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On-Line Ar Extraction System for Rapid High-Precision Routine Analysis

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ABSTRACT

A great increase in the efficiency of radiogenic argon determinations without reduction of the quality of the data has been obtained with a specially designed system. The extraction oven, purification line, ³⁸Ar reservoir, and calibration system are all inter-connected with the mass spectrometer. Getters and adsorption traps are designed for fast operation. Provision is made for storage of up to forty samples within the vacuum system so that they can be analysed in any order.

This system allows the analysis of samples at 50 minute intervals. A typical set of analyses includes ten samples, two spike calibrations and three mass discrimination measurements and requires non-stop operation of the instrument for about 12 hours. The accuracy of the radiogenic argon determination is about 1% (1 σ).

1. Introduction

The potassium-argon method is widely used for age determinations in geology due to the abundance of suitable potassium-bearing minerals in a large variety of rock types. Furthermore the successful use of relatively inexpensive residual gas analysers (such as the AEI MS 10 or the Varian MAT GD 150) for argon measurements has placed the potassium-argon technique within reach of a greater number of investigators.

Several argon dating laboratories quote a precision and accuracy of about 1% (1 σ) (LANPHERE and DALRYMPLE, 1967) and generally have a capacity on the order of two sample analyses per day. The system which will be described here considerably increases this productivity. Extensive work with this system shows that the accuracy is within about 1% (1 σ). Ten sample extractions and analyses, two ³⁸Ar spike calibrations, and three determinations of the isotopic composition of atmospheric argon can be completed in twelve hours. Sample extractions can begin at fifty minute intervals, and the total time required for a complete analysis is 135 minutes. This continuous mode of operation improves efficiency as well as control of blanks, mass discrimination and spiking.

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2. Design

2.1 Essential Features and General Layout

The following features are considered essential for rapid and well-controlled analyses:

a) The extraction oven, sample purification system, ^{38}Ar calibration system, and mass spectrometer should all be part of a single vacuum system. Only with this 'on-line' arrangement the mass spectrometer can be used to evaluate conditions within the entire vacuum system prior to the sample extractions.

b) Spike calibrations and blanks should be carried out both routinely and whenever unusual situations arise.

c) Preliminary results for a given sample should be available rapidly for use in selecting succeeding samples.

d) The sample storage capacity should be large and designed to allow selection of any sample for analysis at a given time.

e) Gas purification procedures must be efficient, complete and reproducible.

The vacuum system is an all-metal construction, in large part stainless steel, and is bakeable to 250°C . The block diagram in Figure 1 shows its general layout. Specific features of the system's components are presented below. Ultra-high vacuum valves and gas pipettes are modifications of designs developed in the Department of Physics, University of Minnesota and will not be discussed here (THORNESS and NIER, 1961). The glass mass spectrometer was designed and constructed by P. EBERHARDT (Physikalisches Institut der Universität Bern).

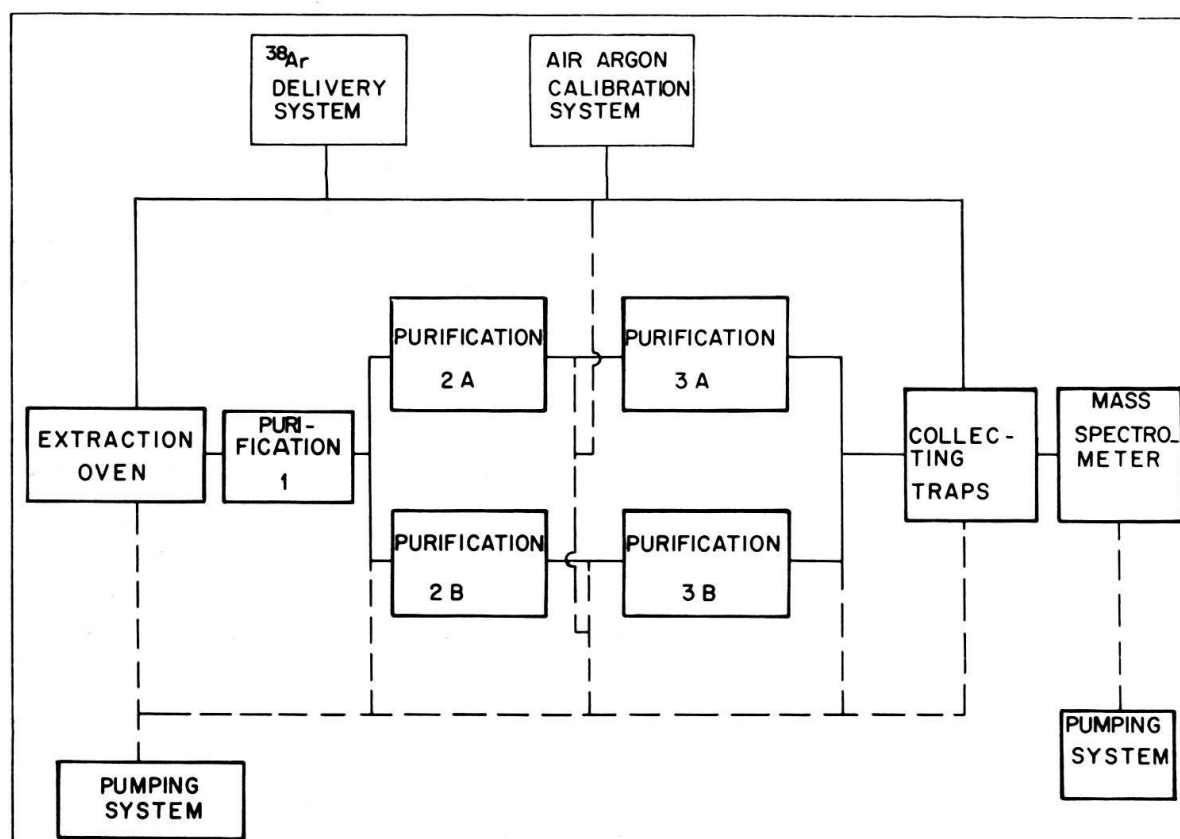


Fig. 1. Block diagram of the 'on-line' argon system.

2.2 Sample Storage Cap

A photograph of the sample storage cap is shown in Figure 2. The 100–500 mg mineral samples are wrapped in 0.001" nickel foil. This nickel wrapping makes the samples magnetically maneuverable and, furthermore, the high melting point of the nickel prevents sample loss due to decrepitation during rapid release of volatiles. The samples are distinguished by the size and shape of the foil package and, if necessary, by felt pen marks.

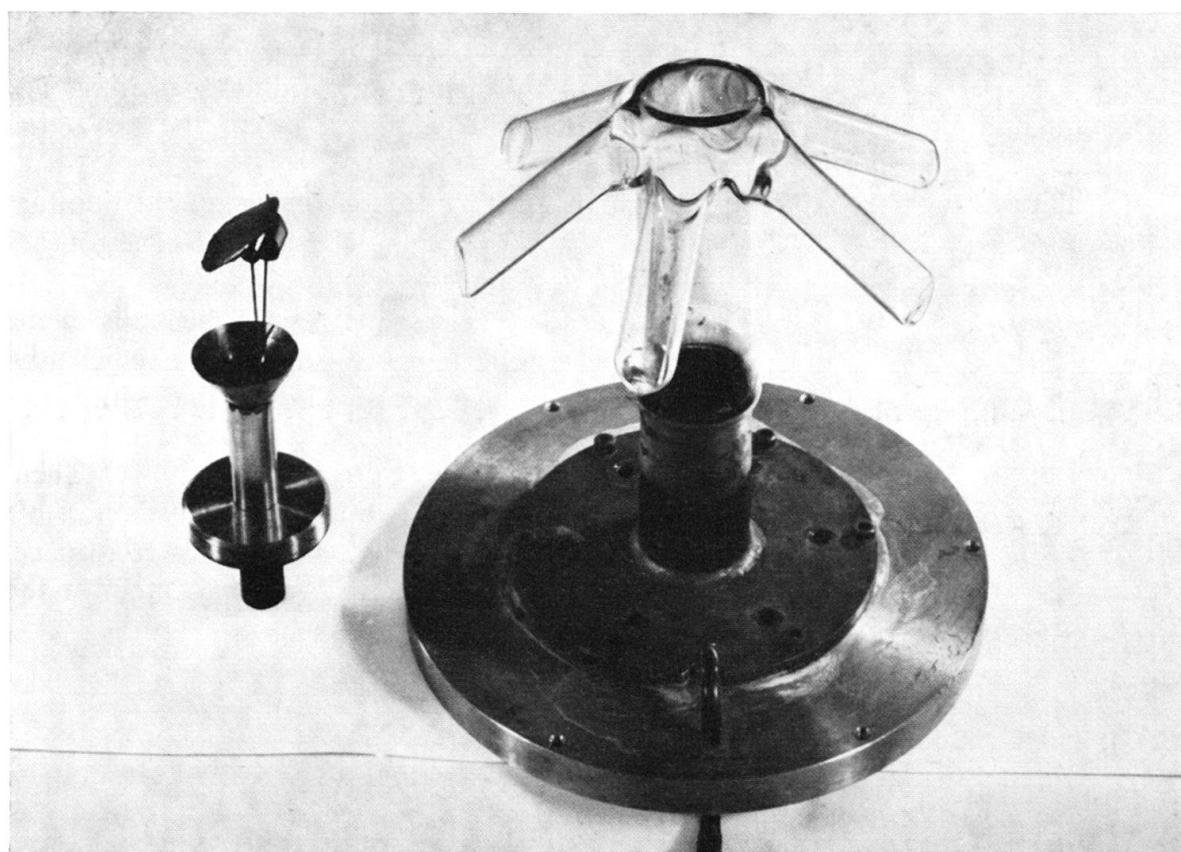


Fig. 2. Sample storage cap and guiding funnel with magnetically operated disc to prevent coating of viewing port with condensates.

The sample to be analysed is separated from the others in the same compartment using two horse-shoe magnets arranged in opposite polarity. Once free, the selected sample is moved to the center of the storage cap and dropped into the extraction crucible, guided by the funnel shown beside the cap in Figure 2. The magnetically operated metal disc on top of the funnel permits observation of sample melting while preventing formation of opaque deposits on the viewing port on top of the storage cap.

2.3 Extraction Oven

The extraction oven consists of a molybdenum crucible heated by radiation from a resistance heated sheet-tantalum element. A thermocouple near the crucible bottom is used to control the crucible temperature within a few degrees. The molybdenum

crucibles used are commercially available (Metallwerke Plansee; cost about \$10.–) and are 2" in height, $\frac{5}{8}$ " o.d., and $\frac{1}{2}$ " i.d. A molybdenum insert to reinforce the lower portion increases the crucible lifetime, which is usually determined by leaks produced by the formation of molybdenum-nickel alloys. When a new crucible or tantalum heater is installed, the assembly is heated in air to about 800°C in order to oxidize hydrocarbons.

The oven is evacuated down to the micron range through a rough pump line before switching to the normal pumping system. Other portions of the vacuum system are independently pumped until the pressure in the extraction oven is below 10^{-6} torr.

Several procedures are used to obtain minimum blanks:

a) Cycling of the oven temperature is more efficient than continuous heating. The maximum cycling temperature (1850°C) is about 50° higher than the extraction temperature.

b) Filling the oven with 1 atm. of high purity nitrogen (any exposed titanium getters must be cold) for one hour is effective in reducing the amount of argon adsorbed on surfaces of both the system and the samples.

c) Cooling the oven with an air stream instead of water allows the walls of the oven volume to reach a much higher temperature and thus degas more efficiently. Of course, in this case, the cycling temperature must be kept lower than with water cooling.

The samples are dropped into the oven at a temperature of about 800°C. Then, the oven temperature is raised to 1800°C within about two minutes. This is possible because no gas discharges can occur as in a radio frequency induction heated furnace. During the extraction and first purification, a Pirani gauge is used to monitor the pressure.

2.4 Purification Units

The purification units contain three components:

Titanium sponge getters

Copper-copper oxide getters

Zeolite adsorption traps

The construction of the titanium and copper-copper oxide getters is the same (Fig.3). The gettering material is distributed on mesh discs spaced along the input tube. The gas must pass through the active material. To prevent alloying between the titanium and stainless steel, a tantalum sleeve is inserted into the outer stainless steel tube. The getters are externally heated.

The titanium getters are first held around 800°C. At this temperature, the metal reacts with hydrocarbons, CO, N₂, C, O₂, and H₂O. The reactions with hydrocarbons and water produce free hydrogen, which reacts when the getter is later cooled to room temperature. The copper-copper oxide getters are operated at 800°C throughout the entire purification procedure. Their function is to convert residual hydrogen to water, which is adsorbed on the zeolite traps.

The all-copper zeolite traps (shown in Fig.4) function as a purification medium and are also used for adsorptive transfer of gases. The zeolite is held in contact with the walls of the trap by copper mesh. This improves the thermal contact and hence adsorption or desorption speed. The baffles assure multiple collisions of the molecules

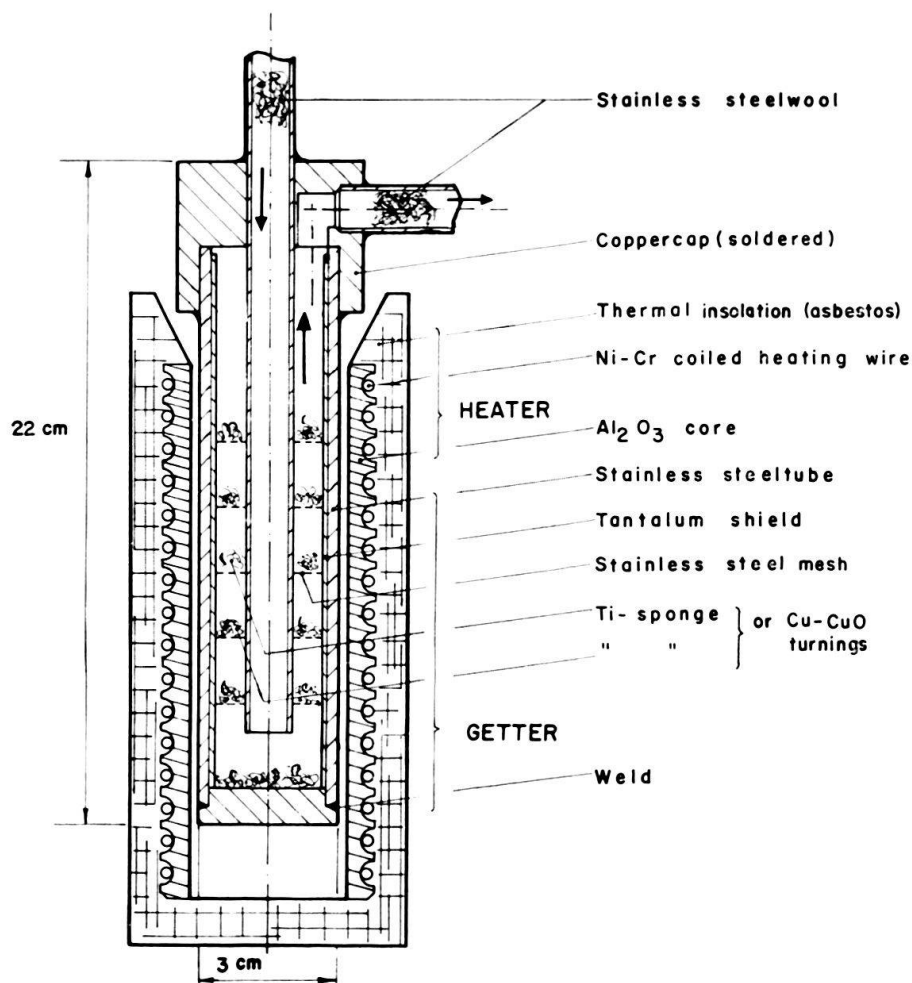


Fig. 3. Construction of titanium getters and getter-heaters. Copper-copper oxide getters are constructed similarly.

with the zeolite. All condensable gases (including argon) are completely adsorbed on the zeolite after ten minutes at liquid nitrogen temperature (-196°C). A dry ice-acetone mixture (about -70°C) is applied to the zeolite for argon desorption without release of water, carbon-dioxide and some other contaminants. It is important to note however, that argon is only partially released at the dry ice-acetone temperature. To obtain total Ar release its partial pressure is kept low by adsorption onto a second trap at -196°C . The Ar desorption from the last transfer trap into the mass spectrometer must be carried out at 80°C . The adsorption and release characteristics of the zeolite traps can be verified with the on-line mass spectrometer. We have found them to be a complex function of the thermal history of the zeolite and the composition and amount of the contaminants. Thus, the advantage of zeolite over well degassed charcoal is not clear.

When the sample gas is expanded into a purification unit, it is exposed to the hot titanium and copper-copper oxide getters for five minutes. Then, it is adsorbed on the zeolite trap for fifteen minutes. Just prior to desorption, the purification unit is pumped for two minutes by the Hg-diffusion pump to remove any gases not adsorbed

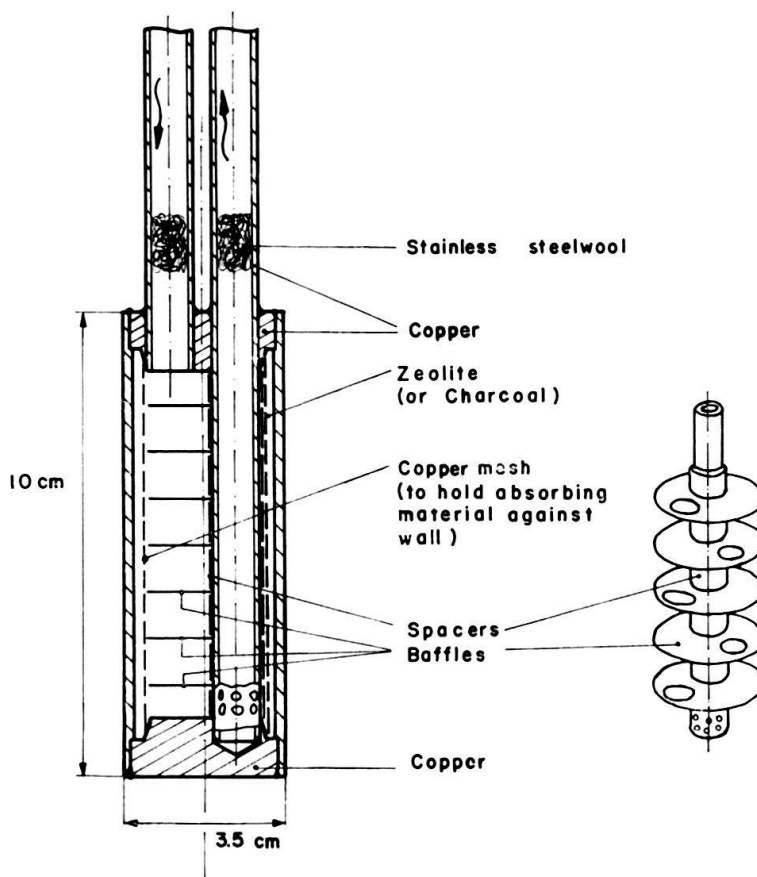


Fig. 4. Construction of zeolite (charcoal) traps.

(H, CH₄, CO). When the sample is desorbed, the titanium getter is cooled below 100°C within about two minutes. This allows an additional gettering action. Only after this operation the gas mixture is expanded into the next segment of the vacuum system.

Each sample passes through two complete purification units of the type described above. Initial rough cleaning is performed by a single titanium sponge getter, which is held at 800°C during the sample extraction and lowered when the extraction oven is cooled. Because of the long residence time of samples in this region of the system, two parallel purification lines of two units each are provided (Fig. 1). Successive samples alternate between these parallel lines, so that the length of the purification procedure does not limit the time interval between analyses. The general arrangement of the purification portion of the system is shown in Figure 5.

2.5 Gas Metering and Dispensing Systems

Both ³⁸Ar spike and high purity atmospheric argon are stored in stainless steel volumes and admitted to the system through the gas pipettes P₃ and P₂, respectively, as shown in Figure 6. Both gases can be delivered either to the mass spectrometer or into the extraction oven.

The air-argon system contains a second gas pipette (P₁) and a mercury manometer. A pressure of 5–10 cm Hg of argon is admitted to the manometer through the stopcock of a primary storage bulb, and is read to ± 0.05 mm using a cathetometer. A known amount of gas is taken with the first gas pipette (P₁) and expanded into a storage

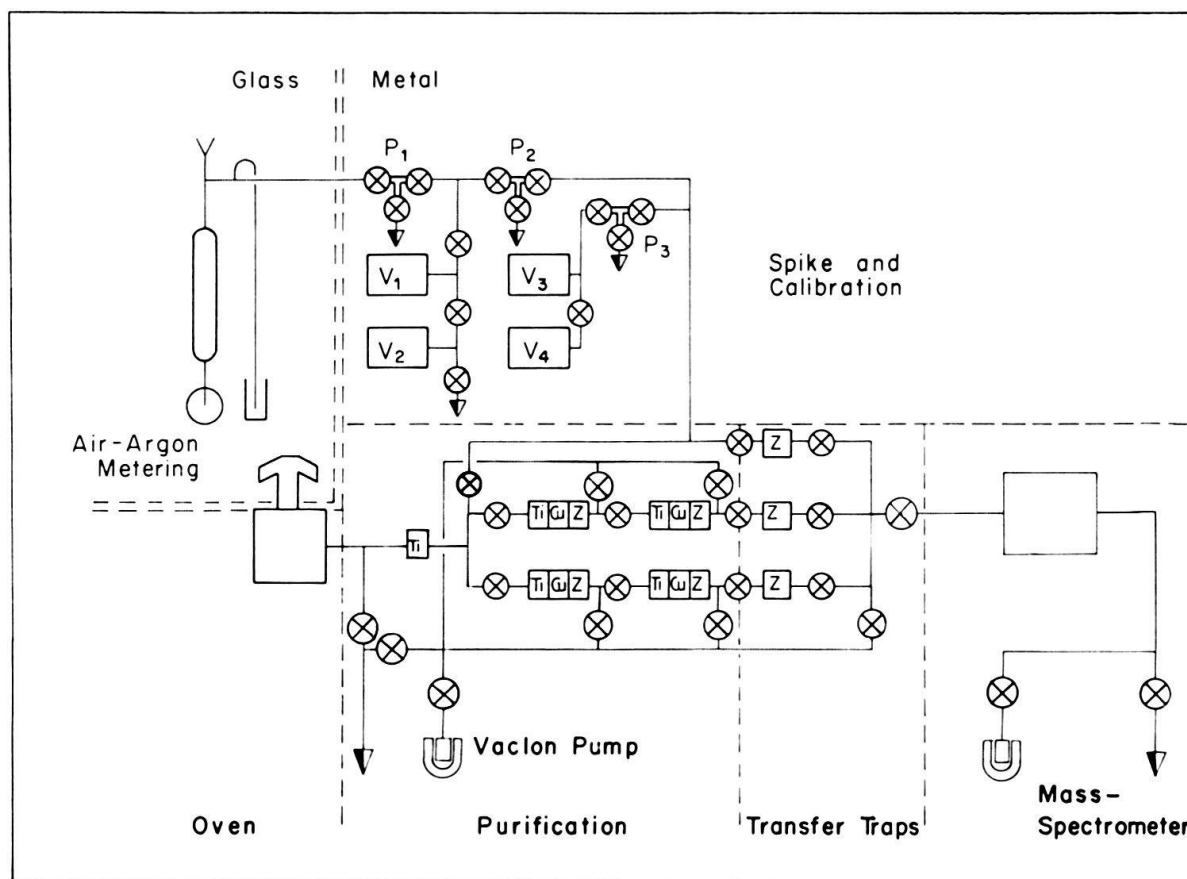


Fig. 5. Operational details of the entire argon system. Half black arrows indicate diffusion pump leads.

volume (V_1 or $V_1 + V_2$ or $V_1 + V_2 + V_3$). Since the volumes of the pipettes P_1 and P_2 and the storage volumes V_1 , V_2 and V_3 are well known, the amount of gas delivered from P_3 as a function of the manometer pressure is known.

The ^{38}Ar delivery system consists of one gas pipette P_3 and the storage volumes V_4 and V_5 . The ^{38}Ar is initially admitted to the system from a glass breakoff. An additional valve with a second storage volume and a zeolite trap provides two possible ^{38}Ar quantities and allows the ^{38}Ar to be removed from the volume adjacent to the pipette if servicing or baking of the pipette is required.

The absolute amount of ^{38}Ar delivered from P_3 is determined by analysing a mixture of a known amount of air argon delivered from pipette P_2 and the unknown amount of ^{38}Ar delivered by pipette P_3 . The air-argon is replaced in the storage volume about every second day of operation. The result of the ^{38}Ar calibration depends on the manometer reading, the measurements of volumes V_1 , V_2 , V_3 and the two gas pipettes P_1 and P_2 . The physical measurement of all volumes are accurate to 0.1% or better. Particular care must be taken to minimize volume change due to distortion of the copper valve seats of the pipettes. Thus, it is essential that the pipettes can be opened for inspection and replacement of the seats and diaphragms. Furthermore, it is important that the pipettes are opened and closed according to a strict time sequence and a reproducible torque. Also, it is essential that the two gas dispensing systems are held constant, because varying or uneven temperatures affect the calibration constants.

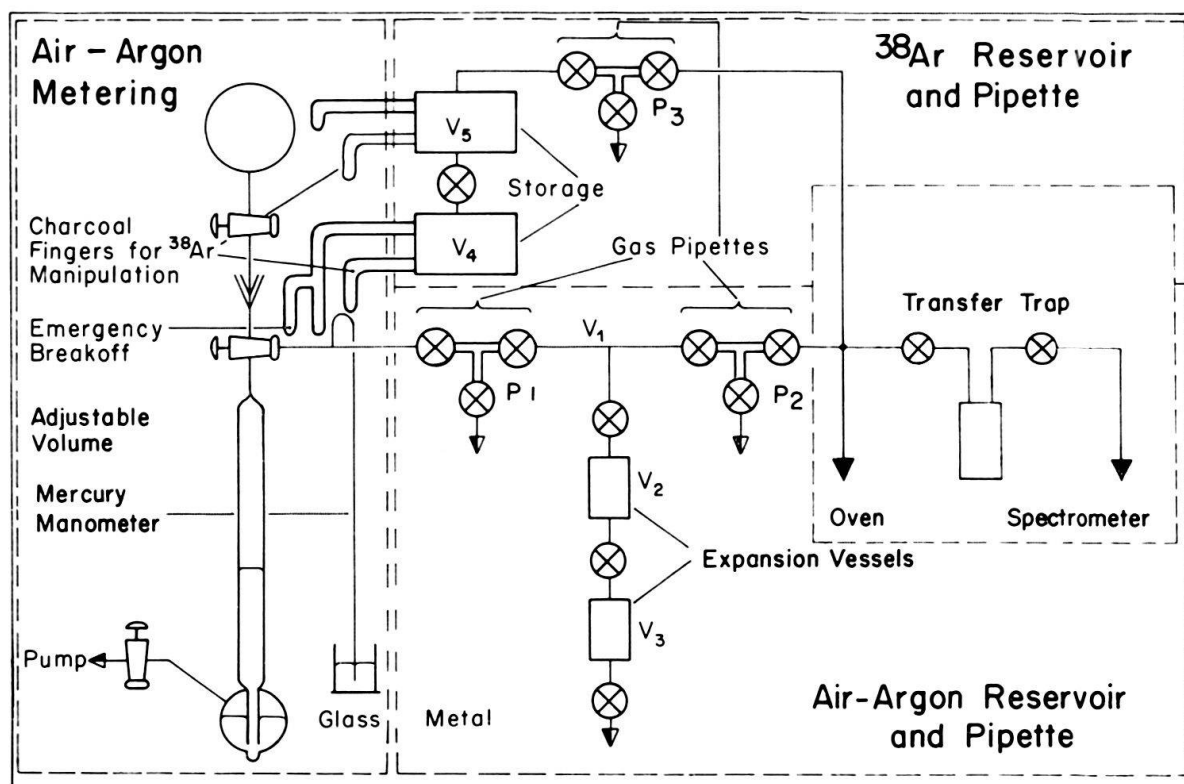


Fig. 6. Details of calibration system, consisting of air-argon metering and both air-argon and ^{38}Ar -dispensing systems. Half black arrows indicate pump leads.

An independent check of the volume constants of our calibration system was made by comparing our system with that used for rare gas studies in meteorites at the School of Physics, University of Minnesota. Agreement to better than 2% was obtained.

2.6 Pumping System

The argon vacuum system is evacuated by three mercury diffusion pumps and two 8 liter/sec sputter pumps. The mercury pumps are used when the system is in operation. The sputter pumps are only used to keep the system under vacuum during stand-by periods. One of the sputter pumps is also used to pump clean parts of the system when the oven or other parts are degassing through the mercury pumps.

3. Operating procedures

1. The operating schedule allows a minimum of ten minutes pumping time between periods of use for any part of the system.
2. At the beginning of an operating period, residual spectra of the isolated system, with the oven at extraction temperature, indicate the condition of the system and the expected blank level.
3. An ^{38}Ar spike calibration is made prior to the sample extractions. The first large ^{40}Ar signal is used to adjust the potentials of the ion source for maximum sensitivity. They are then left unchanged in order not to alter the mass discrimination by variable gas composition due to contaminants. After the source tuning, the data for the initial spike calibration are taken and the first extraction is started.

4. The ^{38}Ar spike is expanded into the extraction oven volume *before* a sample is dropped into the crucible. As the sample is heated, the mean free path of argon is greatly reduced by the rapid rise in pressure of evolving gases. This decrease in the mean free path could cause incomplete equilibrium of the sample argon and spike argon, which would produce erroneous results.

5. The extraction temperature is maintained at 1800°C to insure complete release of argon and to achieve a partial vaporization of sample. Pressure readings are taken with a Pirani gauge during the extraction to monitor the effectiveness of the titanium getter in the oven volume.

6. In order to insure complete release of sample gas from the final zeolite trap, it is held at 80°C for ten minutes. The gas is then allowed to equilibrate through the mass spectrometer input valve before data are taken. The isotope ratios are corrected for memory effects by extrapolation to the time of gas admission.

7. A second ^{38}Ar calibration following the samples and a measurement of atmospheric argon provide three determinations of mass discrimination during an operating day.

8. After about ten sample analyses, contaminants have saturated the first getter. Baking for about 12 hours at 1000°C restores the gettering efficiency of titanium and copper-copper oxide.

4. Results

4.1 ^{38}Ar Calibrations

The determinations of the ^{38}Ar pressure reflect both the reproducibility of delivery of the gas pipettes and the reliability of the manometer readings. The average and standard deviation of the results from each filling of the air-argon storage volume are plotted in Figure 7. Each point represents two to four determinations. Inactive periods of several months have grouped the data into clusters which were averaged for data reduction purposes. Average values and standard deviations for these data groups are also shown in Figure 7, indicating standard deviations of approximately 1%. These include errors in manometer readings, reproducibility of the three pipettes, mass discrimination, and chart reading.

4.2 Extraction Blanks

Randomly spaced determinations of the argon accumulated in the system during the extraction procedure have fluctuated between 0.5 to 2.5×10^{-7} cc STP of ^{40}Ar . These fluctuations may reflect the occasional existence of actual leaks or may be due to insufficient degassing of the oven and/or the whole system. No evidence for significant radiogenic argon memory has been detected in blanks, including those immediately following sample determinations. No systematic difference was found between blanks run prior to sample determinations and those carried out between sample analyses. Comparison of the blank values with the air argon corrections for samples indicates that most of the mica samples analysed for this work contain approximately 1×10^{-6} cc STP air argon per gram.

4.3 Analyses of Standard Samples: P 207 and Bern 4 M

In order to evaluate the accuracy of our analyses, two standard samples were extensively investigated. For our primary standard we chose the widely distributed

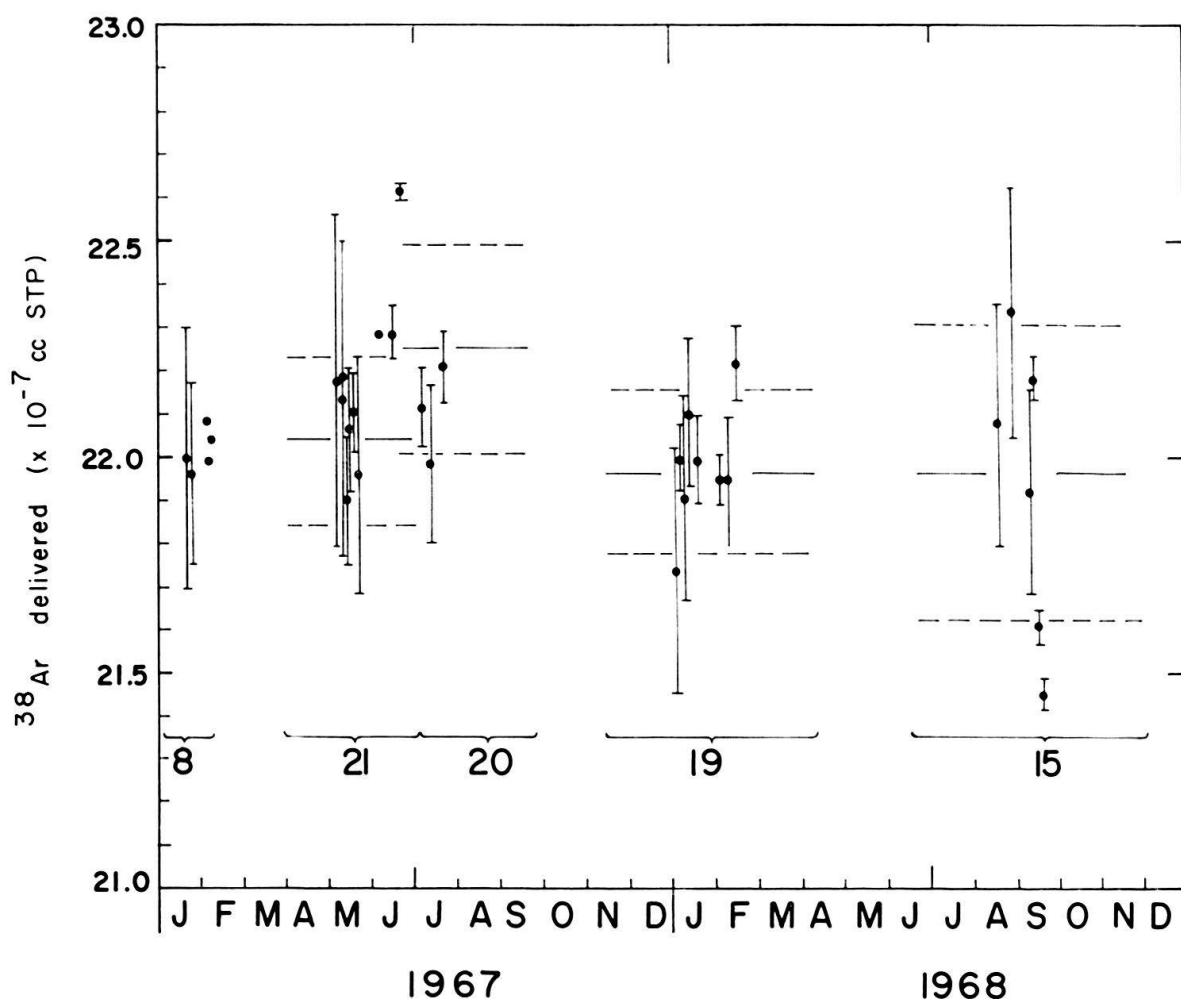


Fig. 7. Summary of ^{38}Ar calibration results. Each point with standard deviations represents the results for a single manometer measurement (see text). The brackets and number of determinations per group show the grouping for calculation purposes. The horizontal solid and dashed lines mark the average and standard deviation for each grouping.

and analysed P-207 muscovite (LANPHERE and DALRYMPLE, 1965, 1967). These results were supplemented by analyses of the 4M muscovite (JÄGER et al., 1963).

These mineral standards were analysed frequently during the first months of operation of our system. Later, analyses of P-207 were included routinely with the unknown samples. We have maintained the alternative of using the P-207 results for ^{38}Ar calibration purposes in case the procedures with air argon proved unreliable. At this time, however, we consider this an extremely unlikely possibility.

In Table I our determinations of the argon concentrations in two interlaboratory standards are given. Comparing our P-207 results with the published average value we estimate our accuracy to be better than 1% for samples of less than 50% atmospheric correction. In view of the lack of suitable mineral standards for biotite, glauconite and hornblende we must assume this accuracy to hold also true for these minerals.

Our results for the 4M standard muscovite scatter more than 1% (mainly due to one high value). Since the results reported by several workers at the Colloquium of Phanerozoic Orogenic Belts appear to be less consistent than for P-207, we do not

Table 1. Analysis of Interlaboratory Standards For Argon

Sample	Weight (mg.)	% Ar ⁴⁰ *	Ar ⁴⁰ * ($\times 10^{-5}$ scc/gm)	ave $\pm 1 \sigma$	Published values
P 207 musc.	213.6	94.9	2.823	2.842 ± 0.029	2.824 ± 0.054 (1)
	183.9	95.3	2.831		
	205.7	95.3	2.825		
	252.2	95.7	2.885		
	203.4	96.2	2.866		
	221.3	96.2	2.776		
	247.8	96.4	2.853		
	224.1	93.8	2.845		
	180.2	95.8	2.846		
	238.9	96.5	2.867		
	188.9	95.0	2.811		
	215.8	90.5	2.852		
	219.1	95.0	2.865		
Bern 4 musc.	390.5	65.5	0.6081	0.6300 ± 0.0263	0.618 ± 0.012 (2)
	342.8	64.0	0.6277		0.642 (3)
	352.5	46.2	0.6153		0.642 ± 0.013 (4)
	351.7	51.8	0.6230		
	354.0	65.4	0.6818		
	344.4	57.2	0.6239		

(1) LANPHERE and DALRYMPLE, 1967

(2) STEIGER, 1964

(3) LANPHERE and DALRYMPLE, 1965

(4) ARMSTRONG, R.L., in prep.

think that our scatter for 4M contradicts the 1% estimate of accuracy based on our P-207 results.

4.4 Replicate Analyses

In two years we have carried out 167 argon determinations on 57 different samples including biotite, muscovite, hornblende, and glauconite with corrections for atmospheric argon of less than 50%. The distribution of these replicate analyses is Gaussian and has a standard deviation of about 1%.

Acknowledgments

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