic technical characteristics are similar to those described above.

Vega Project In the Vega project, the composition of the Venus atmosphere (June, 1985) and the gas composition of Halley's comet (March 1986) were determined [37, 38]. A Sigma-3 gas chromatograph consisted of three injection systems, three columns, and three parallel detectors. The columns were packed with Porapack QA, Porapack N, and Porapack T for the separation and analysis of gases and vapors of sulfuric acid. The first column was connected with a heliumionization detector and a katharometer (carrier gas, helium). The second and third columns were connected with an electron capture detector (carrier gas, highpurity nitrogen). The minimum detectable levels were from 0.1 to 1 ppm (100 ppm for water).

Determination of the composition of Venus' atmosphere (The Pioneer-Venus Project, USA). A gas chromatograph was equipped with a valve, two detectors, and two columns [39]. The gas chromatograph was similar to the instrument used in the Viking project with several improvements. The sample volume was 0.35 mL; a katharometer based on thermistors was used. Columns 15.85 m \times 1.1 mm were packed with Porapack N and provided the separation of mixtures of He, H₂, N₂, O₂, Ar, CO, CH₄, and Kr under isothermal conditions (18°C) at a flow rate of 35 mL/min. The second column (2.1 m \times 1.1 mm) packed with a porous polymer based on polydivinylbenzene (Poly-DVB, particle size 180–220 mesh) was designed for the separation of CO₂, NH₃, H₂O, H₂S, CO₅, C₂H₆, SO₂, HCl, and HF. This sorbent was specially synthesized for the separation of such mixtures [40]. The column temperature was 60°C; the carrier-gas flow rate was 40 mL/min. The minimum detectable levels were 1-60 ppm. The column operated for 30 min. Within this time, three analyses were performed. The chromatograph operated successfully and performed analyses at the heights 51.6, 41.7, and 21.6 km above Venus' surface [41].

The concentrations of CO₂, N₂, H₂O, O₂, Ar, CO, Ne, and SO₂ were measured. The concentrations of H₂, CH₄, Kr, N₂, NO₂, C₂H₄, C₂H₆, H₂S, COS, and C₃H₈ were determined in the vicinity of the upper determination limit.

The gas-chromatographic measurements in the Venera 11–14 and Pioneer–Venus projects gave the following composition of Venus' atmosphere: CO_2 , 96% and N_2 , 4%. The following concentrations were determined (ppm): H_2O 1–1000, CO 20–2000, SO_2 0.1–200, COS 0.35–40, H_2 25, Ar 70, Ne 7, HCl 0.4, and HF 5 × 10⁻³.

In the future, miniaturized gas chromatographs will be used for studying the gas composition of the Titan atmosphere (the largest Saturn's moon) [42, 43] and comets in the next expedition to Mars and other expeditions.

HIGH-SPEED GAS CHROMATOGRAPHY USING PORTABLE CHROMATOGRAPHS

Two tendencies in the development of modern gas chromatography can be clearly seen. These are the shortening of the separation time and rapid analyses as well as the miniaturization of gas-chromatographic instruments [44–48]. In some cases, the required separation takes several seconds [49]. This places more stringent requirements on injection systems, temperature-programming units, and detectors [50, 51], especially for field chromatographs. The author of [52] has considered the capabilities of serial laboratory chromatographs for fast separations and those of portable chromatographs with columns of small diameters. New commercial systems for high-speed chromatography are equipped with small thermostats [53] and are based on a new principle of column heating [54]. The gradient

heating of columns provides the separation of 13 compounds within 3.5 s [55]. A micro gas chromatograph with a katharometer provides the separation of mixtures of alkanes (C₁–C₄) and CO₂ within 30 s [56]. Among the other applications of such instruments in petrochemistry are the determination of H₂S and CO₂ impurities [57] and the fast screening of hydrocarbons from gasoline to diesel oil [58]. A very fast separation of mixtures of light hydrocarbons and permanent gases on PLOT columns with silica gel and Carboxen (carbon sieve) [59] and also of thermally unstable carbamate pesticides [60] was performed.

NEW DEVELOPMENTS IN PORTABLE CHROMATOGRAPHS

Nowadays, it is necessary to create portable chromatographs of the unit-based design for the quick replacement of faulty units and their repair in the field [61]. The most widespread injection method is injection using cryotraps [62] and solid-phase extraction. A pyrolysis device is used to analyze nonvolatile substances. In particular, this approach is used for the determination of microorganisms [63]. To accelerate the analysis, the selective group separation was used (e.g. aromatic compounds, olefin hydrocarbons, and saturated hydrocarbons) [64]. To lower the detection limits and improve the signal-to-nose ratio, thermaldesorption modulation was used [65]. An inexpensive multidimensional portable GC-GC system (tandem) with two short small-weighed columns and low power consumption was developed [66]. For analyses with preliminary identification, portable GC mass spectrometers were designed; they can detect poisonous gases within 20 s [67]. A specially designed CG mass spectrometer for industrial hygiene was reported in [68].

Portable automated instruments for continuous monitoring were developed in [69–71].

APPLICATIONS OF PORTABLE CHROMATOGRAPHS BASED ON RECENT PUBLICATIONS

Gas-chromatographic field determinations of organochlorine pesticides [72], low-volatile organic compounds [73], and carbon dioxide [74] were reported along with the analysis of natural gas [75] and the fast determination of tetrahydrothiophene in natural gas [76]. Gas-chromatographic procedures for the continuous monitoring of methane [77], hydrocarbons C_2 – C_{10} [78], aromatic hydrocarbons [79], and ammonia in air were developed. Small chromatographs were used for the determination of alcohols C_1 – C_5 in blood and urine in forensic examinations [81].

Portable high-speed chromatographs find their basic analytical application in solving environmental problems [82–86]. The latest published data on environmental applications [82, 85] deal with the analysis of resi-

dues of complex pesticide mixtures; gas analyses; the determination of polychlorobiphenyls and aromatic and chlorinated compounds in soil; the determination of benzene in air, polyphosphonates in air; dimethyl sulfide and carbon disulfide in air; freons in the troposphere; isoprene in the atmosphere at the ppm level [87]; analyses of volatile sulfur-containing compounds in air, water and wet precipitations using cryotrapping [88]; the determination of toxic gas in wastes [89]; and analyses of odors [90].

The detection of indoor pollutants (apartments and office buildings) is a very important problem at present. The concentrations of pollutants (mercury, formaldehyde from furniture, and emissions of various organic compounds from linoleum, paints, plastics, and others) indoors are several times higher than their concentrations outdoors (in the city atmosphere). Using a portable instrument, concentrations of toluene, α-pinene, and 1,4-dichlorobenzene were determined at the level of mg/m³ [91]. Using portable chromatographs, pesticides in plasma were determined and thermally unstable steroids and pharmaceuticals were analyzed. Widescale studies were performed using the Photovac Snapshot GC [92]. A miniaturized gas chromatograph with a preconcentrator and two flame photometric detectors [93] was used for the detection of chemical-weapon traces. To determine chemical weapons in air, various detectors were used. Among them pulse flame photometric detector and flameless halogen-selective detectors (requiring no hydrogen) were of great interest. The following detectors were used in portable chromatographs: an argon-ionization detector [94], an acoustic detector, a pulse discharge detector (electron capture and photoionization variants) [95], and a surface-ionization detector [96].

To conclude, it should be noted that the analytical capabilities of portable chromatographs are close to those of stationary instruments. Portable chromatographs are suitable not only for field analysis, but also in laboratories because of lower energy and gas consumption. They also take up less room on laboratory tables. The future seems to belong to chip-based instruments. The next task will be the miniaturization of the whole analytical laboratory to a microchip size [97]. The advantages of capillary chip-based electrophoresis are as follows: the shortening of analysis time by a factor of 50–100 compared to conventional capillary electrophoresis, the reduction of consumption of an eluent by a factor of 100 compared to conventional electrophoresis and by a factor of nearly 1 000 000 compared to HPLC using a column 4 mm in diameter [97].

Reviews devoted to chip-based instruments have already been published. These are reviews on chip-based electrophoresis [98] and reviews devoted to the outlook of chip-based chromatography and electrophoresis [99] (43 references).

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