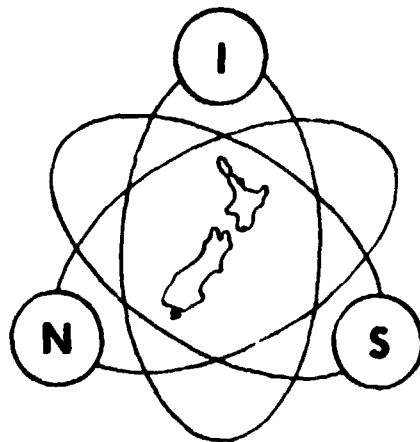
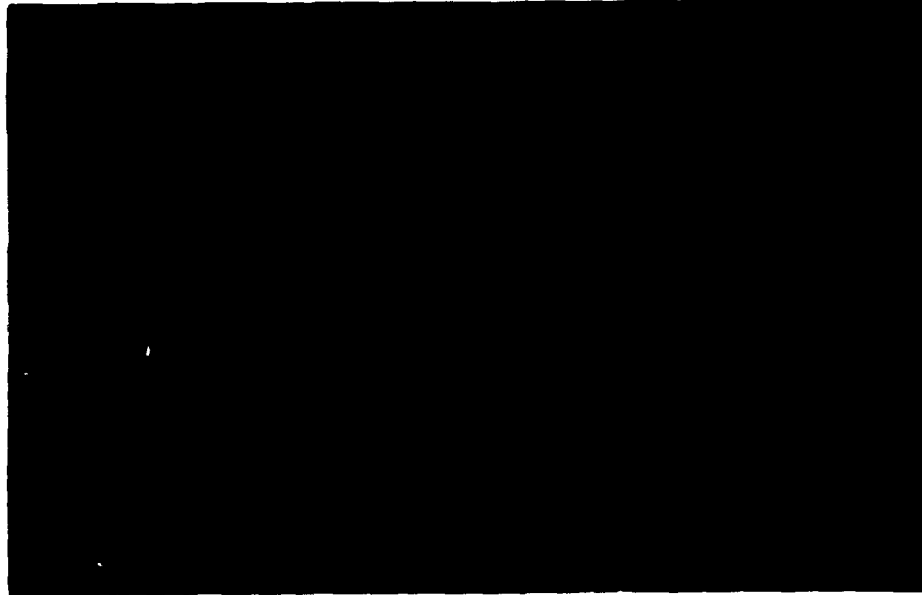


TRN NZ8600358



INSTITUTE OF NUCLEAR SCIENCES

Department of Scientific and Industrial Research

LOWER HUTT, NEW ZEALAND

Institute of Nuclear Sciences INS-R--522

HOT SHOT REDUCTION OF WATER TO HYDROGEN

FOR ISOTOPIC ANALYSIS

by

K. Stanley, G.L. Lyon and N.K. Stewart

February 1984

Institute of Nuclear Sciences, DSIR,

Lower Hutt, New Zealand

ABSTRACT

A simple new technique for quantitative reduction of water to hydrogen gas for isotopic analysis is described. Individual pyrex glass tubes are used as both reaction vessels (for the reaction of zinc shot with water to give hydrogen), and sample bottles (to transfer hydrogen to the mass spectrometer for analysis). The technique is based on that reported by Coleman et al. (1982), but we have added an additional step, in which the zinc shot and tube is heated to the reaction temperature and the resultant gases are pumped away before the water sample is admitted. Results show good precision and memory effects are almost eliminated.

KEYWORDS

DEUTERIUM
HYDROGEN
WATER
SAMPLES

INTRODUCTION

Previous methods for the determination of deuterium content of waters at the Institute of Nuclear Sciences have involved the movement of water by evaporation through a furnace containing either zinc (Lyon & Cox, 1980), or uranium (Stewart & James, 1981), where it is converted to hydrogen gas. The hydrogen gas is then collected in sample bottles by either Toepler pumping or absorption onto charcoal.

In the hot shot method, water is injected into a reaction vessel containing zinc and the vessel itself is placed in a furnace where conversion to hydrogen gas occurs. Since the zinc is used for one sample and no movement of water or hydrogen gas is involved, the problem of memory from previous samples is greatly reduced.

METHOD

Water is converted quantitatively to hydrogen gas by reaction with zinc shot metal at 450°C.

The zinc is BDH AnalaR in shot form (0.5-2 mm, or about 8-30 mesh size), pretreated with nitric acid. About 250 mg of zinc is placed in a dry tube and this is evacuated, then pre-reacted in the block heater at 450°C for 10 minutes. The tube is then re-attached to the vacuum line, evacuated and filled with dry nitrogen. A 5 mg water sample is added by syringe, frozen with liquid nitrogen and the tube is re-evacuated. The water sample is allowed to react with the zinc in the block heater, at 450°C, for one hour. Hydrogen produced by the reaction is then analysed by mass spectrometry.

APPARATUS

A schematic representation of the vacuum line used is given in Fig. 1.

The manifold used for evacuating the tubes is attached to the previously used uranium system (Stewart & James, 1981). Pumps used are a mercury diffusion pump and an oil rotary pump. Pressure in the system is measured by Pirani gauges (G1 and G2).

3.

Reaction tubes (Fig. 2) are 12 mm pyrex with teflon valves. They are 15 cm long and are attached to the manifold with ground glass B10 cones, lubricated with Apiezon 'L' grease. The O-ring seals of the valves are affected somewhat by the heat and care must be taken to ensure they seal effectively to prevent air contamination or loss of hydrogen.

A tygon hose connects the dry nitrogen cylinder to the line. The cold trap between this and T3 may be used to trap water (with a dry ice/ethanol bath) should dry nitrogen be unavailable.

The furnace is an aluminium block with eight holes, 45 mm deep, drilled in it, so that eight samples can be reacted simultaneously. As it takes three hours to heat, it is switched on automatically using a Kambrook timer. The temperature is maintained at $450 \pm 5^{\circ}\text{C}$ by a Shinko temperature controller.

OPERATION

1. System evacuation -

(a) Switch on the rotary pump and then the water inlet tap which operates a pressure switch to turn on the diffusion pump. The diffusion pump cold trap is filled with liquid nitrogen (to be kept topped up during the day).

(b) Open T1.

2. Tube preparation -

(a) Place ~250 mg cleaned AnalaR zinc (metal) shot into a clean and dry tube. A normal water sample is 2-10 μl . For a larger sample use more zinc (e.g. 400-500 mg for 20-30 μl sample). Note weight of zinc and tube number.

(b) Tubes are evacuated four at a time to $G2 = 0.01$ torr (open T2 and tubes to evacuate).

(c) Shut T2 and tubes, and place tubes in the furnace at 450°C for 10 minutes to pre-react any contaminants (a film of zinc should appear in tubes). You may evacuate four more tubes in this time, then pre-react them.

4.

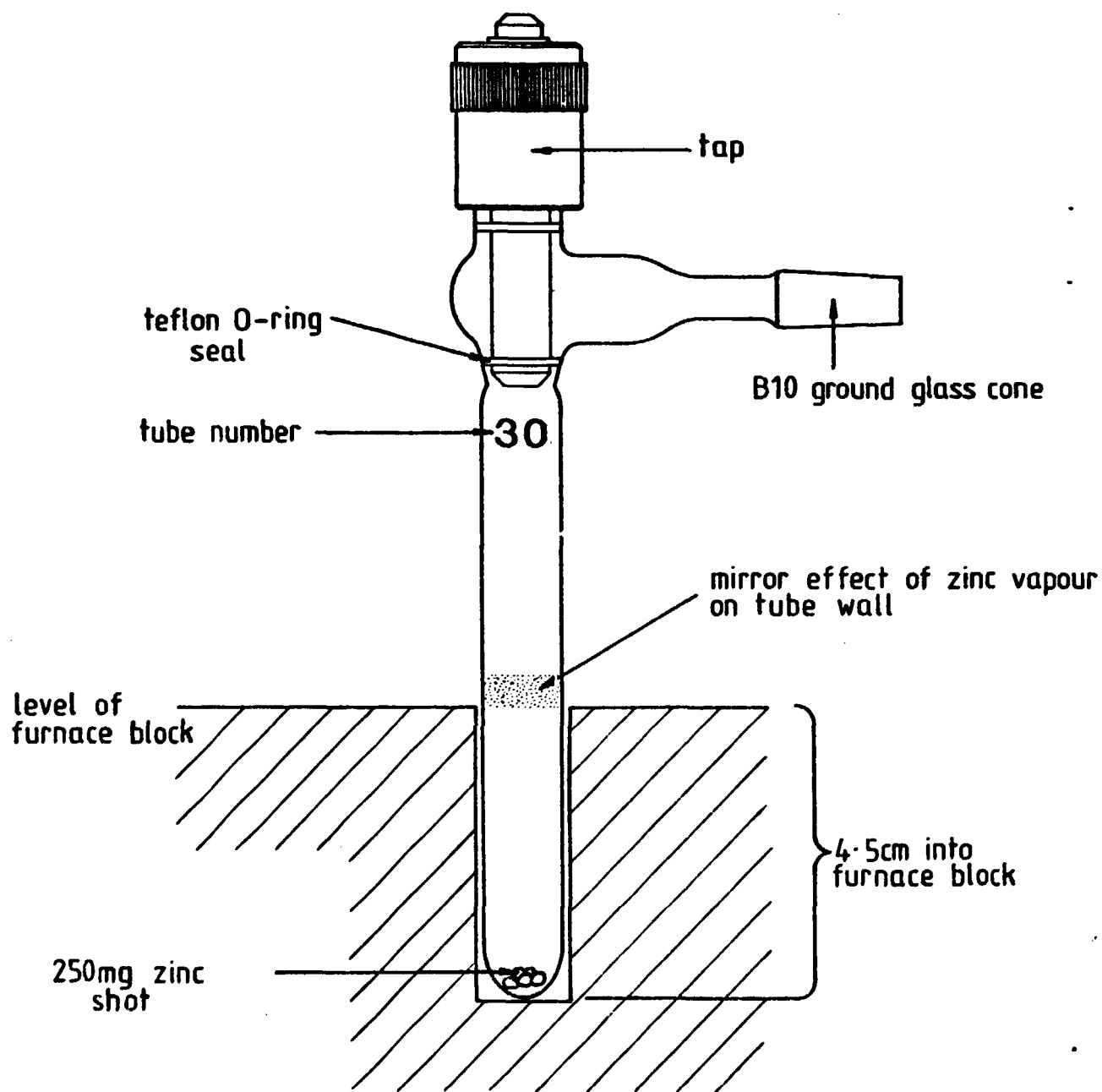


Figure 2. (Actual size)

(d) Place tubes in cooling rack and when cool enough to hold, pump again to $G2 = 0.01$ torr.

3. Dry nitrogen introduction -

(a) When tubes are pumped, close T2. Open T5 (on nitrogen gas cylinder) a little ($\sim 1\frac{1}{2}$ turns). Place one hand lightly against tubes to prevent N_2 pressure forcing them out and open T3 slowly.

5.

(b) Carefully pull one tube out from manifold until you hear a hiss that shows the nitrogen is flowing. Replace tube and close T3. Again pull tube out slightly to release the pressure, replace and remove hand.

(c) Close T5.

4. Sample loading and conversion -

(a) Rinse 10 μl syringe once in water sample, then take 5 μl of sample. Close three tubes and remove stopper completely from the fourth. Working quickly, syringe water into the bottom of the tube (touch large drops on the syringe to the glass), replace and close stopper.

Repeat this procedure for the other tubes, remembering to note the sample details next to tube number.

(b) Place liquid nitrogen dewars about the base of each tube (at present one dewar for two tubes is used), to freeze water. Wait a couple of minutes, check tubes are stoppered and water frozen, top up LN_2 and open T2 and tubes.

Pump to 0.01 torr (G2), keeping LN_2 topped.

(c) Close tubes and T2. Remove LN_2 and place loaded tubes into furnace, at 450°C , for one hour to react the water and zinc.

(d) Cool and attach tubes directly on mass spectrometer for analysis.

5. Cleaning tubes -

(a) Remove stopper. Place used zinc in storage bottle. Fill tube with diluted chromic acid and leave until zinc film comes off the sides of the tube. Rinse several times with distilled water, and place in oven to dry.

6. Preparing (cleaning) the zinc -

Before use the zinc shot is cleaned of its oxidation layer with 30% nitric acid. A teaspoon of zinc shot, placed in a beaker, is a reasonable amount to clean at one time.

6.

(a) Place in a fume cupboard. Pour over just enough acid to cover zinc. When yellow gas has stopped, rinse with distilled water about four times. Repeat. The zinc should be shiny. If not, wash and rinse again - if still dull, make up new acid.

(b) Switch fume cupboard off. Place zinc into a clean tube (some water may be removed first by transferring zinc onto tissue paper and then into tube - this takes longer though) to approximately three-quarters full. Attach tube to S6 and open T4 to pump off the water (do this when not loading samples).

Pump zinc to at least 0.02 torr (G1).

(c) A small "finger" furnace is obtained (from BrF_5 lab.), plugged in and switched on. Place it around the tube and turn to 100°C . Pump for $\frac{1}{2}$ hour, or until G1 = 0.01, turn to 200°C then to 300°C for $\frac{1}{2}$ hour each. G1 should be 0.01 torr.

(d) Remove furnace, switch off and pump zinc till cool. Return furnace.

(e) Close T4 and tube. Remove tube. If zinc is to be used immediately, place in its storage bottle, if not keep in tube under vacuum until needed.

RESULTS

Reproducibility of the system is monitored by the daily measurement of standard INS8. Twenty-five samples analysed over several days from the hot shot method give an average $\delta\text{D}_{\text{SMOW}} = -48.6 \pm 0.6\text{‰}$. The 1977 normalised value of $\delta\text{D}_{\text{SMOW}}$ for INS8 is -48.7‰ . This has been determined on the deuterium mass spectrometer (Micromass 602) using INS8 processed by the Lyon & Cox (1980) zinc-line method.

A series of INS8 samples, differing in the following ways, show no appreciable differences in average or standard deviation (see Table 1). All tubes have approximately 250 mg of zinc shot and (except (f)) are pre-reacted.

(a) Samples reacted and analysed on the same day.

(b) Samples reacted but analysed the next day.

(c) Samples loaded on one day, then reacted and analysed the next day.

(d) Syringe tip was wiped with tissue before placing each water sample into the tube, and special care was taken so that no water droplets adhered to the tube near the top, where they could only partially freeze, causing fractionation. (The standard deviations of the previous tests were higher than expected, and it was considered this type of fractionation may be the cause.)

(e) Samples loaded by injecting each in turn via the septum adaptor (Fig. 2), with the water being distilled into the tubes with liquid nitrogen. (This was the loading method initially used in the development of the technique.)

A set of INS8 samples, (f), loaded into tubes not pre-reacted showed a slightly more negative δD_{SMOW} value, $-51.27 \pm 1.31\text{‰}$, but no increase in variation between samples (Table 1).

A possible area for memory (i.e. contamination of a sample by the previous sample) to occur is by sample carry-over in the syringe. The effects of memory were tested using INS5 and INS3 standards, as they differ substantially in value. 1977 δD_{SMOW} normalised values for INS5 and INS3 are respectively -393.0‰ and $+1.2\text{‰}$. The syringe was rinsed once in each water sample before that sample was loaded. Results (Table 2) do not show any significant memory effects.

The hot shot method is used in analysing the deuterium content of methane and hydrogen in geothermal gases (Lyon & Cox, 1978). Here the resulting waters are frozen directly into the tubes. It is often the case that these samples are either small (0.5-2 mg), or large (up to 30 mg). The zinc hot shot technique shows little impairment of accuracy for either small or large samples. Two INS8 samples of 2 μl volume show δD_{SMOW} of -49.47‰ and -50.20‰ , while two 10 μl INS8 samples are slightly more positive at $\delta D_{SMOW} = -46.19\text{‰}$ and -47.19‰ . These values are within expected variations. Where larger samples (especially 20-30 μl) are anticipated, it is usual to increase the amount of zinc shot used in the reduction. The time for the reaction may also require lengthening, but this has not been tested.

At present 16-20 samples including 2-3 INS8 standards can be converted and analysed in an 8-hour day by one technician. This is compared to a maximum of 10 conversions using the zinc-line method.

DISCUSSION

The zinc hot shot method was developed initially as a way to quantitatively determine the deuterium content of the often small samples (some 1-3 mg of water) obtained from combustion of hydrogen and methane in New Zealand geothermal gases (Lyon & Cox, 1978). Such small samples cannot be converted by the zinc-line method (Lyon & Cox, 1980). However, the new method proved much more efficient than the zinc-line method, and so is now used for all routine deuterium analysis.

The choice of zinc metal used is very important. Experiments with types of zinc, other than the BDH AnalaR zinc shot available to us (coarse zinc powder for filling reductors, by E. Merck, Darmstadt in Germany, and Fisher (USA) 30 mesh zinc metal, previously used in the zinc-line furnace) gave incomplete or no reduction of water to hydrogen, even when left in the furnace block for several hours, or with an increase in amount of zinc. The Fisher zinc metal was tried also in a distilled form obtained from previous zinc-line furnaces. Other authors, Colman *et al.* (1982) and Kendall & Coplen (not in print) have noted the same phenomenon. It is not known why only zinc shot works, but possible reasons are its spherical shape, cavities that increase surface area, and perhaps impurities that may catalyse the reduction process. The size of the shot does not appear to influence the reaction (this was found in preliminary work, using two size fractions - one greater than sieve mesh 14 and the other less, compared to unsieved zinc) (Table 3).

Pre-reaction of the zinc shot and the use of dry nitrogen when loading samples is to eliminate contamination by atmospheric water vapour. Thus it is considered unnecessary to store the cleaned shot under vacuum to keep it away from water vapour contamination.

Table 1: (all values are δD_{SMOW} ‰)

(a) Run reacted on one day	(b) Reacted then run next day	(c) Loaded, then reacted and run next day
-48.05	-48.05	-47.94
-47.85	-52.37	-48.23
-50.35	-48.04	-49.17
-50.02	-47.36	-48.48
-47.09	-48.26	-47.92
-48.37	-50.10	-47.75
<u>-48.58 ± 1.32</u>	<u>-49.03 ± 1.88</u>	<u>-48.19 ± 0.53</u>
(d) Syringe tip wiped	(e) Sample injected via septum adaptor	(f) Zinc not pre-reacted
-46.27	-48.72	-50.20
-50.67	-47.22	-53.67
-48.83	-47.03	-50.57
-48.35	-47.16	-50.61
-47.70	-48.29	-51.85
-46.99	-46.70	-50.72
<u>-48.14 ± 1.54</u>	<u>-47.52 ± 0.80</u>	<u>-51.27 ± 1.31</u>

Table 2: Testing for syringe sample carry-over.

Sample	δD_{SMOW} (‰)
INS5	-400.12
INS5	-394.32
INS3	0.78
INS3	1.61
INS3	2.03
INS5	-397.48

Table 3: Testing size of zinc shot. Here all tubes are not pre-reacted as this was a preliminary test carried out before pre-reacting was used. The shot was sieved using a no. 14 mesh and the two fractions cleaned with nitric acid separately.

Sample (a)	δD_{SMCW} unsieved	δD_{SMOW} , size <u><14 mesh</u>
INS5	-384.21	-384.30
	-388.70	-385.57
	-386.92	-382.51
	-387.56	-387.13
		-382.15
		-386.50
	<u>-386.84 ± 1.91</u>	<u>-384.69 ± 2.07</u>
(b)	δD_{SMOW} unsieved	δD_{SMOW} , size <u>>14 mesh</u>
INS8	-50.91	-51.65
	-53.76	-49.39
	-51.04	-51.73
	-51.50	-51.85
	-51.45	
	-51.48	
	<u>-51.69 ± 1.04</u>	<u>-51.16 ± 1.18</u>

REFERENCES

- Coleman, Max L., Shepherd, Thomas J., Durham, John J., Rouse, Jone E. and Moore, Gillian R. 1982. Reduction of water with zinc for hydrogen isotope analysis. *Analytical Chemistry* 54, 993-995.
- Coplen, Tyler B. and Kendall, Carol. A multi-sample technique for conversion of water to hydrogen for stable isotope ratio determination. (Not in print at March 1984).
- Lyon, G.L. and Cox, M.A. 1978. Stable isotope analysis of hydrogen and methane mixtures. INS-R--254.
- Lyon, G.L. and Cox, M.A. 1980. The reduction of water to hydrogen for D/H ratio analysis using zinc in a matrix of sand. INS-R--282.
- Stewart, M.K. and James, M.R. 1981. Conversion of water to hydrogen for deuterium assay using uranium at 700⁰C. INS-R--292.

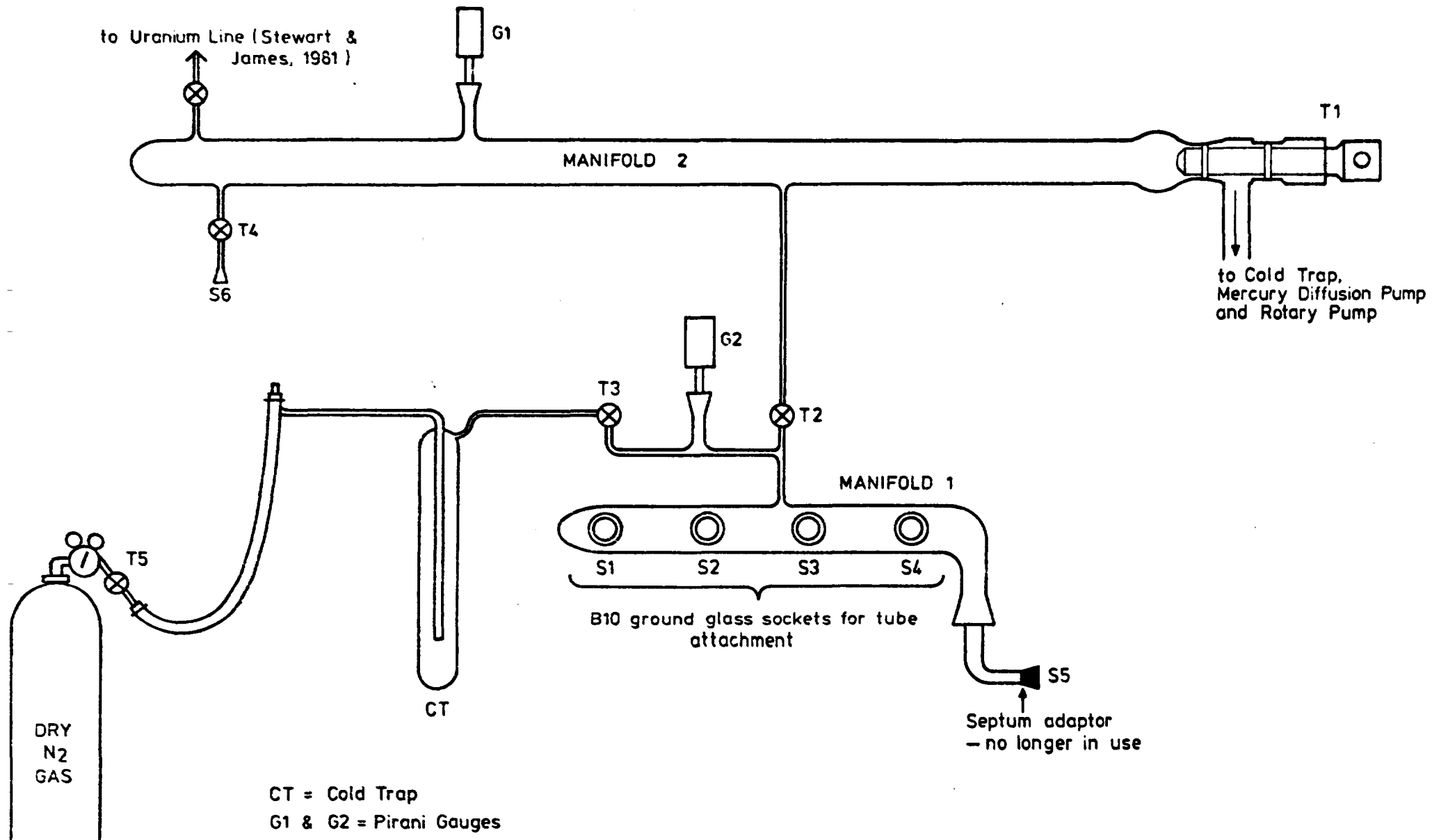


Figure 1.