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An Improved Analyzer for Determining Helium-4 in Parts-Per-Billion Range

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere	min	minute
°C	degree Celsius	Ω	ohm
°C/W	degree Celsius per watt	ppb	part per billion
in	inch	ppm	part per million
KΩ	kilohm	ppm/°C	part per million per degree Celsius
μA	microampere	pct	percent
μF	microfarad	s	second
μH	microhenry	V dc	volt, direct current
μV	microvolt	V ac	volt, alternating current
μV/°C	microvolt per degree Celsius	W	watt
μV/ppb	microvolt per part per billion		

AN IMPROVED ANALYZER FOR DETERMINING HELIUM-4 IN PARTS-PER-BILLION RANGE

By Charles A. Seitz¹ and Philip W. Holland¹

ABSTRACT

The Bureau of Mines has modified its parts-per-billion helium-4 analyzer to improve the analytical capabilities of the instrument. The modifications resulted in the following improvements: (1) The analytical precision of the instrument for 10 consecutive analyses was improved to ± 1 ppb at the 5,000-ppb helium-4 level, (2) the helium-4 sensitivity was increased almost tenfold, and (3) the minimum detectable limit for helium-4 was improved to 0.5 ppb. The modifications made to improve the instrument included replacing the ion-source control circuit with a direct-current solid-state design, controlling the temperature of the ion source, stabilizing and reducing the pumping rate of the vacuum system, and optimizing peak integration.

INTRODUCTION

The modifications described in this report were performed to improve the analytical capabilities of the Bureau's parts-per-billion helium² analyzer (1).³ The analyzer consists of a modified helium leak-detector mass spectrometer, a laboratory-built sample inlet system utilizing an O-ring-sealed chromatographic valve, and a liquid-nitrogen-cooled charcoal trap. A programmable reporting integrator and event-control module are used to automate sample valve switching and to determine the helium peak heights. The analyzer was originally developed for trace helium analysis in the 5- to 20,000-ppb range. The instrument is used for determining the helium content of pure gases (excluding neon and hydrogen), laboratory-prepared standards, and atmospheric samples.

The modifications to the analyzer were undertaken in an effort to improve the analytical precision. Replacement of the mass spectrometer ion-source control circuit is considered to be the most significant improvement. The new circuit is unique in that an operational amplifier and two transistors are used for regulation of direct current to the filament. Since the new control circuit eliminates overshoot of filament current, the life of the filament is expected to be lengthened.

Performance tests showed the precision for 10 analyses of a sample containing about 5,000 ppb helium to be routinely ± 1 ppb. Prior to the modifications, the precision ranged from ± 4 to ± 8 ppb.

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²"Helium" in this report refers to the isotope helium-4.

³Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

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ion-source control circuit. Mr. Lucich, formerly with the Bureau of Mines, is with the Air Force, U.S. Department of Defense, McClellan AFB, CA.

ION-SOURCE CONTROL CIRCUIT

COMPONENTS

A schematic diagram of the ion-source control circuit is shown in figure 1. Main components of the circuit include an operational amplifier (A),⁴ four power supplies (PS₁, PS₂, PS₃, and PS₄), two 10-turn potentiometers (P₁ and P₂), and two transistors (Q₁ and Q₂). The circuit also includes four diodes (D₁-D₄), seven capacitors (C₁-C₇), 12 resistors

(R₁-R₁₂), a pilot light (PL), a micro-ampere meter (M), and an inductor (L). A list of the components used in the circuit and their specifications is given in the appendix.

DESIGN AND OPERATION

The control circuit was designed to provide a constant ionizing current by regulating direct current through the mass spectrometer filament. The described circuit provides adjustment and control of the ionizing current up to 150 μ A; however, the upper limit of the

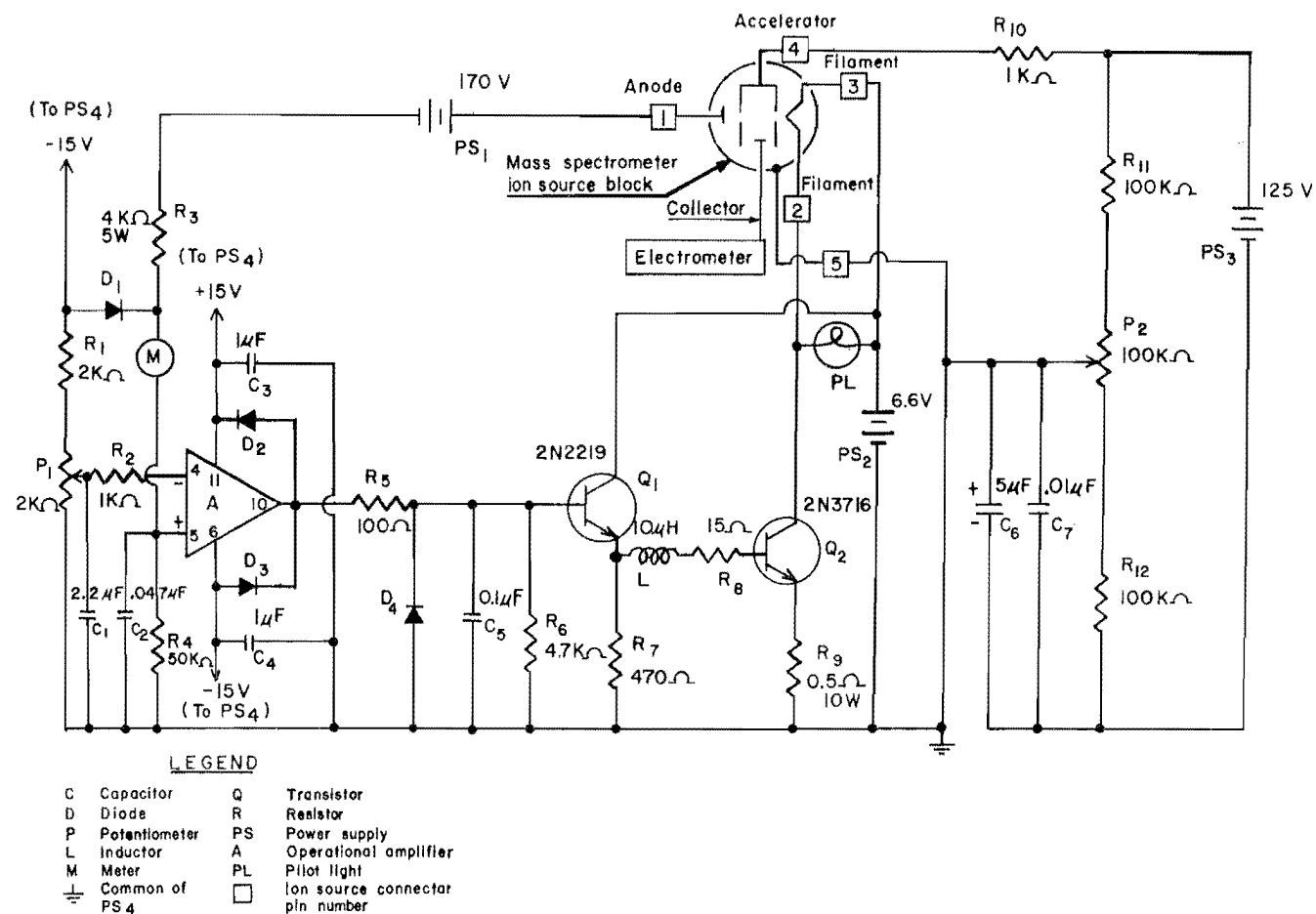


FIGURE 1. - Schematic diagram of ion-source control circuit for mass spectrometer.

ionizing current can be extended by using resistors of less than 50 K Ω for R_4 . An ionizing current of 50 μ A was arbitrarily chosen to be a good operating point when conducting the performance tests described in this report.

Current through the mass spectrometer filament is controlled by the operational amplifier and transistors Q_1 and Q_2 . (Refer to figure 1.) Electron flow from the filament to the anode (ionizing current) causes a sensing voltage to be developed across resistor R_4 and at pin 5 of the amplifier. The difference between the voltage at pin 5 and the set point voltage supplied from the wiper of potentiometer P_1 at pin 4 is amplified. The output from the amplifier at pin 10 controls the current through Q_1 and, likewise, through Q_2 and the filament. The control of the current through the filament regulates the temperature of the filament and the rate at which electrons are emitted. Thus, the voltage developed at pin 5 as a result of the electron flow from the filament to the anode and through R_4 occurs to such an extent that it balances the control set point voltage at pin 4.

The control circuit is phased in such a manner that a random increase in ionizing current will cause the sensing voltage at pin 5 (non-inverting input) of the amplifier to become more negative relative to circuit ground. When this occurs, the output from the amplifier becomes less positive, thereby causing Q_1 and Q_2 to be less conductive. As Q_2 becomes less conductive, current through the filament is reduced, thereby reducing the temperature of the filament. Thus, the ionizing current is reduced toward the control set point. The converse of the above description occurs when there is a random decrease in ionizing current. By adjusting P_1 , a different ionizing current can be established.

Table 1 shows the operational parameters of the circuit for three set point voltages. The values of the filament current at the three operating points were calculated by measuring the current through R_9 and subtracting the base current of Q_2 (the current through R_8). It should be noted that a filament current of 4.09 A produces an ionizing current of

about 52 μ A and that an increase in the filament current to 4.21 A (a 3-pct increase) results in an ionizing current of 150 μ A (about a 300-pct increase). Thus, exact and precise control of the filament current is critical in maintaining a constant ionizing current.

TABLE 1. - Operational parameters of control circuit for three set point voltages

Set point voltage at pin 4 of amplifier, V	Ionizing current, μ A	Filament current, A
-2.59	51.8	4.09
-5.07	101.4	4.17
-7.51	150.2	4.21

The ionizing voltage (anode voltage) operating point was arbitrarily selected to be 170 V. Anode voltages from 125 to 175 V should have little or no effect on circuit performance; however, no data were obtained at different anode voltages.

Transistor Q_1 was selected for use in the circuit based on its ability to match the relatively low current output of the amplifier and to provide adequate current for driving Q_2 . The current gain for Q_1 as used in the circuit is calculated to be 135. The heat sink used with Q_1 has a maximum temperature rise of 25° C/W.

Transistor Q_2 was selected for its 150-W power rating. This rating provides an adequate safety factor when considering that approximately 11 W is dissipated by Q_2 when the 4-A filament current flows through it. As used in this circuit, the current gain of Q_2 is calculated to be 60. The heat sink for Q_2 has a maximum temperature rise of 0.5° C/W.

Diode D_1 was installed to protect the amplifier in the event that the ion source anode is shorted to ground. Diodes D_2 and D_3 were installed to protect the amplifier from any voltage spikes that might be picked up on the output of the amplifier.

Power supplies PS_1 , PS_2 , PS_3 , and PS_4 are used to furnish voltages to the ion source anode, filament, accelerator, and operational amplifier, respectively. The accelerator voltage is set at 70 V above circuit ground using potentiometer P_2 .

The pilot light was installed in parallel with the filament to indicate filament operation. The light glows dimly under control conditions but glows

very brightly when the filament is open. The microampere meter indicates the value of the ionizing current.

OTHER IMPROVEMENTS

ION-SOURCE TEMPERATURE CONTROL

Another modification that contributed to improving the analytical precision of the mass spectrometer was establishing temperature control of the ion source. Heating of the ion source was accomplished using a 50-W mantle heater as shown in figure 2. A laboratory-built proportional temperature controller (2) was used to control the temperature of the heater and block to $75.0 \pm 0.1^\circ \text{C}$. After initial power up of the heater, about 40 min is required to achieve temperature stabilization and control.

VACUUM SYSTEM MODIFICATIONS

The vacuum system of the mass spectrometer was modified by installing a 1/16-in-diameter orifice between the liquid nitrogen cold trap and the intake of the oil diffusion pump (fig. 2). Installation of the orifice reduced the pumpout rate of the helium in the ion source resulting in the following improvements: (1) approximately a tenfold increase in helium sensitivity, (2) an improved minimum detectable limit for helium, and (3) an improved helium peak shape. The pumpout rate of the ion

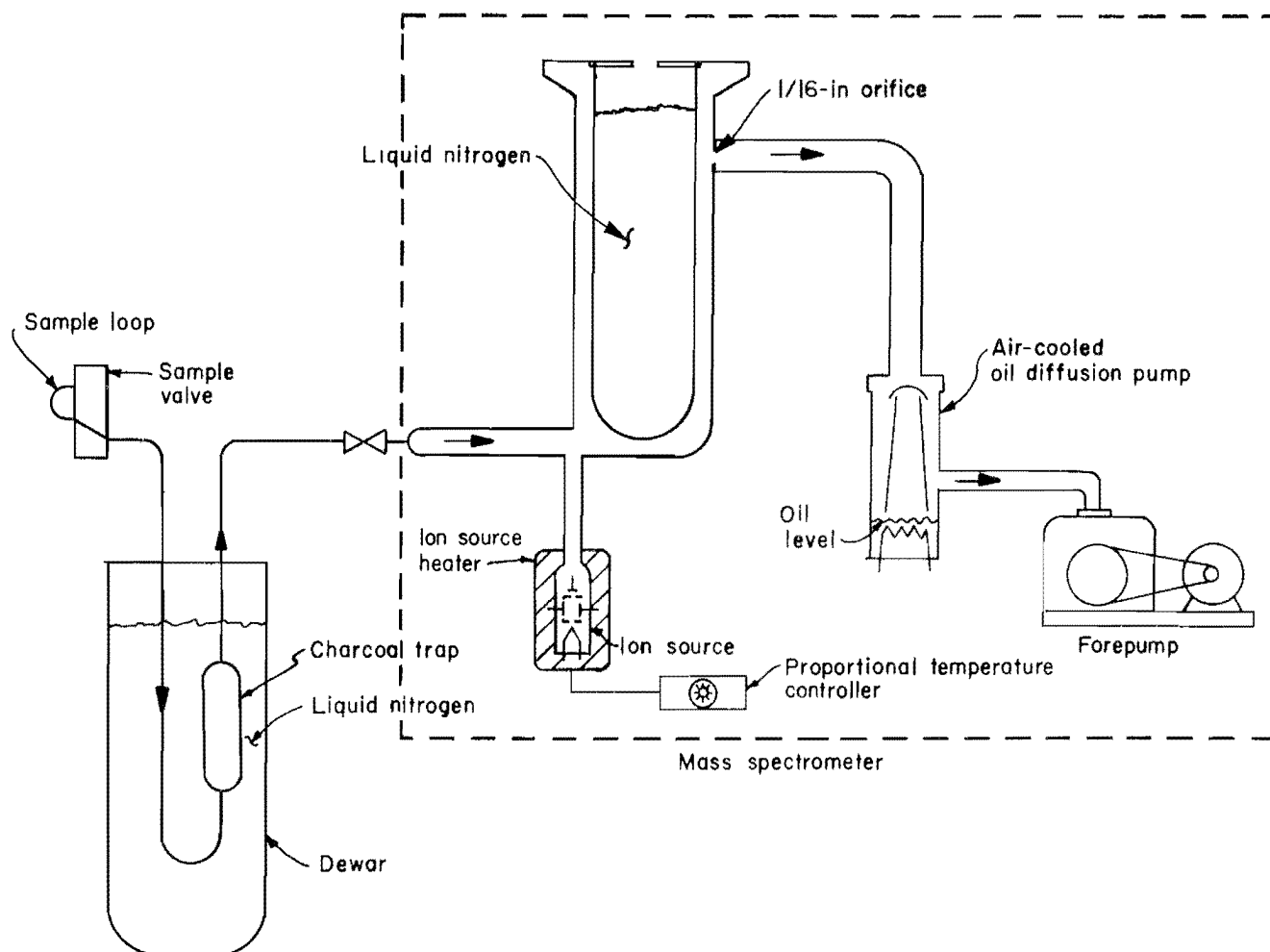


FIGURE 2. - Schematic diagram of analytical flow system for parts-per-billion helium analyzer.

TABLE 2. - Time-programmed integrator commands for sample-valve sequencing and peak quantization¹

Integrator time-programmed command	Time of execution (from start of run), min	Action of executed command
PK WD 0.01.....	0.01	Set time width of peak at half height to be 0.01 min.
THRSH 3.....	.02	Set threshold discrimination level for detection of peaks to 2 ³ .
INTG #0.....	.50	Immediately declare the present baseline as a baseline reference point.
INTG #5.....	.51	Extend the baseline horizontally from the last declared baseline reference point.
EXT #5.....	.52	Shift sample valve to admit sample for analysis.
EXT #-5.....	1.52	Return sample valve to purge position in preparation for next sample.
STOP.....	3.00	Stop run sequence and cause digitized peak height to be printed out.

¹The time-programmed integrator commands are for a Hewlett-Packard Model 3390A integrator.

source was further stabilized by regulating the electrical power supplied to the oil diffusion-pump heater element. The line voltage supplied to the element was reduced and regulated at 105 V ac using a power stabilizer.

OPTIMIZATION OF HELIUM-PEAK INTEGRATION

The improvement in the helium-peak shape resulted in more consistent peak-height quantization by the programmable

reporting integrator. The increase in the pumpout time of the ion source caused the start-to-apex time interval for the helium peak to be increased from about 1 s to 11 s, thereby allowing a more consistent start-of-peak detection and a more accurate peak-height measurement. The peak-height determination is based on the measurement of the height at the apex from an extended pre-peak baseline. The time-programmed valve sequencing commands and integration parameters used in an analysis are given in table 2.

HELIUM ANALYZER PERFORMANCE TESTS

PRECISION

The precision was determined by comparing two helium-in-nitrogen weighed standards. The standards were prepared by successive dilution of helium with analyzed nitrogen⁵ until the desired concentration in the parts-per-billion range was achieved (3-4). For the test, a weighed standard containing 4,654±3 ppb

helium was considered as an unknown sample and compared to a weighed standard containing 5,480±3 ppb helium. The "unknown" was analyzed a total of 40 times: 10 analyses per day on 4 different days. Each analysis of the unknown was bracketed by analyses of the standard. The precision (standard deviation) for each 10-analysis set was ±1 ppb, as shown in table 3. The absolute accuracy of an analysis depends on the accuracy of the weighed standard used for calibration.

⁵Cylinders of "pure" nitrogen used in preparing the standards were analyzed to contain as low as 1 ppb helium.

TABLE 3. - Analyses of weighed standard containing 4,654±3 ppb helium

1st set of analyses	2d set of analyses	3d set of analyses	4th set of analyses
4,653	4,652	4,651	4,653
4,653	4,653	4,653	4,652
4,652	4,652	4,652	4,652
4,654	4,652	4,652	4,653
4,653	4,652	4,652	4,652
4,653	4,654	4,652	4,653
4,652	4,654	4,653	4,652
4,652	4,652	4,652	4,652
4,652	4,652	4,653	4,654
4,652	4,653	4,652	4,653
4,653 ¹	4,653	4,652	4,653

¹Mean value.

NOTE.--Standard deviation = ±1.

LINEARITY AND SENSITIVITY

The linearity and sensitivity of the analyzer were evaluated by comparing a series of six helium-in-nitrogen weighed standards. For the evaluation, the mean helium peak heights for the weighed standards were determined by analyzing each standard 10 times. The helium contents of the weighed standards and their

corresponding mean peak heights are compared in table 4. From these results, it is concluded that the analyzer is linear over the range of 52 to 7,040 ppb helium to within about 0.02 pct of absolute linearity. Since the method of analysis requires that each unknown sample be bracketed by a standard of essentially the same helium level, absolute linearity is not needed. The mean helium sensitivity is 41.79 $\mu\text{V/ppb}$, almost a tenfold increase over the previously observed helium sensitivity (1). The minimum detectable limit for helium was calculated to be 0.5 ppb, which corresponds to a peak that is twice the height of the baseline noise.

TABLE 4. - Linearity of parts-per-billion helium analyzer

Helium content of weighed standard, ppb	Mean helium peak height, μV	Mean helium peak height, $\mu\text{V/ppb}$
52.5±2.5.....	2,190	41.71
889.8±1.1.....	37,220	41.83
4,654±3.....	194,600	41.81
5,480±3.....	229,200	41.82
6,121±4.....	255,800	41.79
7,040±4.....	294,300	41.80

CONCLUSIONS

The newly devised, solid-state circuit for control of the ionizing current of the mass spectrometer was considered to be the most significant factor in improving the precision of the analyzer. Performance tests showed the precision for 10 consecutive analyses at the 5,000-ppb helium level to be ±1 ppb. This precision represents a fourfold improvement.

The analyzer was shown to be within about 0.02 pct of absolute linearity over the range of about 52 to 7,040 ppb

helium. Since the method of analysis used requires each unknown sample to be bracketed by a standard of essentially the same helium level, the need for absolute linearity is eliminated.

The sensitivity and minimum detectable limit for helium were demonstrated to be 41.79 $\mu\text{V/ppb}$ and 0.5 ppb, respectively. The improvement in each of these analytical capabilities was approximately tenfold.

REFERENCES

- Holland, P. W. An Analyzer for Determining Helium-4 in the Parts-Per-Billion Range. BuMines RI 8853, 1984, 9 pp.
- Lucich, G. M., and P. W. Holland. A Proportional Temperature Controller With Automatic Shutoff. BuMines RI 8423, 1980, 8 pp.
- Loya, E. W., C. A. Seitz, and D. E. Emerson. Gravimetric Preparation of Primary Standard Gas Mixtures in the Parts-Per-Trillion Range. BuMines RI 8643, 1982, 4 pp.
- Miller, J. E., A. J. Carroll, and D. E. Emerson. Preparation of Primary Standard Gas Mixtures for Analytical Instruments. BuMines RI 6674, 1965, 10 pp.

APPENDIX.--LIST OF CIRCUIT COMPONENTS AND SPECIFICATIONS

- A - operational amplifier, input offset $<75 \mu\text{V}$, input noise voltage $<0.6 \mu\text{V}$ peak-to-peak, input offset drift $<1.3 \mu\text{V}/^\circ\text{C}$, long-term input offset stability $1 \mu\text{V}$ per month.
- C_1 - capacitor, $2.2 \mu\text{F}$, 25 V, electrolytic type.
- C_2 - capacitor, $0.047 \mu\text{F}$, 25 V, ceramic type.
- C_3 - capacitor, $1 \mu\text{F}$, 25 V, tantalum type.
- C_4 - capacitor, $1 \mu\text{F}$, 25 V, tantalum type.
- C_5 - capacitor, $0.1 \mu\text{F}$, 25 V, ceramic type.
- C_6 - capacitor, $5 \mu\text{F}$, 200 V, electrolytic type.
- C_7 - capacitor, $0.01 \mu\text{F}$, 200 V, ceramic type.
- D_1 - diode, type 1N4004, low-leakage tested.
- D_2 - diode, type 1N4002.
- D_3 - diode, type 1N4002.
- D_4 - diode, type 1N4002.
- L - inductor, $10 \mu\text{H}$.
- M - meter, 0 to 200 μA .
- P_1 - potentiometer, $2 \text{ K}\Omega$, 10-turn, temperature coefficient = $\pm 20 \text{ ppm}/^\circ\text{C}$.
- P_2 - potentiometer, $100 \text{ K}\Omega$, 10-turn, temperature coefficient = $\pm 20 \text{ ppm}/^\circ\text{C}$.
- PL - pilot light, incandescent, No. 47.
- PS_1 - power supply, adjustable, 125 to 175 V.
- PS_2 - power supply, adjustable, 5 to 9 V.
- PS_3 - power supply, adjustable, 125 to 175 V.
- PS_4 - power supply, dual, +15 V and -15 V.
- Q_1 - transistor, NPN, type 2N2219.
- Q_2 - transistor, NPN, type 2N3716.
- R_1 - resistor, $2 \text{ K}\Omega$, 0.25 W, temperature coefficient = $\pm 8 \text{ ppm}/^\circ\text{C}$.
- R_2 - resistor, $1 \text{ K}\Omega$, 0.25 W, temperature coefficient = $\pm 8 \text{ ppm}/^\circ\text{C}$.
- R_3 - resistor, $4 \text{ K}\Omega$, 5 W.
- R_4 - resistor, $50 \text{ K}\Omega$, 0.25 W, temperature coefficient = $\pm 8 \text{ ppm}/^\circ\text{C}$.
- R_5 - resistor, 100Ω , 0.25 W.
- R_6 - resistor, $4.7 \text{ K}\Omega$, 0.25 W.
- R_7 - resistor, 470Ω , 0.25 W.
- R_8 - resistor, 15Ω , 5 W.
- R_9 - resistor, 0.5Ω , 10 W.
- R_{10} - resistor, $1 \text{ K}\Omega$, 0.25 W.
- R_{11} - resistor, $100 \text{ K}\Omega$, 0.25 W, wire-wound type.
- R_{12} - resistor, $100 \text{ K}\Omega$, 0.25 W, wire-wound type.