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Improved Resolution and Precision of Argon Analysis Using an MS 10 Mass Spectrometer.

by DAVID C. REX and MARTIN H. DODSON

ABSTRACT

The resolution and peak shape obtained on argon using an A.E.I. MS 10 mass spectrometer are improved by using a 4.1 kG permanent magnet in place of the standard 1.8 kG magnet. The precision obtained with a digital out-put and peak switching system is considered with special reference to young K-Ar ages.

The AEI MS 10 mass spectrometer is a small bakeable metal instrument with 180°, 5 cm radius analyser section. It was first applied to argon isotope analysis by FARRAR, MACINTYRE, YORK and KENYON from Toronto. They described their experience at the 12th Annual ASTM meeting on mass spectrometry. We understand that since then 20–30 laboratories have bought MS 10's for argon isotope analysis. We wish to summarise here our experience in the last few months at Leeds with this instrument using a more powerful magnet and digital output. We hoped that digital output would improve precision of measurement of high atmospheric argon contamination.

We use a 25 litre per sec. ion pump to evacuate the mass spectrometer. A pressure of 10^{-8} torr is easily obtained. The whole system can be baked at 400 °C with the filament off and can be given what we call a "cool bake" at 150 °C with the magnet in position and the filament on. After this very little background is seen in the mass spectrometer and none at masses 36 to 40. (The detection limit for argon is of the order 10^{-12} std.cc. with the digital output.) The tube unit can be isolated from the ion pump by a high vacuum valve (Fig. 1) and all samples are run statically. The system is roughed out with a sorption pump which is then isolated from the high vacuum system.

The argon extraction system is directly linked to the MS 10 through a variable leak valve with a conductance of 1 litre per sec. fully open. The system (Fig. 2) is built in pyrex glass with metal high vacuum valves. The samples are heated by a R.F. generator using Molybdenum crucibles. The system is pumped with a mercury in glass diffusion pump backed by a rotary pump. The Ar-38 spike is aliquotted into the system through a double metal closure valve designed by staff at the Cambridge geochronology laboratory.

In its simplest version the MS 10 is fitted with a permanent magnet, masses being selected by variation of the acceleration voltage. Using the usual 1.8 kG magnet with 0.025 cm collection slit, argon peaks are well resolved, but the peak shapes are usually rather poor (Fig. 3). Recently a 4.1 kG magnet has been introduced. This means increasing the accelerating voltage from 100 volts to 420 volts to tune to Ar-40. We

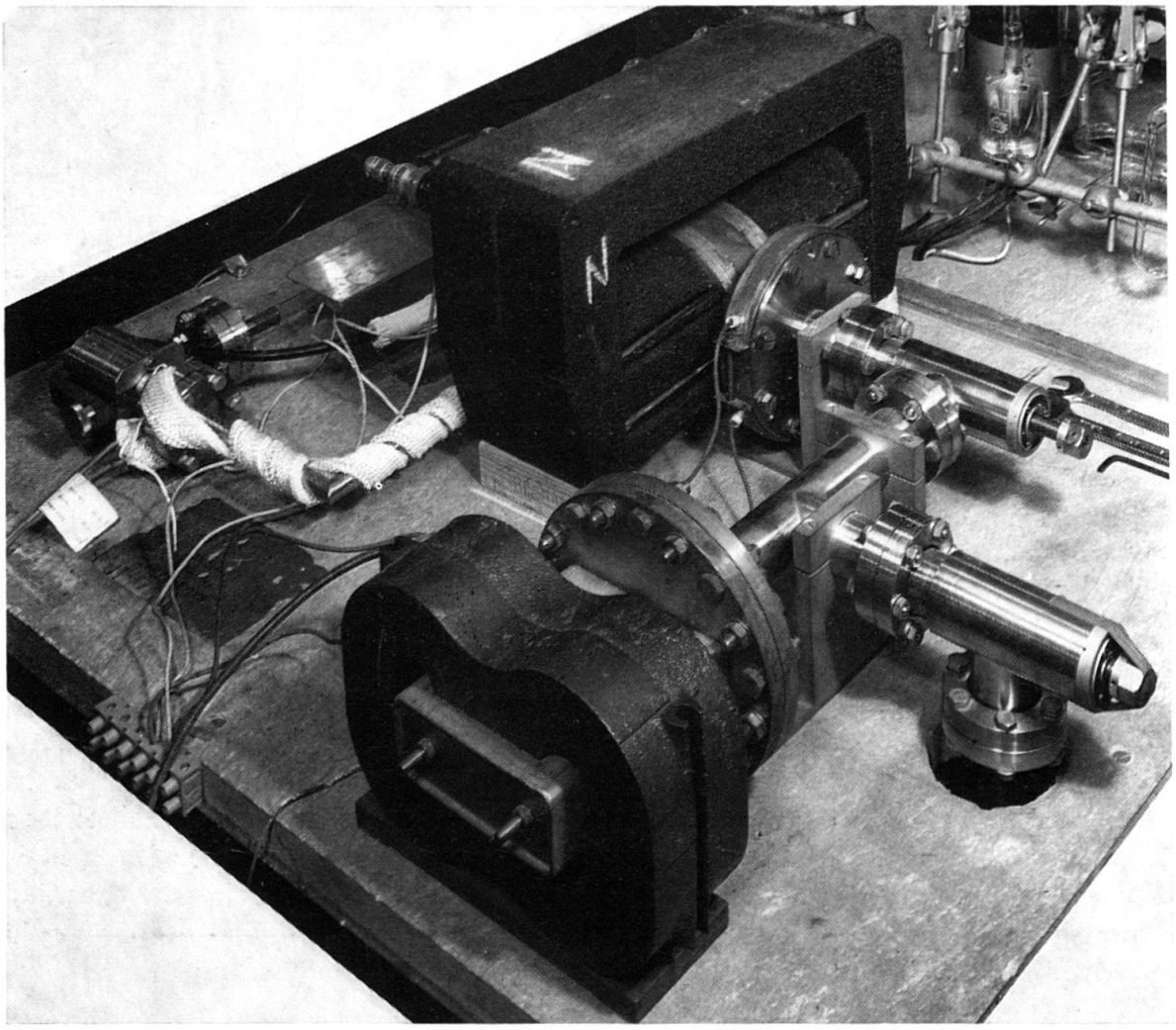

Fig. 1. MS10 with large magnet and pumping system. Ion pump in foreground, isolation valve at upper right. Valve at lower night leads to sorption pump.

have found that focussing is greatly improved (Fig. 3) so that a 0.050 cm collector slit can be used. Resolution is approximately 45 at the 0.1 % level and 67 at the 1 % level. We feel that this resolution would enable the MS10 to be used for Ar-40/Ar-39 method, though a 0.040 cm slit might usefully improve the unit mass separation.

The increase of the accelerating voltage to 420 V has introduced a small memory effect but this has not caused us serious difficulties (Fig. 4). It can be seen that the memory for 40/38 is only 0.05 % per min. compared with approximately 1 % per min. on the Reynolds mass spectrometer, which uses 2000 volts acceleration voltage. This spiked run was analysed after running samples of atmospheric argon, and the memory figure corresponds roughly to the rate of exchange of this sample with those previously analysed.

The output from the MS10 has been digitised, using a Hewlett-Packard voltage-to-frequency converter (Model 2212A) connected to an Advance TC6 timer counter. The displays are printed out on a Kienzle printer.

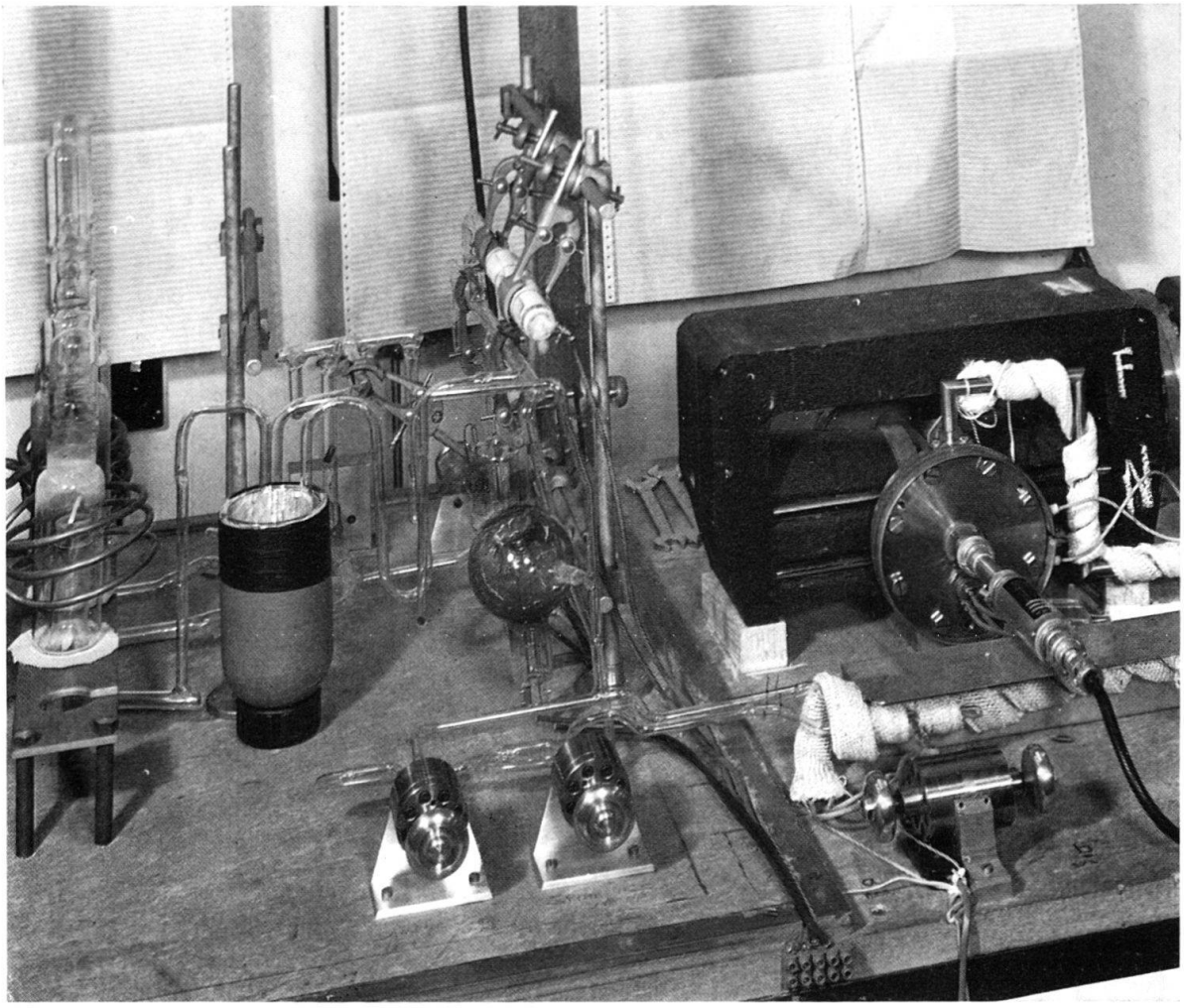

Fig. 2. MS10 with argon extraction system. Spike aliquotting valve right of centre, with Ar-38 reservoir below table.

We have found that by using a 10 sec. counting time all measurements can be made using the one amplifier sensitivity, namely 10 V F.S.D. This range and counting time gives 2–3000 pulses for the Ar-36 peak in atmospheric argon.

To help make best use of the digital system Mr. Dickinson of our department has built a peak-switching control which enables the peaks 40, 38 and 36 to be selected as well as the base line between peaks. Tuning of the peaks is checked by using a switch which displaces the beam to either side to give roughly half the peak height. The good peak shape previously mentioned makes this operation easy. Since the initial tuning it has only been necessary to tune to one peak, to have all in tune. The acceleration voltage supply is stable enough for the peaks to remain in tune for an hour or more. We have been able to include masses 28 and 16 in our peak-switching system but unfortunately hydrogen cannot be observed, as it would require 8400 volts when the large magnet is employed. When running a sample we measure at 40-38-36$^1/_2$-36-35$^1/_2$-40 etc., with 10 sec. count time at 7 sec. delay time. The peak heights and base-line measurements are interpolated linearly to obtain 40/36 and 40/38 ratios. To show the precision of the digital output we have measured 40/36 ratios in atmospheric argon

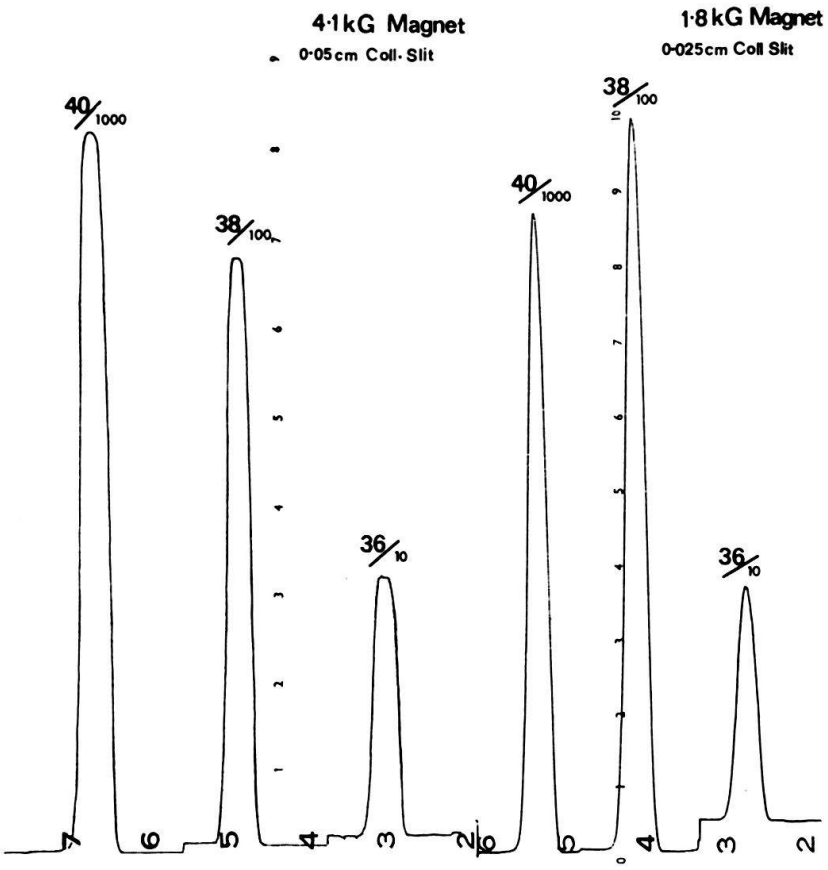

Fig. 3. MS10 argon spectra with different analyser magnets.

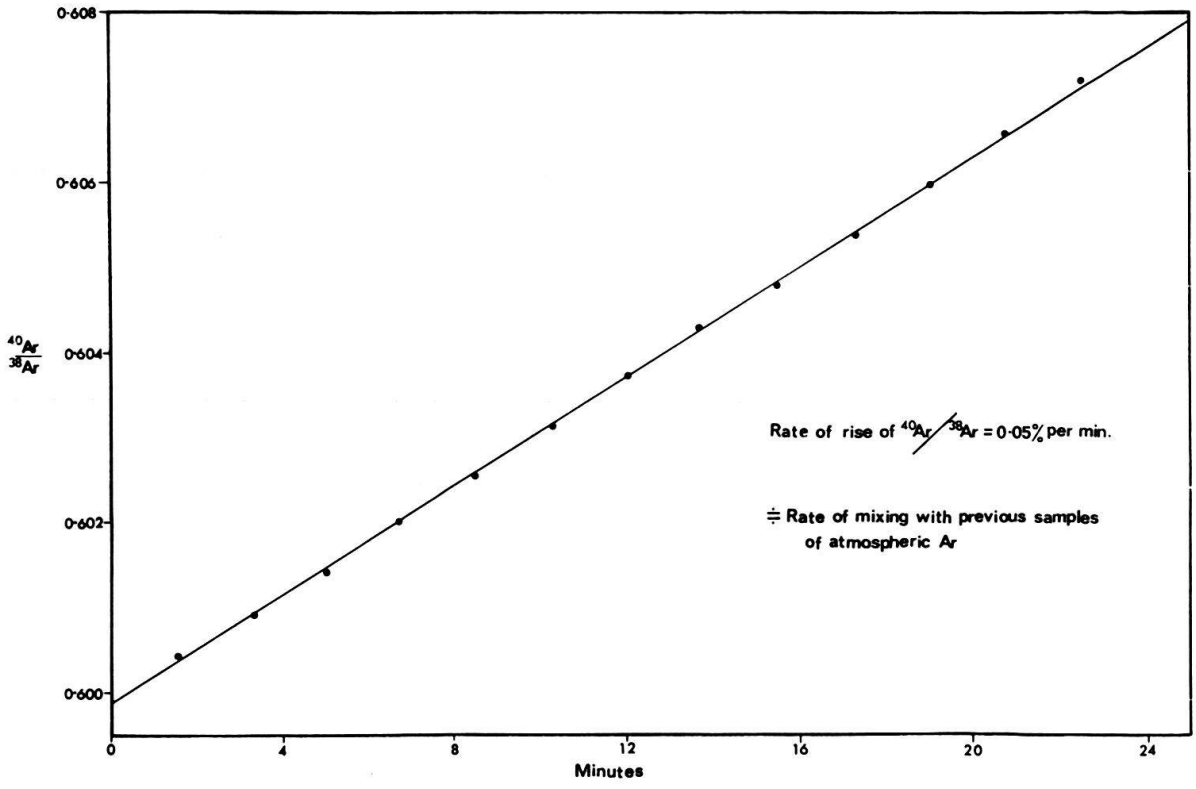

Fig. 4. Memory effect of a MS10 fitted with a 4.1 KG magnet.

Table 1. Atmospheric argon isotope ratios obtained with digital output on MS10.

Date 1969	$^{40}Ar/^{36}Ar$	Std. error on mean
2nd June	289.36	0.08
4th June	288.80	0.06
13th June	288.73	0.06
18th June	289.21	0.09
30th June	288.81	0.08
30th June	288.96	0.07
10th July	288.52	0.09
16th July	288.40	0.08

Mean $^{40}Ar/^{36}Ar$ 288.85

Std. deviation amongst analyses $\pm$ 0.30

(Table 1). The standard error within each run is between 0.02 and 0.03% while the standard deviation of the set of eight analyses is 0.1%. The latter is probably caused through the variation of the mass discrimination effect over a period of days.

Variation of the ion repeller voltage affected the beam intensity and the 40/36 ratio. We chose a value of + 5 V wrt cage which was on a flat part of the curve where small variation in the voltage would least affect the 40/36 ratio. The electron volts were kept to the recommended 70 V and the trap current at 50 μA. The ratio of 288.85 for the 40/36 has been corrected for fractionation into the mass spectrometer by multiplying by $\sqrt{40/36} = 1.054$. This factor has been checked by allowing a small volume of atmospheric Ar to equilibrate between the MS tube and the extraction system and it agreed with theory to 0.2%. This error may be due to poor gas conductance in the pipes to and from the leak valve.

The contribution to the standard error in radiogenic argon determination on samples with low atmospheric contamination is about 0.05% due to determination of the 36 peak height. With the apparatus described we hope to measure very small amounts of argon. We have run some samples giving an age of about 12 m.y. and obtained good reproducibility. We have also run two recent lavas unspiked, a 1961–2 Tristan da Cunha lava and a 1969 Deception Island lava, to test the problems of measuring large atmospheric contamination. With the Tristan lava we found an apparent excess of Ar-40. This agrees with the recent work of DALRYMPLE (1969). With the apparatus it is possible to freeze the argon down onto charcoal in a small volume which can be isolated from the rest of the system. This connects to the mass spectrometer via the leak valva. The small volumes of gas can therefore be leaked rapidly into the mass spectrometer. Using this method the Tristan da Cunha lava gave

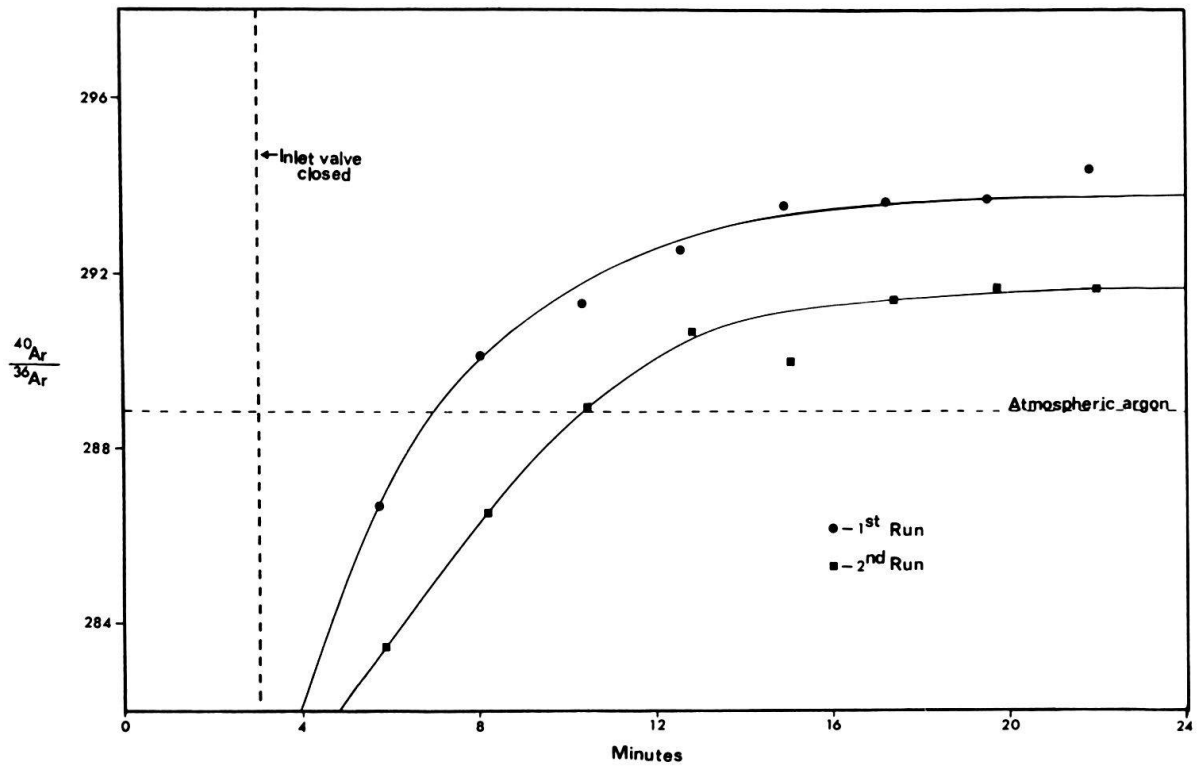

Fig. 5. Changes in measured $^{40}Ar/^{36}Ar$ ratio when argon from Tristan 1961–62 lava was equilibrated between extraction system and MS10.

40/36 ratios of 296.7 and 294.8, while the Deception Island Lava gave 289.2. The fractionation correction is so important with these ratios that we tried equilibrating samples of the gas with the mass spectrometer tube. The results for the Tristan da Cunha lava are shown on Figure 5. The rise in the 40/36 ratio is believed to be due to clean up of initial hydrocarbon contamination since peaks were observed at masses 37, 39, 41, although the methane peak was below 10% of the 40 peak. When the sample of gas was left in the mass spectrometer for half an hour a 40/36 ratio of 294.6 was obtained showing no rise over 10 scans, so the contamination is apparently cleaned up by the mass spectrometer. We are unable at present to explain the differences between two successive runs on the same gas sample.

Our clean up procedures are a liquid nitrogen trap, Cu-CuO furnace heated to 450°C., and Ti sponge heated by the RF generator to dull red heat and allowed to cool slowly. If on examination it is found that peak 16 is high we use a tungsten filament heated to approximately 2000°C to crack the hydrocarbons followed by another Ti sponge clean up. We have recently found that active charcoal at — 117°C (frozen ethyl alcohol) will hold down CO and methane, allowing argon to pass on. We have not used any molecular sieve as a clean-up agent yet.

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