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^{222}Rn-in-water standard at NPL

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The Development of a ^{222}Rn-in-water Standard at NPL

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ABSTRACT

The design and characterisation of a unit for dispensing ^{226}Ra-free aqueous solutions of ^{222}Rn, with activity concentrations traceable to UK national standards of radioactivity, is described. The unit consists of a polyethylene-encapsulated ^{226}Ra solution immersed in distilled water enclosed within a metal accumulation chamber fitted with a central bellows. The accumulation chamber has metering valves at both ends and is attached to a motor-driven mechanism which serves to contract and expand the bellows. The solution is dispensed via a needle positioned beneath the lower valve. The unit, operated by a Microprocessor Control Unit (MCU), is characterised in terms of the activity concentration of ^{222}Rn dispensed when a specified operating procedure is followed. The unit has been intercompared with a similar system held at the National Institute of Standards and Technology (NIST), Gaithersburg, USA.

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1 INTRODUCTION

The radionuclide ^{222}Rn (and its short-lived daughters) is now well established as a major contributor to the overall radiation dose to the general public. Most attention has been given to the dose arising from inhalation of airborne $^{222}Rn/^{222}Rn$ daughters but in some circumstances there may be a significant dose from ^{222}Rn dissolved in domestic/occupational water supplies. By 1993 NPL had already developed a ^{222}Rn gas standard[1] but evidence was growing of a need for a related standard for ^{222}Rn in aqueous solution. A project to develop such a standard was therefore initiated.

This report describes the background to the project, the design and characterisation of the ^{222}Rn dispensing unit, and the results of an international intercomparison exercise with a similar system developed at the National Institute of Standards and Technology (NIST), Gaithersburg, USA. Recommendations for future work are made.

This project formed part of the Ionising Radiation Metrology Programme (1995-1998) of the National Measurement System Policy Unit of the United Kingdom Department of Trade and Industry.

2 BACKGROUND TO THE PROJECT

In 1993 it became clear that there was a requirement in the UK for a means of standardising systems for the assay of ^{222}Rn dissolved in water. This requirement stemmed from the water industry although there was also evidence from the Health and Safety Executive (HSE) that such measurements should also be carried out in industries in which large quantities of water are used (e.g. paper manufacturing). NPL contacted users in the water industry and elsewhere to determine the required specification for such a standard.

The radionuclide ^{222}Rn (when dissolved in water) may be assayed by a variety of techniques such as liquid scintillation (LS) counting and γ-ray spectrometry (of ^{222}Rn and its daughters). In all cases, the loss of ^{222}Rn from solution during the sampling procedure introduces significant analytical uncertainties and this has implications for any potential standard; for example, the solution must be introduced into the detection system in such a way that losses of dissolved ^{222}Rn are minimised. The use of sealed glass ampoules, normally used for radionuclide standards, is impractical due to potential ^{222}Rn losses during filling, sealing and reopening, as well as the partitioning of the ^{222}Rn between the gaseous and liquid phases in the ampoule. The most straightforward practical solution to this problem is to design a portable unit to generate standardised aqueous ^{222}Rn solutions and to dispense the aliquots directly into the user's system. Such a unit would have to be operated by NPL staff or loaned to the customer with a suitable operating procedure. Potential customers in the UK were agreeable to such a scheme and requested a system with the capacity to deliver total ^{222}Rn activities in the range 10 - 150 Bq. Such a standard would have to be traceable to primary standards of radioactivity via the NPL ^{222}Rn gas standard.

3 DESIGN OF UNIT

The only example of such a dispensing unit in the literature is that described by Hutchinson et al.[2] (NIST). Their unit consists of a polyethylene-encapsulated ^{226}Ra solution source in a low-volume accumulation chamber (containing aged, deionised water) and an ancillary mixing and dispensing system consisting of glass tubing, stopcock valves and gas-tight, motor-driven syringes. The ^{222}Rn dissolved in the ^{226}Ra solution partitions between the solution and the polyethylene capsule wall and subsequently diffuses into the accumulation chamber. This results in a ^{226}Ra-free aqueous solution of ^{222}Rn (and its short-lived daughters) in the accumulation chamber. The water in the chamber is then

extracted, homogenised and dispensed via a needle. The NIST unit is certified in terms of the ^{222}Rn concentration in an aliquot dispensed when a detailed operating procedure is followed.

It was felt that UK customer requirements could be met by the construction of a similar system. However, several improvements were considered, namely:

(i) the NIST system was considered very bulky and a more compact design would facilitate transportation;
(i) could be achieved by mixing the solution in, and dispensing it directly from, the accumulation chamber;
a metal bellows could form part of the accumulation chamber; this would remove the need for motor-driven syringes to dispense the solution, as well as plastic components such as taps (which could absorb ^{222}Rn);
the bellows could be motor-driven by a programmable dedicated control unit.

The development of such a unit, by NPL and Oxford Sensors and Controls, Oxfordshire, UK, is described below.

3.1 FINAL SPECIFICATION

The dispenser (see Figure 1) consists of a cylindrical accumulation chamber with a central electroformed stainless-steel bellows. The chamber has isolating valves at each end and a dispensing needle at the lower end (when in the upright position). The chamber is fixed to a back-plate at one end whilst the other is attached to a moveable carriage assembly mounted on a high precision slide. The carriage assembly is connected to a lead screw which is driven by a stepper motor also mounted on the back plate. The stepper motor is controlled by a microprocessor control unit (MCU) which is shown in Figure 2; it can be set to compress or to extend the bellows in programmable steps.

The accumulation chamber contains a polyethylene capsule enclosing an aliquot of a ^{226}Ra standard solution. It also encloses a number of loose glass beads which assist the mixing operation. The capsule was manufactured at NIST by heat-sealing a weighed aliquot (approximately 0.1g, corresponding to a total ^{226}Ra activity of approximately 1.4 kBq) of the ^{226}Ra solution into a section of narrow polythene tubing (the final dimensions of the capsule were approximately 20 mm long x 4 mm diameter). The ^{226}Ra solution, provided by NPL, had been calibrated at NPL using a secondary standard ionisation chamber. The capsule is mounted on a metal clip located on the inside wall of the accumulation chamber. In normal operation the remaining volume in the accumulation chamber is filled with deionised water, which dissolves the ^{222}Rn as it emanates from the capsule walls. All air is excluded from the chamber as its presence would result in partitioning of ^{222}Rn between the liquid and gaseous phases. The ^{222}Rn solution is dispensed by opening the lower valve (with the dispenser in the upright position) and compressing the bellows.

The variable volume bellows is designed to produce a linear relationship between the change in compression of the bellows and the mass of water dispensed. The bellows, carriage and stepper motor assembly is supported on a stand with a detachable V-shaped base. Prior to any accumulation period or dispense cycle the carriage must be at the 'datum' position (corresponding to the bellows being fully extended) to ensure the accuracy of the mass dispensed and a constant mass for accumulation of ^{222}Rn in solution.

The MCU enables the operator to accurately dispense a range of masses up to 50 g, in increments of 5 g, by sending a number of pulses to the stepper motor on the dispenser. The unit is calibrated for

the mass of solution dispensed by weighing aliquots of dispensed solution on a calibrated microbalance and then inputting the correct masses (if necessary) to the MCU. The number of pulses sent is dependent on the mass selected for dispensing. An optical device (the 'Opto Switch'), located in the carriage housing of the dispenser, detects if the carriage assembly is high or low relative to the datum position in which case an audible and visual warning is given by the MCU. When this warning is given the carriage assembly must be manually reset to the datum position.

For filling or flushing the dispenser (see 4.2 below), a reservoir tank (of about 5 l capacity) is connected to the inlet port (at the opposite end of the dispenser from the needle) by a polyethylene hose. See Figure 3.

The coupling between the dispenser and the stand enables rotation through 180° in the vertical plane. A spring-loaded catch locks the dispenser in the upright position (needle pointing down) or in the filling position (needle pointing upwards to aid air removal). The coupling also enables the dispenser to be rotated back and forth, to agitate the glass beads to ensure homogeneity of the ^{222}Rn solution, prior to dispensing. When rotating the dispenser the catch must be manually disengaged and great care taken not to handle the bellows.

4 CHARACTERISATION OF THE DISPENSING UNIT

The characterisation of the unit comprised the following stages:

(i) optimisation of the mixing process;
(ii) determination of the procedure required to achieve a reproducible starting condition for ^{222}Rn ingrowth;
(iii) construction of a ^{222}Rn ingrowth curve;
(iv) intercalibration against the NPL ^{222}Rn gas standard.

4.1 OPTIMISATION OF THE MIXING PROCESS

The ^{222}Rn in the dispenser emanates from the polyethylene capsule which is located at the upper end of the accumulation chamber (upright position). It was thought that this may give rise to variations in the ^{222}Rn concentration within the water volume and that a mixing process would be required to ensure that dispensed aliquots were reproducible in terms of ^{222}Rn activity concentration; accordingly, six loose glass beads, which can be agitated by rotating the dispenser around its central pivot, were enclosed within the accumulation chamber to assist the mixing process.

A number of experiments were performed in which ^{222}Rn was allowed to diffuse into the water for a nominal period of four days; the dispenser was then rotated through 360^0 n times, n varying from 0 to 16. In each run, the ^{222}Rn solution (in 5 g aliquots) was dispensed to a series of ten liquid scintillation vials, diluted to 20 g with 'Uniscint BD' liquid scintillant (Mensura Technology plc, Lancashire, UK) and counted on a Wallac 1219 Liquid Scintillation Spectrometer. The standard deviation of the observed count-rates of the ten samples from each run was calculated and is given in Table 1. The mixing procedure adopted consists of 12 rotations of the unit.

4.2 DETERMINATION OF THE PROCEDURE REQUIRED TO ACHIEVE A REPRODUCIBLE STARTING CONDITION FOR RADON INGROWTH

NIST have demonstrated[2] that a completely reproducible ^{222}Rn activity concentration for a given ^{222}Rn ingrowth period can only be achieved if the ingrowth commences with all ^{222}Rn removed from the

water volume and from the polyethylene capsule wall. This can never be completely achieved but the ^{222}Rn content of the polythene can be minimised by a 'flushing' procedure in which water is slowly passed through the accumulation chamber over a period of hours and is then rapidly passed through for a short period (of the order of seconds). Insufficient flushing will give rise to excess ^{222}Rn in the water over that normally expected for a given (subsequent) ingrowth period.

The optimum flushing procedure (for the NPL dispenser) was determined by flushing water through the accumulation chamber at a fixed rate but for varying periods of time, allowing ingrowth for a fixed period of time and then observing the count-rate per gram of water as in Section 4.1 above. The count-rate was plotted as a function of the flushing time (see Figure 4). On the basis of these experiments, the following flushing procedure was adopted:

(i) Five rapid cycles of dispensing 50 g from the generator;
(ii) Flushing for six hours at a flow-rate of approximately 10 g/minute (bellows fully extended);
(iii) Flushing for 20 seconds with the two valves fully open (bellows fully extended).

Experimental runs carried out under different ambient temperatures but with identical flushing periods demonstrated that the flushing process was temperature dependent, so all subsequent runs were carried out in a temperature controlled environment (approx. $22^{o}C$).

4.3 CONSTRUCTION OF A ^{222}RN INGROWTH CURVE

The ingrowth of ^{222}Rn in the water volume of the accumulation chamber at any time following complete removal of ^{222}Rn is described by the following equation:

$$A_{Rnt} = A_{Ra0} f(1 - e^{-\lambda t})/v \qquad (1)$$

where A_{Rnt} is the ^{222}Rn concentration (in Bq/g) in the accumulation chamber at time 't',
A_{Ra0} is the total ^{226}Ra activity (in Bq) in the polyethylene capsule,
f is the emanation coefficient (i.e. the fraction of ^{222}Rn generated within the capsule which diffuses into the accumulation chamber),
λ is the decay constant (in s^{-1}) for ^{222}Rn,
t is the time (in s) since the complete removal of ^{222}Rn,
and v is the volume (in ml) of the accumulation chamber when fully extended (always the case during flushing and ingrowth).

The decay constant was derived from an assumed half-life[3] of (3.8235 ± 0.0003) days (1σ).

Assuming the dispensed ^{222}Rn solution is then assayed by Liquid Scintillation Counting, the observed count-rate will be dependent on the detection efficiency, 'ε', giving:

$$K = (A_{Ra0} f\varepsilon/v) \times (1 - e^{-\lambda t}) \qquad (2)$$

where K is the observed count-rate per gram.

A plot of K versus $(1 - e^{-\lambda t})$ should therefore yield a straight line with a slope equal to $A_{Ra0} f\varepsilon/v$.

In order to determine whether the ^{222}Rn concentration in the accumulation chamber follows this equation, ^{222}Rn was allowed to ingrow (following the flushing procedure described above) for a range

of time periods varying from 1 to 29 days before being mixed, dispensed as 5 g to each of ten liquid scintillation vials and counted. The results are given in Table 2 and are plotted in Figure 5.

4.4 INTERCALIBRATION AGAINST THE ^{222}Rn GAS STANDARD

The ingrowth experiments described in Section 4.3 above were run in parallel with a series of similar experiments in which some of the solution from the dispenser was quantitatively transferred to a Drechsel bottle (containing nitrogen-flushed deionised water). The remaining solution in the dispenser was transferred to LS vials as in Section 4.3. The ^{222}Rn in the Drechsel bottle was then flushed into a pulse ionisation chamber previously calibrated for ^{222}Rn using a standardised ^{226}Ra solution (see Tables 3 and 4). This enabled the determination of the ^{222}Rn concentration of the water in the dispenser and thus the ^{222}Rn concentration in the LS vials. The detection efficiency, ε, for ^{222}Rn in the LS counter could thus be determined. This value should be in the vicinity of 5 counts per second per Bq of ^{222}Rn due to the presence of ^{222}Rn itself and its four short-lived daughters. The results are summarised in Tables 5 and 6.

The slope derived from equation (2) can be used in conjunction with known values of A_{Ra0}, ε and v to derive f. The value thus derived was **0.69** with an uncertainty of **2.71%**. Table 7 summarises the associated uncertainties.

5 CONDUCT OF THE INTERCOMPARISON EXERCISE

5. PROCEDURE

The NPL dispenser was shipped by air to NIST in January 1997. The unit was transported in its custom-built carrying case in a section of the aircraft maintained at a temperature of 4 - 18°C and a pressure of approximately 100 kPa. The bellows, filled with water, was compressed to its lowest volume prior to packing to minimise lateral motion.

On arrival at NIST, the bellows was fully extended (deionised water was admitted via the upper valve during this process to maintain an air-free internal volume). The unit was then flushed, and ^{222}Rn allowed to ingrow, as described in Sections 4.2 and 4.3 above. An ingrowth period of approximately 40 hours was used. At approximately the same time, the NIST ^{222}Rn-in-water dispenser was flushed and ^{222}Rn was allowed to ingrow for a similar period. After the ingrowth periods, ^{222}Rn samples (5 g) from both systems were dispensed to LS vials containing Uniscint BD; the vials were counted on a LS counter using the NIST/CIEMAT efficiency tracing technique[4].

Later on the same day, a second ingrowth was begun on both systems, and ^{222}Rn was allowed to ingrow for approximately 43 hours. Again, this was preceded by a 6-hour flushing period. The results are given in Table 8.

5.2 INTERCOMPARISON RESULTS AND DISCUSSION

The results are given in Table 8. The mean value of 'f' obtained by NIST for their system is consistent with previous measurements obtained from both their primary ^{222}Rn standard and by LS counting using the NIST/CIEMAT method. A value of 0.625 ± 0.84% was quoted in an earlier publication[5]; the mean value of 0.627 obtained in the current exercise for the same NIST system was consistent with this value and was regarded as providing confirmation of the validity of the NIST/CIEMAT technique under the same experimental conditions as were used for assaying the NPL samples.

The two values of 'f' obtained by NIST for the NPL dispenser (0.748 ± 0.1% and 0.703 ± 0.2%) differ by 6.0%, suggesting that there is a significant difference between the two results. All procedures involved in the operation of the NPL dispenser (flushing, ingrowth, dispensing and counting) were identical for both experimental runs, so the discrepancy cannot readily be explained. It may be significant that the second of the two results is in agreement with a previous NPL measurement of 0.69 (a difference of 1.8%, yielding a u-statistic[6] of 0.9 when uncertainties due to LS counting efficiency alone are considered), whereas the first result (giving a difference of 7.8% and a u-statistic of 3.8) is not. The latter was carried out immediately following air transport of the dispenser, which may have been a contributory factor. The dispenser had been transported at a temperature in the range 4 - 18°C (to prevent freezing of the water in the accumulation chamber), in a cargo aircraft, with the bellows at full linear compression (to minimise lateral motion). Retrospectively, it was thought that compressing the bellows in this way prior to flushing of the dispenser may have influenced the starting conditions for the flushing process. To check this, a further experiment was carried out at NPL in which the dispenser was stored with the bellows in a fully compressed configuration for a period of 10 days (longer than the transportation period used). The bellows was then re-extended and then flushed in the normal way prior to ingrowth, dispensing and Liquid Scintillation Counting as per the normal procedure. This experiment revealed that compression of the bellows prior to flushing has no effect on the starting conditions for flushing and ingrowth. However, air transportation was not carried out and this is still a possible cause of the observed discrepancy.

6 CONCLUSIONS

1 The observed discrepancy between the values of the emanation coefficient, f, for the two intercomparison experimental runs on the NPL dispenser demonstrates that there are still unknown factors affecting the distribution of ^{222}Rn within the accumulation chamber, possibly related to the air transport process.

2. These factors must be identified before a comprehensive operating procedure and associated uncertainty budget can be compiled. An initial approach would be to subject the dispenser to a series of air journeys, following each with a flushing/ingrowth/dispensing cycle.

3. In the meantime, the dispenser may be used as the basis of a calibration service provided that road transport only is involved. The value of 'f' is **0.69** with an expanded uncertainty (k=2) of **5.6%**. Air transport of the dispenser must be followed by a flushing/ingrowth/dispensing cycle to confirm the value of f before the dispenser is next used for calibration inland.

7 ACKNOWLEDGEMENTS

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Table 1 - Results of solution mixing tests

Number of rotations of unit	Standard deviation (expressed as percentage of mean observed count-rate of a set of samples)
0	1.66
4	0.47
8	0.49
12	0.38
16	1.23

Table 2 - Results of ingrowth experiments

Nominal ingrowth period (days)	Actual ingrowth period, 't' (seconds)	Observed count-rate per gram at reference time (counts/s/g)	$e^{-\lambda t}$
1	85080	8.606	0.8365
2	173660	15.878	0.6946
3	259200	21.561	0.5805
4.9	422400	30.041	0.4122
5	433200	30.525	0.4029
6	516540	33.626	0.3383
7	604920	36.539	0.2810
10	843360	42.508	0.1704
14	1215300	46.637	0.07808
21	1792740	49.475	0.02325
29	2489940	50.436	0.005383

Table 3 - ^{222}Rn detection efficiency of pulse ion chamber

Date	^{222}Rn activity transferred to pulse ion chamber from standardised ^{226}Ra solution (Bq)	Reference time	Ion chamber response (cps)	Calibration factor (cps/Bq ^{222}Rn)
26/2/97	9.47	1217 GMT	17.000	1.7938
28/2/97	4.78	1200 GMT	8.7923	1.8374
5/3/97	9.47	1216 GMT	17.050	1.7996
				1.8103

Table 4 - Uncertainty on pulse ion chamber ^{222}Rn detection efficiency

Source of uncertainty	Uncertainty
Standard Deviation of the Mean	0.756%
Weighing of ^{226}Ra standard solution	0.03%
Activity concentration of ^{226}Ra standard solution	1.23%
Half-life of ^{226}Ra	0.15%
Half-life of ^{222}Rn	0.01%
Type B Combined Standard Uncertainty	1.240%
Combined Standard Uncertainty	1.452%

Table 5 - ^{222}Rn (+ daughters) efficiency of LS counter 'ε'

Date	Pulse ion chamber response (cps)	Reference time	^{222}Rn in pulse ion chamber (Bq)*	^{222}Rn concentration of water in dispenser (Bq/g)	LS counter response (cps/g)	LS counter calibration factor (cps/Bq ^{222}Rn)
7/1/97	58.333	1522 GMT	32.223	6.4446	30.52	4.7357
24/3/97	64.309	1529 GMT	35.524	7.1048	33.63	4.7334
					Mean	4.7346

* Assuming a calibration factor of 1.8103 cps/Bq ^{222}Rn

Table 6 - Uncertainty on LS counter ^{222}Rn (+ daughters) efficiency 'ε'

Source of uncertainty	Uncertainty
Standard Deviation of the Mean	0.025%
Detection efficiency of pulse ion chamber	1.452%
Homogeneity of dispensed aliquots	1.5%
Type B Combined Standard Uncertainty	2.088%
Combined Standard Uncertainty	2.088%

Table 7 - Uncertainty on emanation coefficient 'f'

Source of uncertainty	Uncertainty
LS counter response	0.1%
LS counter detection efficiency, ε (4.73 cps/Bq ^{222}Rn)	2.088%
Volume of accumulation chamber, v (90.3 ml)	1.2%
Specific activity of ^{226}Ra standard solution, A_{Ra0} (1.4 kBq)	1.23%
Type B Combined Standard Uncertainty	2.705%
Combined Standard Uncertainty	2.707%

Table 8 - Intercomparison results

	NPL (1)	NPL (2)	NIST (1)	NIST (2)
f	0.748 ± 0.1%	0.703 ± 0.2%	0.633 ± 0.2%	0.621 ± 0.2%

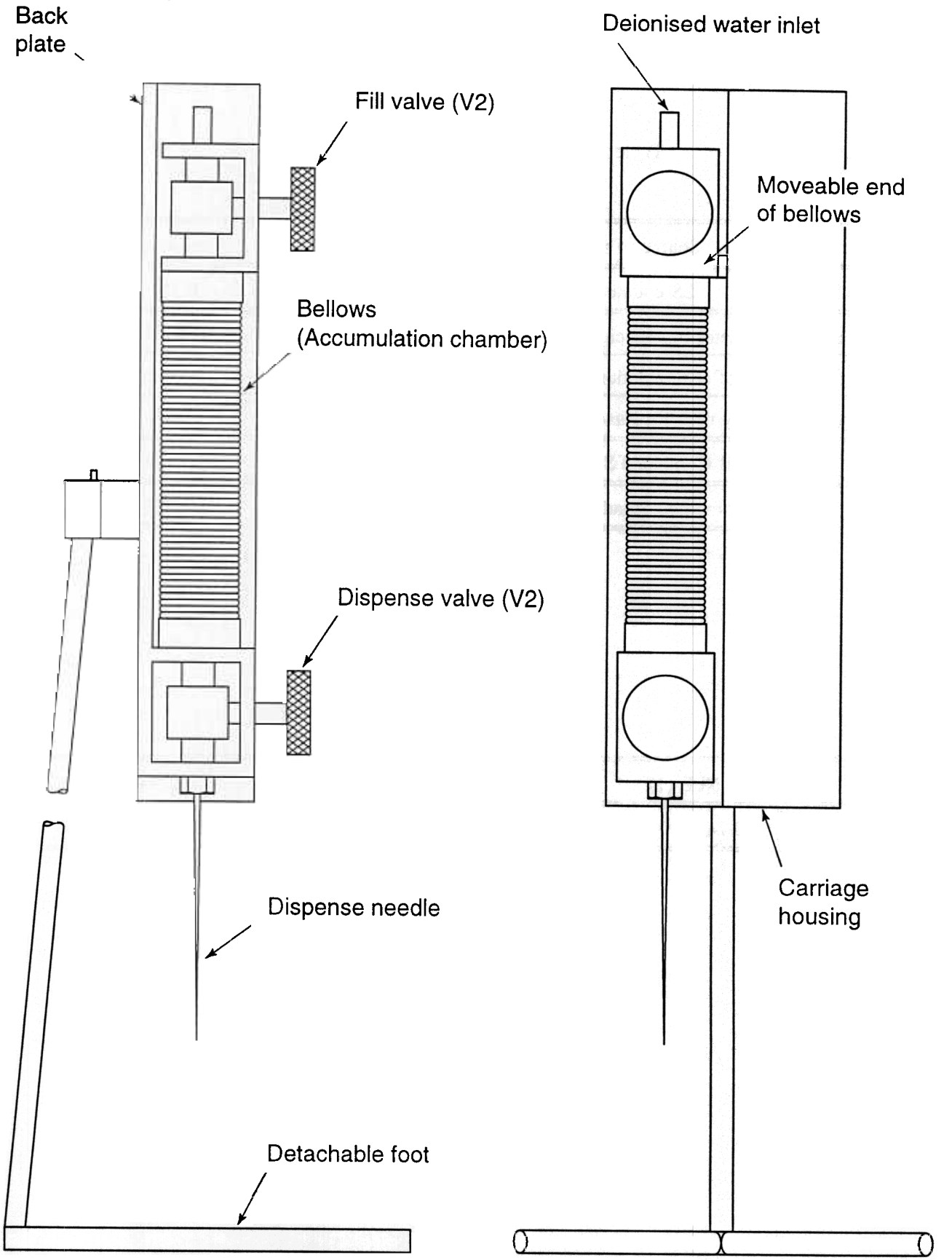

Figure 1 Schematic diagram of the NPL ^{222}Rn-in-water dispenser

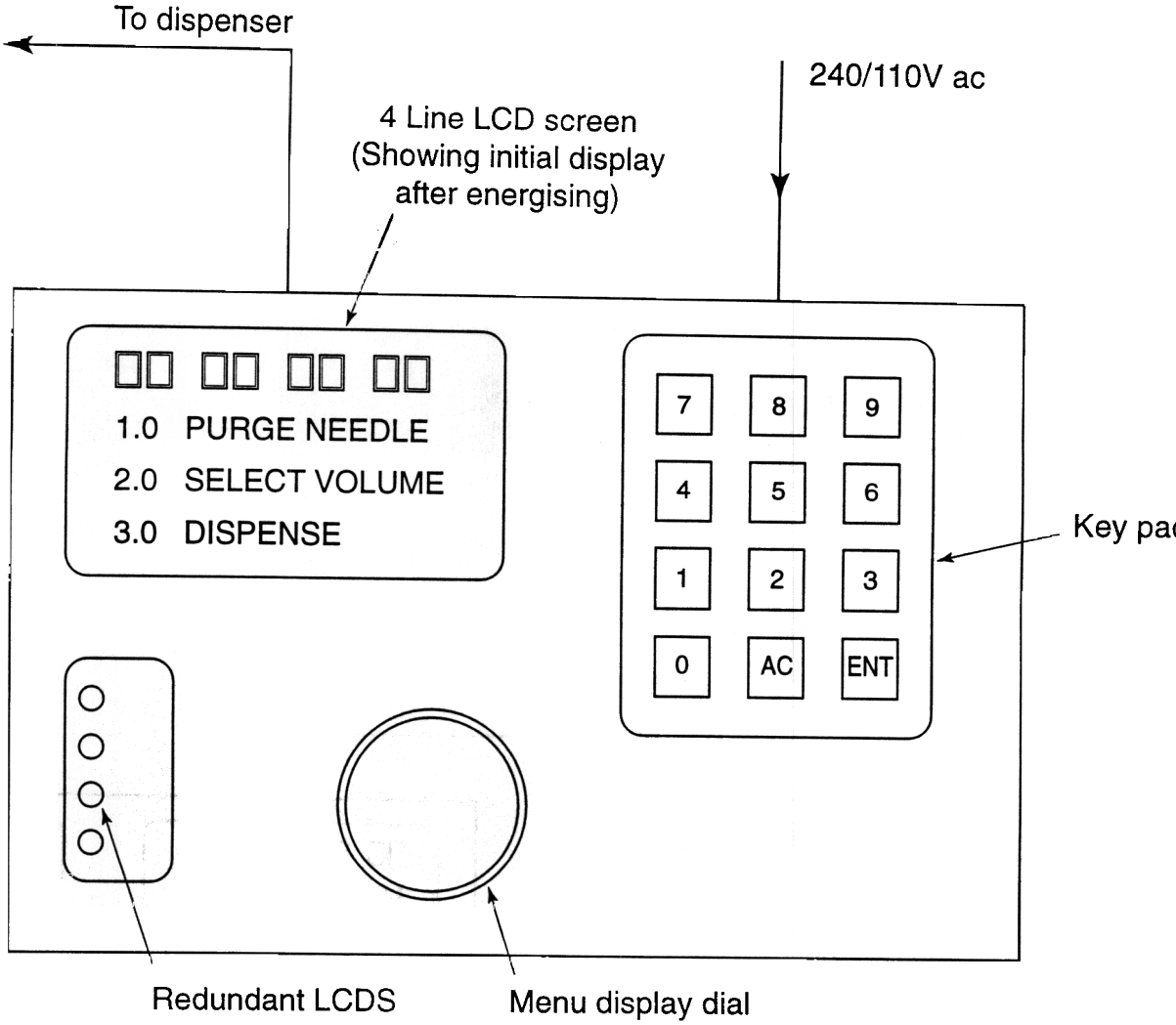

Figure 2 The Microprocessor Control Unit, MCU

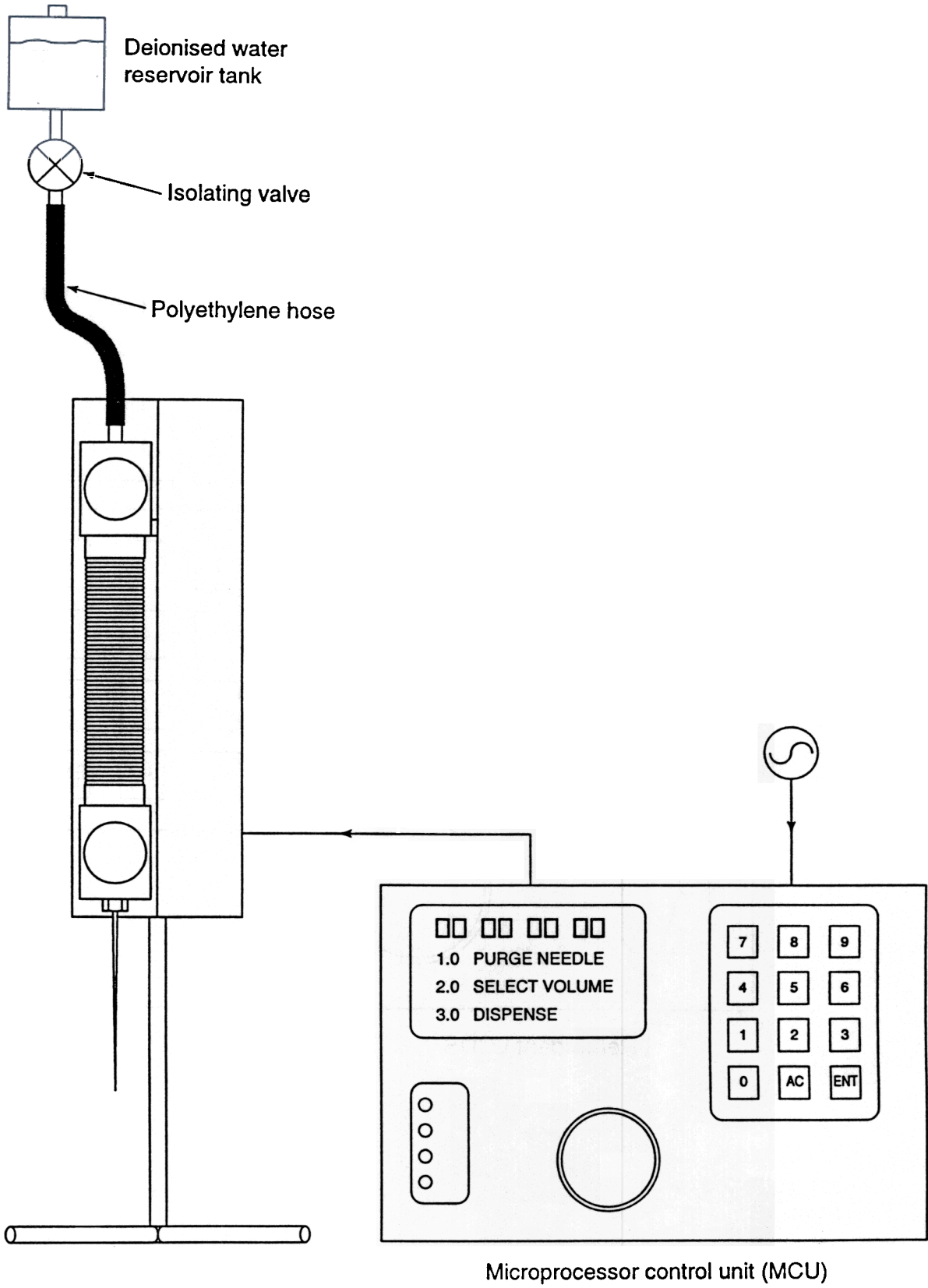

Figure 3 Schematic diagram of the dispenser connected to the reservoir tank and MCU

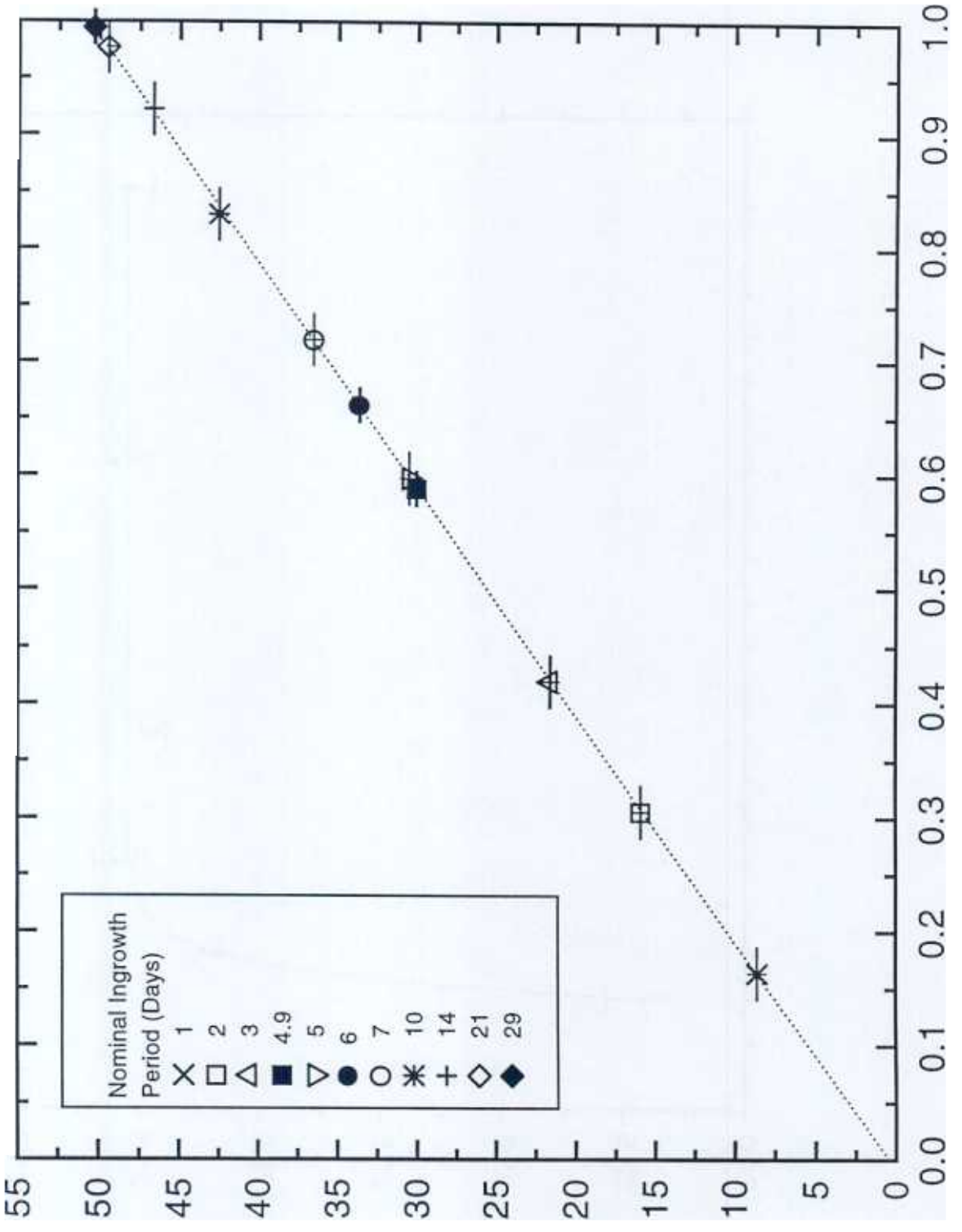

Figure 5 Ingrowth curve for ^{222}Rn dispenser