

A Method for Determining Argon Isotopes in a Continuous Helium Flow for K/Ar Geochronology

A. V. Ignat'ev, T. A. Velivetskaya, and S. Yu. Budnitskii

*Far East Geological Institute, Far East Division, Russian Academy of Sciences,
pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia
e-mail: ignatiev@fegi.ru*

Received November 17, 2008; in final form, March 30, 2009

Abstract—A new method for the measurement of the argon isotope composition in a continuous helium flow using isotope mass spectrometers is described for potassium–argon geochronology. Argon was extracted from the samples in a chamber with a multiple-sample holder by successively heating the samples with a continuous infrared laser. Argon extracted in the chamber was preconcentrated in a capillary, separated on a chromatographic capillary column in a helium flow, and then injected into the ion source of a mass spectrometer through an open splitter. Measurements of the ^{36}Ar , ^{38}Ar , and ^{40}Ar isotopes were carried out on isotope mass spectrometers in a dynamic mode using a triple-collector ion detector and three electrometric amplifiers. Preliminary experiments on the developed device for measuring argon isotopes in a continuous helium flow have shown that the proposed method can be used for the determination of radiogenic argon in an amount of $n \times 10^{-12}$ g with the accuracy satisfying the solution of many geochronological problems. In sensitivity and reproducibility, the proposed method is highly competitive to the isotope dilution method for measuring argon and simpler than the conventional methods for measuring radiogenic argon.

Keywords: K/Ar geochronology, argon isotopes, stable isotopes, mass spectrometer

DOI: 10.1134/S1061934810130071

INTRODUCTION

Measurement of low concentrations of radiogenic argon in the determination of the age of breeds by the K/Ar method is among the most difficult problems in isotope geology. The development of this method passed on the way of decreasing the error of mass spectrometric measurements, reducing the amount of argon necessary for the analysis, and improving methods of extraction and argon purification. Up-to-date methods for measuring small amounts of radiogenic argon consist of a complex of blocks satisfying a number of hard requirements. The complex includes specialized blocks of high-vacuum pumping out and purification of argon from any extraneous gases, including a high-precision system of dozing the ^{38}Ar monoisotope. Special attention is given to a block of the high-temperature heating of a sample to 1700–2000°C for the complete extraction of argon with a very low background. Such a system of gas extraction from samples with a high-temperature heater vacuum-isolated from the zone where the sample was melted was developed by a group of German researchers [1]. The system allows reaching the level of the total working background up to thousands of fractions of nanogram for the ^{40}Ar isotope [2]. The determination of the isotope composition of argon is carried out on high-sensitivity mass spectrometers in a static mode (without pumping out the chamber of an analyzer, ion source, and the

system of argon admission to a high vacuum). The static mode of mass spectrometric measurements allows a tenfold reduction of the amount of the measured gas in comparison with the dynamic mode [3]; however, the maintenance of the static mode of measuring argon is far from a trivial problem. Recently, laser systems of the extraction of argon have become increasingly widely distributed [4]. In these systems one can much more easily achieve a low dark experiment ($n \times 10^{-14}$ ng of ^{40}Ar) (**blank** in what follows) and reach a temperature of sample heating for the complete extraction of argon for some tens of seconds [5].

Assessing the present-day procedure of K/Ar geochronology, one needs to note that methods of the extraction of argon isotopes, their purification of extraneous gases, and the process of the mass spectrometric determination of small amounts ($n \times 10^{-12}$ ng) of radiogenic argon ensure the necessary error for the solution of some applied questions [2]. However, extraction, purification, and determination of small amounts of argon are extremely labor-intensive and expensive methods.

Mass spectrometers used to determine the distribution ratios of stable isotopes of polyisotope elements (hydrogen, nitrogen, oxygen, carbon, etc.) and argon isotopes are similar in many respects. Therefore, attempts to carry out such measurements for the case of ultra small amounts of gases (tens of nanograms) in

a static operating mode of a mass spectrometer [6] were undertaken. The achieved reproducibility of the measurements (isotope mass spectrometry with a double admission system admission) was much worse than classical methods [6, 7]. At the same time, mass spectrometry for the determination of the distribution ratios of stable carbon isotopes, in contrast to the K/Ar method, was radically improved. Thus, a new device was proposed in [8], which allows the direct admission of the analyzed gas into the mass spectrometer in a continuous helium flow after the gas chromatograph (CF-GC-IRMC, continue flow-gas chromatograph-isotope ratio mass spectrometer) for the determination of the ratios of stable carbon isotopes. For more than ten years after improving the principles of measuring isotope ratios in a constant helium flow, the CF-GC-IRMS method was introduced into the practice of each laboratory dealing with sensitive measurements of the stable isotopes of oxygen, carbon, and nitrogen [9, 10] and recently, hydrogen and sulfur [11, 12].

Because of the simplicity of sample preparation in comparison with the tiresome and laborious methods that prevailed before the appearance of the CF-GC-IRMS method, the new technology has surpassed classical methods for the determination of isotope ratios in many cases. The main reason for its rapid success was that the method is highly competitive compared to the classical procedures of measuring isotope ratios in reproducibility, as well as being three orders of magnitude more sensitive and several times more rapid [13].

In the classical system, the distribution ratios of isotopes are determined in pure gases. In the CF-GC-IRMS method, the analyzed gas is injected into a source of a mass spectrometer from a chromatograph column in a helium flow as a short impulse usually of 10–30 s. The use of capillary columns considerably simplifies the procedure of the purification of the analyzed gas in comparison with the cryogenic separation of gases in the classical methods. A device with an open input with flow splitting is used for the admission of the analyzed gas from a capillary column into an ion source of a mass spectrometer [14]. This device was developed specially for quartz capillary columns with a diameter not exceeding 0.5 mm.

An important condition for reliable measurements of stable isotopes is the standardization of the measurement process based on the principle of the identity of the conditions of measuring the sample and the standard (IT Principle) [15]. In CF-GC-IRMS, helium is used as a gas-carrier of the sample and standard, the last one is injected into a helium flow using a special device [16]. In K/Ar geochronology, a dosed amount of the ^{38}Ar monoisotope (method of isotope dilution) [17] is usually used as the standard.

To determine $\delta^{13}\text{C}$ as the characteristic of the isotope composition of carbon in CO_2 relative to the international standard (PDB) using the CF-GC-IRMS method with an error of 0.05‰, less than one

nanogram of the gas was sufficient [18]. Usually, in K/Ar geochronology, the necessary error of the measurement of the distribution ratios of isotopes is essentially below the specified value and the determination of an amount of radiogenic argon is permissible with an error close to 1%. According to the Poisson statistics, at such an error of the analysis, the registration of 10000 ions is sufficient ($1\sigma = 1/N^{0.5}$, where N is the number of the ions measured by the ion detector). Taking into consideration the sensitivity of the up-to-date isotope mass spectrometers, which is achieved by less than 1000 atoms per ion (i.e., only one ion from 1000 atoms reaches the Faraday cylinder), for a signal measurement with an error no worse than 1%, 10^7 atoms of an analyzed isotope should enter into the source. So, it is possible to determine, for example, ^{36}Ar in the amount of $36 \times 10^7 / 6.24 \times 10^{23} = \sim 5 \times 10^{-16}$ g on a up-to-date isotope mass spectrometer in a continuous helium flow with an error close to 1%. First of all, in K/Ar geochronology the measurement of the amount of radiogenic argon is of interest, and the determination of the amount of ^{36}Ar is necessary for introducing the correction on the concentration ^{40}Ar in air. The abundance of ^{36}Ar in air is 295.5 times lower than that of ^{40}Ar . In this case, for the determination of the amount of radiogenic ^{40}Ar by CF-GC-IRMS with an error of 1%, one should have a sample portion containing only 1.5×10^{-13} g of radiogenic ^{40}Ar . In real conditions, other sources of errors, such as amplifier noise, the instability of ion current, contributions from isobaric weights of impurity substances, and the ratio of air to radiogenic argon will affect the error limits of calculating the amount of radiogenic argon. Considering the estimation analysis carried out above, the use of the CF-GC-IRMS method for the determination of argon isotopes seems a rather promising and attractive problem.

The purpose of the work was to create a complex for the determination of the isotope composition of argon in a helium flow on a MAT-253 mass spectrometer, elaborate a procedure for the extraction of small amounts of argon, and determine appropriate analytical parameters of the proposed installation used in K/Ar geochronology.

EXPERIMENTAL

The installation for argon analysis consisted of several consistently connected systems: a high-vacuum line, a cryofocusing system, a gas chromatograph, and a MAT-253 mass spectrometer (Fig. 1).

The high-vacuum line was collected from bellows valves (B1–B5) connected with stainless steel tubes of an external diameter of 6 mm. The U-tube cryogenic nitric trap was made from a corrosion-proof tube. The system was pumped out to 10^{-8} torr using a turbo-molecular pump. Argon was extracted with an infrared laser with continuous multimode operation at a wavelength of 1.06 μm with a maximum capacity of

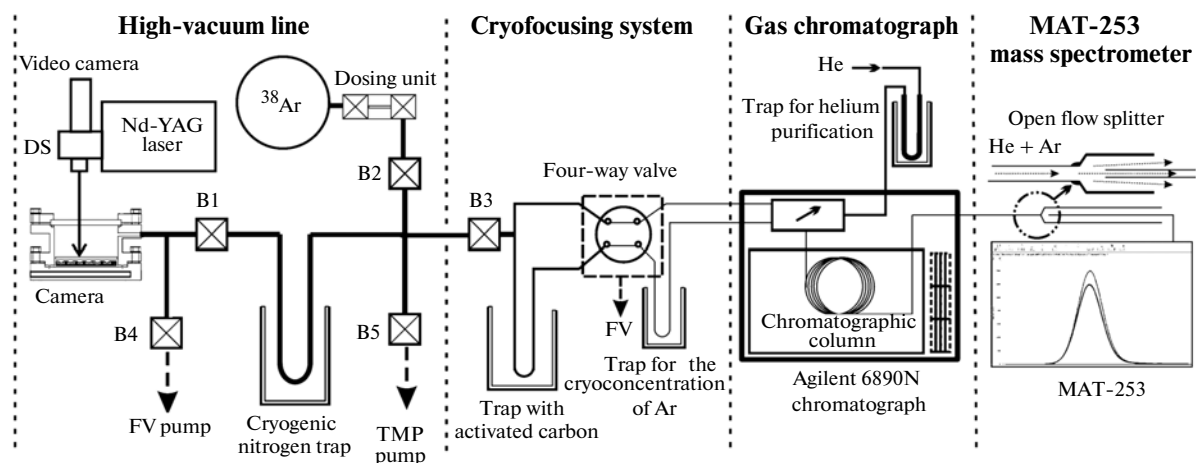


Fig. 1. Basic scheme of installation for the extraction and determination of the argon isotope composition in a continuous helium flow on a MAT-253 mass spectrometer: DS is the system of the deviation and focusing of a laser beam; B1–B5 are high-vacuum bellows valves; FV is a forevacuum pump; TMP is a turbo-molecular pump.

100 W. The deviation and focusing of the laser beam were carried out by means of a DS system (system of deviation and focusing of the laser beam). In the system of the deviation and focusing of the laser beam, we used an objective with a focal distance of 10 cm and an eyeglass allowing the observation of an object with a sevenfold magnification and field-of-view of a diameter of up to 10 mm on the display. A chamber for argon extraction was placed above the point of focusing of the laser beam at a distance that allowed us to obtain the diameter of the laser beam on a sample of about 1 mm.

In the system of the admission of the ^{38}Ar monoisotope, we used a cylinder of the volume 1000 cm^3 . The inner surface of the cylinder was covered by enamel, which guaranteed the long-term use of the ^{38}Ar monoisotope without a change in the isotope composition. The cylinder was heated before the installation and degassed by pumping out to a high vacuum, then it was filled with the tracer, the ^{38}Ar monoisotope, in an amount of $\sim 2000\text{ ng}$. Between the cylinder and the vacuum system, there was a dosing unit with a dosing volume of about 0.2 cm^3 .

In our system, argon was extracted from samples in a high-vacuum chamber with a holder for several test samples. The chamber was made of stainless steel (Fig. 2) and consisted of a cylindrical body (1), a top flange (2) for the vacuum sealing of a quartz window, and a bottom flange (5). The sample holder (4) was installed on a bottom flange. In the bottom flange, the heater was installed, which allowed heating the chamber to 250°C (9). At the switched on heater, a heat-insulation cover was put on the chamber for uniformly warming up the whole volume of the chamber. For vacuum sealing of the chamber window, a gold ring (5) was used, and for sealing the bottom flange, a copper lining (6) was used. The internal diameter of the

chamber was 32 mm and its height was 40 mm. The entrance window was made of quartz glass of a thickness of 5 mm (7), transparent at the wavelength of the emission of the Nd-YAG laser.

The holder of small samples (no more than 5 mg) was made from nickel; its diameter was 30 mm and its thickness, 5 mm. The holder had 30 holes of a diameter of 3 mm and depth of 3 mm. Separate quartz weighing bottles of an outer diameter of 10 mm and height 5 mm were used for samples of a higher weight not exceeding 20 mg. The chamber could simultaneously hold 9–10 weighing bottles; hence, the total weight of one sample could achieve 200 mg. To prevent the emission of seeds from the holes in heating the samples, the multicharge holder and weighing bottles were coated with a screen from the quartz glass of a thickness of 2 mm (8).

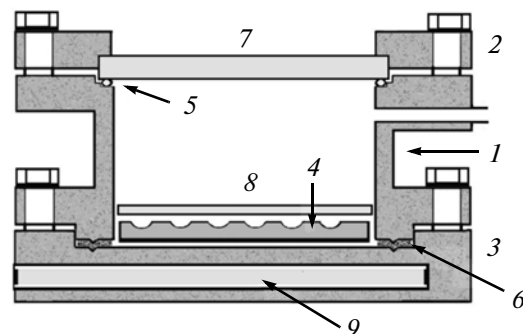


Fig. 2. Basic scheme of a high-vacuum chamber with a sample holder: 1, chamber case; 2, 3, bottom and top flanges, respectively; 4, sample holder; 5, 6, vacuum sealing gold and copper rings, respectively; 7, 8, quartz glasses; 9, chamber heater.

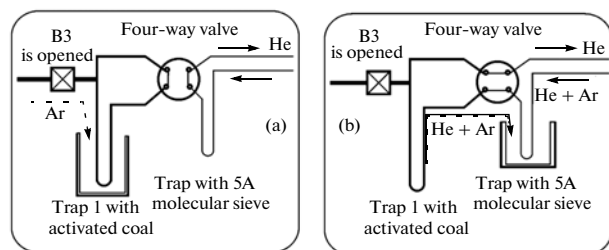


Fig. 3. Scheme of helium and argon flows: (a) in the concentration of argon from the extraction system; (b) in the cryoconcentration of argon before injection into the chromatograph.

The cryofocusing system (interface for connecting a high vacuum line to the line of the continuous helium flow) included a bellows valve B3, a four-way valve, a trap with activated coal, and a trap for argon cryoconcentration. A trap with activated coal was made from a corrosion-proof steel tube with an external diameter of 1.6 mm. Part of the tube cooled with liquid nitrogen was filled with activated coal. The valve B3 cuts frozen argon in the trap from the high-vacuum installation part. The trap with activated coal was filled with helium upon switching the four-way valve. To obtaining the amount of argon for which the amplitude of its ion current in the mass spectrometer is the greatest, argon from the cryogenic nitric trap was transferred into the helium flow and condensed in the trap of the argon cryoconcentration. This trap was made from a piece of a HP-MOLSIV 5A OD 0.32 chromatograph capillary column and directly connected to a capillary chromatograph column.

Gas chromatograph. After defrosting the trap with a molecular sieve, a gas mixture was filled into a capillary column of an Agilent 6890N gas chromatograph. The impurity gases were separated on the chromatograph column and pure argon in a helium flow moves through an open flow splitter to the ion source of the mass spectrometer. An HP-MOLSIV 5A OD 0.32 capillary column of the length 25 m was used. The working temperature of the thermostat was 25°C, and the rate of helium flow through the capillary chromatograph column was 2 cm³/min. The helium flows through the capillary column and the cryofocusing system were set and controlled using an Agilent 6890N gas chromatograph. Helium (grade 99.9999%) was admitted to the chromatograph through the cryogenic trap with activated coal for additional purification and, in particular, for freezing small impurities of argon in helium. It is necessary to note that, at a helium flow rate of 2–4 cm³/min, one cylinder of a volume of 40 L will be sufficient for use for over one year.

The MAT-253 mass spectrometer worked in a dynamic mode. The isotope composition of argon was determined simultaneously on three collectors linked

to amplifiers vs. input resistances 1×10^{12} , 3×10^{11} , and $1 \times 10^{11} \Omega$ for ³⁶Ar, ³⁸Ar, and ⁴⁰Ar, respectively.

To admit the analyzed gas to the ion source of the mass spectrometer, the open inlet device with a flow splitter (CF-GC-IRMS) was used [14]. The analyzed gas was admitted into the mass spectrometer source with a helium flow. The mass spectrometer was equipped by an additional module of differential pumping, which ensured the optimum vacuum conditions even at large inflows of helium into the ion source and allowed measurements of isotope ratios in the helium flow to 0.5 cm³/min. Such a flow was achieved using a soaking up capillary from melted quartz of a length of 1.5 m with an inner diameter of 0.1 mm. Under these conditions, the vacuum in the chromatograph column was not achieved and its resolution remains invariable. Upon passing helium through the open input device, the flow was separated and only part of it reached the ion source. In the given configuration of the open flow splitter, the efficiency of argon recycling achieved up to 25%. The decrease in the rate of the helium flow through the chromatograph column allowed increasing the efficiency of argon supply into the mass spectrometer source. However, for the satisfactory work of the capillary chromatograph column used by us, the rate of argon flow should be no less than 2–4 cm³/min. At the same time, an excess of the helium flow was necessary for the complete screening of the absorbing capillary in the open flow splitter from the penetration of ions of atmospheric air into the source. Therefore, the minimum helium flow through the column 2 cm³/min was used in the device.

The determination of the values of the peak areas of ion currents from three isotopes on the coordinates peak time vs. the efficiency of ions/their intensity was carried out using the ISODAT-NT software. Taking into account the input resistances of amplifiers, the values of peak areas of ion currents from ³⁶Ar, ³⁸Ar, and ⁴⁰Ar corresponded to the quantitative composition of argon isotopes admitted into the ion source from the extraction system. Knowing the absolute amount of the dosed calibration ³⁸Ar monoisotope, we calculated the amount of radiogenic argon by the standard procedure [19].

Operation principle of the installation for the analysis of argon isotopes. Before putting in samples, the holders were dried in air at 120°C. Samples were consistently put into holes of the nickel holder or in weighing bottles and placed in the chamber. The high-vacuum system was pumped out to 10⁻⁸ torr and warmed up at 200–250°C. After cooling the chamber and the high-vacuum system to the room temperature, the blank signal from the whole system was checked. Before the beginning of melting the next sample, the monoisotope was let into the high-vacuum system. After the inflow of the tracer, we put on a Dewar vessel with liquid nitrogen onto the cryogenic trap and trap-1 with activated coal (Fig. 3). The laser was

directed to the investigated sample and switched on. Gradually the capacity of the laser beam was increased to the maximum. Usually less than one minute was sufficient for the complete melting of the sample in the nickel holder. The time of the complete melting of the whole sample in a quartz weighing bottle can be as long as 5 min because of the big weighed portion of the sample. Upon melting the sample, the extracted gases pass through the cryogenic trap, in which water and carbon dioxide were condensed. Residual gases together with argon passed through open valve B3 and were frozen in trap-1 with activated coal (Fig. 3a). The complete freezing of the extracted argon lasted for 5–6 min, then a Dewar vessel with liquid nitrogen was put into the trap with the molecular sieve, valve B3 was closed, and the four-way valve was switched (Fig. 3b). The trap with the molecular sieve was pumped with helium for 1 min, and the Dewar vessel was removed from trap1. The trap was refrozen and the liberated argon in the helium flow was condensed in the capillary trap with the molecular sieve for 1 min. Then, we switched the four-way valve and removed the Dewar vessel; the liberated gases with the helium stream were admitted into the chromatograph capillary column. Here, the initial multicomponent mixture was separated by the elution times to give a number of binary mixtures consisting of the carrier gas and one of the components. Argon separated from the other gases in the helium flow was passed from the chromatograph column through the open flow splitter to the ion source of the mass spectrometer. Measurements of ion currents on the mass spectrometer were carried out in a three-beam mode using electrometric amplifiers connected to amplifiers with input resistances 1×10^{12} , 1×10^{11} , and $3 \times 10^{11} \Omega$ for ^{36}Ar , ^{40}Ar , and the ^{38}Ar tracer, respectively. The signal from electrometric amplifiers was digitized and registered as peak areas of ion currents for ^{36}Ar , ^{40}Ar , and the ^{38}Ar tracer (Fig. 4) under the control of the Isodat Acquisition program, part of the ISODAT NT software for the MAT-253 mass spectrometer.

The mass spectrometer was calibrated for registering the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio by measuring argon with an atmospheric isotope composition. The measured $^{40}\text{Ar}/^{36}\text{Ar}$ ratio was equal to 297.3 (taking into account input resistances). The difference of the obtained ratio from the standard ratio, 295.5, is caused by an insignificant difference of input resistances of electrometric amplifiers for ^{40}Ar and ^{36}Ar and the discrimination of weights.

After the adjustment of the ion source, the absolute sensitivity of the MAT-253 mass spectrometer was one ion per 790 atoms of ^{40}Ar at an emission of 1.5 mA. The isotope's sensitivity limit of the mass spectrometer was no more than 2×10^{-6} . The background was traditionally reduced by warming up the whole complex. For the MAT-253 mass spectrometer, it was sufficient to singly warm up the ion source at 200–250°C for two days. The, upon admitting helium of the grade

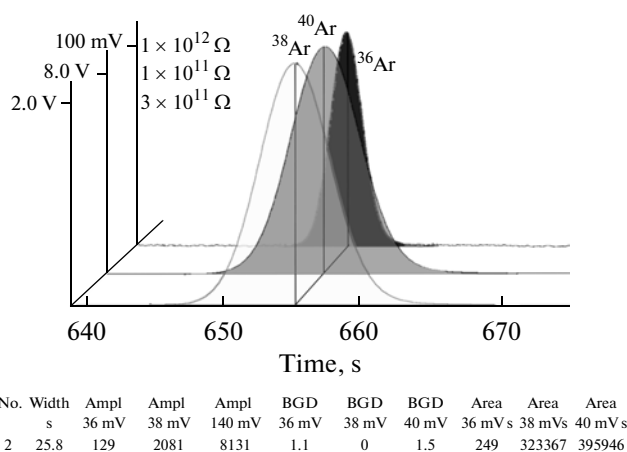


Fig. 4. Example of recording the results of measurements of the biotite interlaboratory standard. The weight of the sample is 0.27 mg; intensity and corresponding input resistances of electrometric amplifiers are given along the axis of ordinates (peaks of ^{36}Ar , ^{40}Ar , and the ^{38}Ar tracer are shifted for clarity). The values of the peak area of ion currents of argon isotopes are given recalculated to the resistance $1 \times 10^{12} \Omega$. Width, s is the peak width in seconds; BGD are background values in mV; Ampl, mV is an amplitude in mV; and Area, mV s is the value of peak area in mVs; 36, 38, 40 mean ^{36}Ar , ^{38}Ar , and ^{40}Ar , respectively.

He-6.0 (purity 99.9999%) and additionally purifying on the trap with activated coal at the temperature of liquid nitrogen, the background signal was lowered to $1.5 \times 10^{-15} \text{ A}$ for the ^{36}Ar isotope, almost to zero for ^{38}Ar , and to $15 \times 10^{-15} \text{ A}$ for the ^{40}Ar isotope. The achieved background signal of the device was stable for more than one year.

RESULTS AND DISCUSSION

The developed measuring complex for argon isotopes allowed the significant simplification of the scheme of sample preparation for isotope analysis with the preservation of high sensitivity and specificity. This was achieved by carrying out the following operations. A necessary condition for the measurement of small amounts of argon isotopes is the minimum blank signal from air argon. A high-vacuum system together with a multiply charged chamber were warmed after each change of samples at 200–250°C for 10–12 h to achieve a blank signal with a low concentration of air argon. The results of a series of measurements of the blank signal for 10 min are presented in Table 1. Here and below all results are given as peak areas for ^{36}Ar in mV and for ^{38}Ar , ^{40}Ar , in V, recalculated to the $10^{12} \Omega$ input resistance.

The obtained values of the blank signal virtually coincide with the results of the hot blank experiment 10×10^{-3} – $3 \times 10^{-3} \text{ ng}$ on the measurement complex mass spectrometer plus a device of argon extraction with a vacuum-isolated heater [21], but rank below the best blank signals for laser systems of argon extraction.

Table 1. Results of measuring the blank signal of the laser extraction of argon in a continuous helium flow on MAT-253 mass spectrometer

Measurement data	^{36}Ar , mV s	^{36}Ar , g	^{40}Ar , V s	^{40}Ar , g
06.07.2007	29		8.85	
07.08.2007	29		8.58	
08.10.2007	32		9.59	
01.23.2008	34		10.5	
02.14.2008	21	$\sim 2 \times 10^{-15}$	6.38	$\sim 6 \times 10^{-12}$
03.05.2008	22		6.42	
04.09.2008	23		6.90	
05.17.2008	22		7.19	
06.03.2008	23		6.99	
07.22.2008	22		6.38	

A certain portion of argon in the blank signal of our system is due to the residual concentration of argon in helium. The valve B3 was closed in measuring this portion and a four-way valve for helium supply throughout the entire system of cryofocusing (Fig. 3b) was switched. The Dewar vessel with liquid nitrogen was put into the trap with a molecular sieve and argon in the helium flow was condensed in the capillary trap with the molecular sieve for 10 min. The frozen amount of argon did not exceed 0.6 V s or $\sim 5 \times 10^{-13}$ g ^{40}Ar , which is 10 times lower than the amount of argon in the blank signal of the whole system.

A series of measurements of the ratios of argon isotopes in the tracer on the mass spectrometer with a double system of isotope admission was carried out for the correct estimation of the amount of radiogenic argon, and the following distribution ratios of isotopes were calculated: $^{38}\text{Ar}/^{36}\text{Ar}$ 1656 ± 3 and $^{38}\text{Ar}/^{40}\text{Ar}$ 1451 ± 4 .

A series of calibration measurements of the amount of dosed ^{38}Ar was carried out after the necessary information on the background conditions, the values of the blank signal, and the ratios of argon isotopes in the tracer was obtained. The following interlaboratory standards with a known concentration of radiogenic argon were used: Biotit–Black salma ($^{40}\text{Ar}_{\text{rad}} = 1689$ ng/g), Muskovit–Black salma ($^{40}\text{Ar}_{\text{rad}} = 1861$ ng/g) [22], and Hornblend–MMhb-1 ($^{40}\text{Ar}_{\text{rad}} = 65.04$ ng/g) [23] (Table 3). The weight of the standards was varied from 9 to 0.2 mg, which corresponded to the amount of extracted radiogenic argon from 7.8 to 0.13 ng. Samples were weighed on an MC-5 balance with an error of ± 0.1 μg . The amount of radiogenic argon (in V s) was calculated by the equation:

$$^{40}\text{Ar}_{\text{rad}} = ^{40}\text{Ar}_{\text{mea}} - ^{38}\text{Ar}_{\text{mea}}/1451 - (^{36}\text{Ar}_{\text{mea}} - ^{38}\text{Ar}_{\text{mea}}/1656)297 \quad (1)$$

and the amount of ^{38}Ar in ng was

$$^{38}\text{Ar}_{\text{ng}} = P_{\text{st}} ^{40}\text{Ar}_{\text{st}} ^{38}\text{Ar}_{\text{mea}}/^{40}\text{Ar}_{\text{rad}} \quad (2)$$

Here, P_{st} is the weight of the standard sample and $^{40}\text{Ar}_{\text{st}}$ is the amount of radiogenic argon in the standard. The results of measurements of the amount of the tracer are presented in Table 3; they take into account the correction for its gradual decrease in the dosed samples.

The results of the calibration of tracer (Table 2) by MMhb-1, Biotit–Black Salma, and Muskovit–Black Salma are equal to $4.10 \times 10^{-4} \pm 4 \times 10^{-12}$, $4.12 \times 10^{-10} \pm 9 \times 10^{-12}$, and $4.08 \times 10^{-10} \pm 7 \times 10^{-12}$ ng, respectively. The data obtained are actually estimates of the error of measuring the amount of argon by the proposed procedure. The error of the determination of the amount of argon is a function of several values determined experimentally. The error of the determination of $^{40}\text{Ar}_{\text{rad}}$ in Eq. (1) is equal to the sum of the errors of measuring $^{40}\text{Ar}_{\text{mea}}$, $^{38}\text{Ar}_{\text{mea}}$, and $^{36}\text{Ar}_{\text{mea}}$. The error of the measured values is the sum of errors due to measuring the ion current on the mass spectrometer and errors from the system of argon extraction. The error of measuring the peak area of the ion current of $^{36}\text{Ar}_{\text{mea}}$ depends mainly on the signal-to-noise ratio. For example, a signal of 100 mV at a peak width of 5 s was measured with an error no worse than 0.2 mV in up-to-date mass spectrometers with an electrometer with the input resistance $R = 10^{12} \Omega$ [18]. The values of the peaks areas of $^{36}\text{Ar}_{\text{mea}}$, presented in Table 3, vary within the limits of 220–2384 mV, i.e., they are measured with an error of less than ± 0.1 mV. The peaks areas of $^{40}\text{Ar}_{\text{mea}}$ and $^{38}\text{Ar}_{\text{mea}}$ are several hundred times as high as that of $^{36}\text{Ar}_{\text{mea}}$ and, respectively, the error of their measurements will be dozens of times less than that in [18]. The errors of the determination of the ratios of $^{38}\text{Ar}/^{36}\text{Ar}$ and $^{38}\text{Ar}/^{40}\text{Ar}$ isotopes in the tracer and the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio in air in calculations are regular errors. Hence, the total error of the determination of the amount of radiogenic argon is determined by the measurement error of $^{36}\text{Ar}_{\text{mea}}$, because the sum of other errors is tenfold lower. The maximum error of $^{40}\text{Ar}_{\text{rad}}$ will be equal to $\sim 0.1 \times 297$ mV s or $\sim 4 \times 10^{-14}$ ng. The error 4×10^{-14} ng is an internal error of the mass spectrometer in measuring $^{40}\text{Ar}_{\text{rad}}$.

Errors of the system of argon extraction basically consist of the error of the completeness of the extraction of radiogenic argon, the error of tracer dosage, and in our case, of the stability of the helium flow. There was no doubt about the complete extraction of radiogenic argon, because the extraction of radiogenic argon was not observed in repeatedly heating samples. The instability of the helium flow influences simultaneously the registration of both ^{38}Ar and ^{40}Ar (IT Principle). As was already noted above, the measurement error of ^{38}Ar at the peak area equal to 324 V s will be negligibly small. The design of our dosing unit is similar to that described in [20]. According to the author's data, the maximum error of the volume of the dosed

Table 2. Results of calibration by the amount of the ^{38}Ar monoisotope contained in one dose of the tracer

Standard	Weight of sample, mg	$^{36}\text{Ar}_{\text{mea}}$, mV s	$^{38}\text{Ar}_{\text{mea}}$, V s	$^{40}\text{Ar}_{\text{mea}}$, V s	$^{40}\text{Ar}_{\text{rad}}$, V s	$^{40}\text{Ar}_{\text{air}}$, %	Tracer ^{38}Ar , ng
Biotit–Black salma $^{40}\text{Ar}_{\text{rad}}$ 1689 ng g ⁻¹	0.1735	225	319	244	234	4	0.399
	0.2107	223	322	294	286	3	0.401
	0.3898	243	327	523	509	3	0.423
	0.5143	214	323	682	676	1	0.415
	0.8032	248	323	1093	1077	1	0.407
	1.0719	369	324	1445	1394	4	0.421
	2.0722	306	323	2739	2706	1	0.418
	3.9687	1533	328	5713	5317	7	0.414
Average							0.412 ± 0.009
Muskovit–Black salma $^{40}\text{Ar}_{\text{rad}}$ 1861 ng g ⁻¹	0.5053	242	322	744	730	2	0.415
	0.6028	250	324	931	915	2	0.397
	0.7428	247	325	1121	1106	1	0.406
	1.0005	465	325	1553	1473	5	0.411
	4.1466	702	327	6287	6137	2	0.411
Average							0.408 ± 0.007
Hornblende–MMhb-1 $^{40}\text{Ar}_{\text{rad}}$ 65.04 ng g ⁻¹	2.0248	392	326	163	105	36	0.409
	2.0642	221	321	114	106	7	0.407
	3.6038	225	326	197	189	4	0.405
	4.0364	282	324	231	205	11	0.414
	4.0453	435	325	277	206	26	0.415
	5.4131	229	325	290	280	3	0.408
	9.0909	235	325	477	465	3	0.413
Average							0.410 ± 0.004

Table 3. Results of K/Ar dating based on the results of measuring argon by the CF-GC–IRMS method and datings obtained in other laboratories by the standard procedure

No.	Sample	Rock, mineral	CF-GC–IRMS method			Other laboratories million years
			$^{40}\text{Ar}_{\text{air}}$, %	$^{40}\text{Ar}_{\text{rad}}$, ng	million years	
1	F-899/6	Biotit	15	0.213	80 ± 3	82 ± 2
2	P-517/9	Obsidian	5.6	0.126	29 ± 2	24 ± 5
3	P-571	Basalt	56.1	0.006	13 ± 2	14 ± 5
4	Yu-02-17	Basalt	24.3	0.099	37 ± 2	38 ± 2
5	Yu-02-19	Basalt	9.5	0.120	43 ± 2	41 ± 2
6	Yu-02-21	Basalt	13.6	0.065	30 ± 1	31 ± 2
7	GV-412	Muscovit	9.2	0.086	67 ± 3	67 ± 2
8	GV-18	Biotit	21	0.154	104 ± 3	102 ± 2
9	A-185	Biotit	23	0.053	67 ± 2	65 ± 2

gas is equal to $\pm 0.03\%$. In this case, the error of dosing the tracer in calculations of the amount of radiogenic argon should not exceed $\pm 1.3 \times 10^{-13}$ ng. The amount of an impurity of air argon also affects the error of the calculation of radiogenic argon in the measured standards. The contribution of air argon varied from 36 to 1% (Table 2). At such amounts of air argon, the error of the calculation of radiogenic argon virtually does not influence the final result [21, 24]. As a result, the total error of the determination of the amount of $^{40}\text{Ar}_{\text{rad}}$ should not exceed $\sim 2 \times 10^{-13}$ ng in our system.

It is seen from Eq. (2) for calculating the amount of ^{38}Ar of the tracer in nanograms that the error combines the error of the determination of the amount of $^{40}\text{Ar}_{\text{rad}}$, which is equal to 2×10^{-13} ng; the error of the determination of $^{38}\text{Ar}_{\text{mea}}$; and the error of weighing the sample. For a sample with the minimum weight of the standard (0.1735 mg), the weighing error is equal to 0.06%, which corresponds to the determination error of the amount of argon of $\sim 1.8 \times 10^{-13}$ ng in this sample. The weighing error for other samples is several times lower; correspondingly, taking into account the errors of $^{38}\text{Ar}_{\text{mea}}$ and $^{40}\text{Ar}_{\text{rad}}$, the maximum error of the calculation of the amount of the ^{38}Ar tracer in nanograms will be equal to $\sim 4 \times 10^{-13}$ ng.

We obtained that the reproducibility of the calibration of tracer (Table 2) is, on the average, equal to $\pm 7 \times 10^{-12}$ ng, which is one order of magnitude higher than the error of measuring one dose of the ^{38}Ar tracer, $\sim 4 \times 10^{-13}$ ng. This is possibly due to the heterogeneity of the standards Bioti–Black Salma, Muskovit–Black Salma, and for MMhb-1 at sample weights less than 10 mg.

The heterogeneity of the concentration of radiogenic argon in the standard MMhb-1 was often noted in the literature [25–27]. Because of the heterogeneity of the MMhb-1 standard sample weighing less than 10 mg, the measurement error increases to $\pm 1\%$ [28]. Data on the variations of the amount of radiogenic argon with the sample weight for the standards Biotit–Black Salma and Muskovit–Black Salma are absent and, at the same time, the divergence of the ages calculated by the results of calibration using these standards in different laboratories reaches $\pm 5\%$ [22].

Errors of the results of the determinations of radiogenic argon in geological samples depend on the sample features, and the empirical error of age calculation can significantly differ from those obtained in the analysis of standards. The results of the determinations of the age of some samples obtained in other laboratories were compared with the results of measurements of the same samples by CF-GC–IRMS using our system (Table 3). In the age calculations, we used constant values accepted in the world and recommended by the IUGS Subcommittee on Geochronology [29]. Concentrations of potassium in the studied samples were taken from results of measurements in other laboratories where argon analyses were carried

out. In our experiments, the weight of samples was varied from 31.3 to 2 mg and the amount of the extracted radiogenic argon was varied from 0.2 to 0.006 ng. All samples were analyzed at least three times. For all samples, the ages calculated by the results of argon measurements by CF-GC–IRMS coincided with the ones obtained in other laboratories within the limits of the measurement error.

Experiments on the extraction of argon from standards and real samples in measuring Ar in a helium flow on a MAT-253 mass spectrometer have shown that the CF-GC–IRMS method can be used for the determination of radiogenic argon in an amount of 6×10^{-12} g (for example, the P-571 sample weighing 15.606 mg) with an error appropriate for solving many geochronological problems. Measurement of such an amount of radiogenic argon is not the limit of the possibilities of the method, as it follows from the calculation given to substantiate the CF-GC–IRMS method. In our installation, we used a flow splitter with an efficiency of argon recycling of about 25%. For the more effective utilization of the interface, it is desirable to transfer most of the flow into the source of the mass spectrometer. However, the maximum helium flow rate of ~ 0.5 cm³/min in the mass spectrometer is limited by the breakdown potential of the ion source. On the other hand, the efficiency of using the interface can be increased by reducing the helium flow rate through the column of a gas chromatograph to ~ 0.5 mL/min, which would allow achieving 100% efficiency of the use of the amount of argon extracted from a sample. A column of the inner diameter of 0.2–0.18 mm is required for the optimum operation of the chromatograph column at a helium flow rate of 0.5 mL/min. Unfortunately, commercial MOLSIV 5A capillary columns of a diameter of 0.32 mm are not produced now, and other types of columns are ineffective in the separation of argon, oxygen, and nitrogen. The other possible way to decreasing the amount of argon can be by the replacement of the Faraday cup for ^{36}Ar with an electronic multiplier. The use of the electronic multiplier will possibly allow the reduction of the amount of argon measured in CF-GC–IRMS by more than one order of magnitude.

CONCLUSIONS

Experiments on measuring argon isotopes extracted from standard and real samples in a helium flow on a MAT-253 mass spectrometer have shown that the CF-GC–IRMS method can be used for the analysis of small amounts of radiogenic argon (6×10^{-12} g) with an error sufficient for solving many geochronological problems. Basically, CF-GC–IRMS is an alternative to the method of determining argon isotopes in a static mode. The results of these preliminary experiments have shown that the CF-GC–IRMS method used for the determination of argon isotopes has a number of positive moments. In terms of sensitivity and errors, it

is highly competitive in comparison to the classical method of measuring argon with isotope dilution. At the same time, in a dynamic mode using a continuous helium flow, measurements are much easier and more reliable compared to the whimsical method of measurements in a static mode. The measurement of a small amount of radiogenic argon does not provide the limit of the possibilities of the method, as it follows from the general representation substantiated by the use of the CF-GC-IRMS method for potassium argon geochronology. First of all, to realize the potential of this method, it is necessary to increase the efficiency of the open splitter to 100% and use an electronic multiplier instead of a Faraday cylinder in measuring ^{36}Ar . Obviously, the method of measurements in a continuous helium flow can be easily adapted to the $^{39}\text{Ar}/^{40}\text{Ar}$ method of absolute geochronology and to studies of the isotope composition of krypton and xenon.

ACKNOWLEDGMENTS

This work was supported by the Far East Division of the Russian Academy of Sciences (grant no. 09-1-ONZ-02).

REFERENCES

- Standacher, Th., Jessaberger, E.K., Dorflinger, D., and Kiko, J., *J. Phys. E. Sci. Instrum.*, 1978, vol. 11, no. 8, p. 781.
- Karpenko, M.I. and Ivanenko, V.V., *Geokhimiya*, 1993, no. 10, p. 1492.
- Reynolds, J.H., *Rev. Sci. Instr.*, 1956, vol. 27, no. 11, p. 928.
- McDougall, I. and Harrison, T.M., *Geochronology and Thermochronology by the $^{40}\text{Ar}/^{39}\text{Ar}$ Method*, New York: Oxford Univ. Press, 1999.
- Dalrymple, G.B., in *New Frontiers in Stable Isotope Research: Laser Probe, Ion Probe, and Small-Sample Analysis*, Shanks III, W.C. and Criss, R.E., Eds., 1989, p. 89.
- Wright, I.P. and Pillinger, C.T., in *New Frontiers in Stable Isotope Research: Laser Probe, Ion Probe, and Small-Sample Analysis*, Shanks III W.C. and Cris R.E., Eds., 1989, p. 9.
- Franchi, L.A., Boyd, S.R., Wright, I.P., and Pillinger, C.T., in *New Frontiers in Stable Isotope Research: Laser Probe, Ion Probe, and Small-Sample Analysis*, Shanks III W.C. and Cris R.E., Eds., 1989, p. 51.
- Matthews, D.E. and Hayes, J.M., *Anal. Chem.*, 1978, vol. 50, no. 11, p. 1465.
- Brand, W.A., *J. Mass Spectrom.*, 1996, vol. 31, no. 3, p. 225.
- Fry, B., *Rapid Commun. Mass Spectrom.*, 2007, vol. 21, no. 5, p. 750.
- Gehre, M., Geilmann, H., Richter, J., Werner, R.A., and Brand, W.A., *Rapid Commun. Mass Spectrom.*, 2004, vol. 18, no. 22, p. 2650.
- Yun, M., Mayer, B., and Taylor, S.W., *Rapid Commun. Mass Spectrom.*, 2005, vol. 19, no. 11, p. 1429.
- Ghosh, P. and Brand, W.A., *Int. J. Mass Spectrom.*, 2003, vol. 228, no. 1, p. 1.
- Werner, R.A., Bruch, B.A., and Brand, W.A., *Rapid Commun. Mass Spectrom.*, 1999, vol. 13, no. 13, p. 1237.
- Brand, W.A., in *Handbook of Stable Isotope Analytical Techniques*, de Groot, P.A., Ed., Amsterdam: Elsevier, 2004, p. 835.
- Brand, W.A., in *Adv. Mass Spectrom.*, Karjalainen, E.J., Hesso, A.E., Jalonen, J.E., and Karjalainen, U.P., Eds., Amsterdam: Elsevier, 1998, p. 661.
- Inghram, M.G., Brawn, H., Patterson, C., and Hess, D.C., *Phys. Rev.*, 1950, vol. 80, no. 5, p. 916.
- Merritt, D.A. and Hayes, J.M., *Anal. Chem.*, 1994, vol. 66, no. 14, p. 2336.
- Dalrymple, G.B. and Lanphere, M.A., *Potassium-Argon Dating Principles, Technique and Applications to Geochronology*, San Francisco: Freeman, 1969.
- Mille, A.P., *J. Res. Natl. Inst. Stand. Technol.*, 2006, vol. 111, no. 5, p. 335.
- Chernyshev, I.V., Lebedev, V.A., and Arakelyants, M.M., *Petrology*, 2006, vol. 14, no. 1, p. 62.
- Starik, I.E., *Yadernaya geokhronologiya* (Nuclear Geochronology), Moscow: Akad. nauk SSSR, 1961.
- Sampson, S.D. and Alexander, E.C., *Chem. Geol.*, 1987, vol. 66, nos. 1–2, p. 27.
- Cox, A. and Dalrymple, G.B., *J. Geophys. Res.*, 1967, vol. 72, no. 10, p. 2603.
- Baksi, A.K., Archibald, D.A., and Farrar, E., *Chem. Geol.*, 1996, vol. 129, nos. 3–4, p. 307.
- Ingamells, C.O. and Engels, J.C., *Natl. Bur. Stand. Spec. Publ.*, 1976, vol. 422, no. 1, p. 403.
- Renne, P.R., Swisher, C.C., Deino, A.L., Karner, D.B., Owens, T.L., and DePaolo, D.J., *Chem. Geol.*, 1998, vol. 145, nos. 1–2, p. 117.
- Spell, T.L. and McDougall, I., *Chem. Geol.*, 2003, vol. 198, nos. 3–4, p. 189.
- Steiger, R.H. and Jager, E., *Earth Planet. Sci. Lett.*, 1977, vol. 36, no. 3, p. 359.