

THE SUITABILITY OF DENSITY AND REFRACTIVE INDEX INSTRUMENTS TO THE ON-LINE
MEASUREMENT OF HEAVY WATER CONCENTRATIONS*

by

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ABSTRACT

The requirements for heavy water analyses in Canadian power reactors have been compared to the capabilities of commercially available density and refractive index monitors. It has been concluded that although these instruments do not have sufficient sensitivity for leak detection or process control applications at the extremes of the concentration range, they could be considered for less demanding applications in the intermediate range (1-95 wt% D₂O). The Agar (Model FD800) vibrational densitometer was considered to be the most suitable of the 39 different instruments that were reviewed and laboratory tests have confirmed that its performance matches that predicted from the manufacturer's specifications.

1. INTRODUCTION

Heavy water is a major component of the capital cost of CANDU nuclear reactors, and if leaked or downgraded, can add significantly to the cost of electric power. Leaks have been minimized so that heavy water upkeep now accounts for only about 5% of the total unit energy cost [1]. This results in part from extensive monitoring programs and the record would undoubtedly slip if the established monitoring procedures were relaxed.

Accurate methods are required for determining the isotopic concentration of water samples over the entire range of D₂O concentrations. These analytical measurements can be divided into two major categories; on-line monitoring of process streams and chemical laboratory analyses of grab samples.

On-line isotopic analyzers offer many advantages over manual sampling, including:

- timely protection against heavy water leaks to the environment,
- continuous data for process control,
- accurate accounting for heavy water inventory,
- reduction in routine staff work-loads,
- reduction of personnel radiation exposures, and
- operational convenience.

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To date, the only instruments which have proven reliable in the field are the infrared spectrometers manufactured by Barringer Research Limited. These instruments are based on developments by Atomic Energy of Canada Limited (AECL) over the past 20 years [2]. However, plant environmental conditions, and the stringent requirements for sample conditioning to achieve the resolution of 0.0001% D₂O have pushed the basic instrument cost to approximately \$50,000. In addition, the currently available instruments are limited to measurements at the extremes of the D₂O concentration range.

Manual sampling remains the status quo for those process streams for which:

- no suitable on-line instrument has been qualified (e.g. the intermediate range), or
- the high precision infrared monitors are not cost effective.

These streams are considered to be of secondary importance in the overall operation of the reactor. Thus, the cost of developing special-purpose heavy water monitors for these applications has not been justified.

The alternative of applying general purpose analytical equipment which is commercially available has been given serious consideration. Of the physical properties that distinguish light from heavy water and that are amenable to measurement for analytical purposes, density and refractive index have been used in the laboratories for wide range applications. Since on-line density and refractive index monitors are commercially available, an in-depth survey was undertaken to assess the suitability of these instruments to monitoring heavy water concentrations in process streams of CANDU power reactors.

As a first step, in this review, it was necessary to establish the detailed analytical requirements for comparison with the instrument specifications. Thus, all heavy water concentration measurements which are made at Canadian nuclear generating stations or that are to be made in stations now under construction were tabulated, and those systems for which on-line monitoring is desirable were identified.

This documented comparison of the quoted instrument specifications with the detailed monitoring requirements identified one vibrational densitometer that was suitable for further review. The selected instrument was procured and subjected to an intensive laboratory evaluation to assess its applicability to this unique application.

This paper summarizes the review, presents the experimental data from the laboratory evaluation and draws general conclusions about the analysis of heavy water both in the laboratory and in process streams.

2. HEAVY WATER CONCENTRATION MEASUREMENTS IN CANDU REACTORS

An important aspect of this instrument assessment program was to assemble information on current practices for heavy water analysis in Canadian nuclear generating stations. This data was required to identify those systems for which on-line monitoring is either needed or desirable and to quantify the detailed analytical specifications for an appropriate monitoring system.

Data on current and proposed practices were obtained from the appropriate technical staff in New Brunswick Electric Power Commission, Hydro Quebec and Ontario Hydro. To simplify the analysis the monitoring requirements were divided into three isotopic range categories 0-1 wt%, 1-95 wt% and 95-100 wt% D₂O. It was generally found that the accuracy quoted by operating stations is less stringent than the accuracy demands of the stations under construction. For the purposes of this study, the specified accuracies are those usually achieved in operating reactors.

The high concentration range (>95 wt% D₂O) includes the moderator, the heat transport system and the heavy water supply (see Table 1(a)). Analysis in this range is required to an accuracy of ± 0.01 wt% D₂O for both fuel economy and inventory control. Except for the analysis of fresh drum supplies, these systems are amenable to on-line isotopic monitoring. The concentration of the upgrader product and the main heat transport system are dynamically variable, and are candidates for on-line monitoring in the traditional sense. Transfer of water from the collection tanks is a batch process, and the reasons for considering on-line monitoring are discussed later. Laboratory infrared analysis is the normal analytical technique applied to this range with an on-line infrared monitoring system available for the upgrader product. It should be noted that on-line infrared monitors have been applied to the heat transport system in Douglas Point GS and to the moderator systems in NRU and WR-1.

The vapour recovery and cleanup systems, the feed to the upgrader, and the deuteration/dedeuteration units for the ion exchange columns generate most of the samples in the range 1-95 wt% D₂O (see Table 1(b)). Of these, the recovery and cleanup systems generate the majority of samples. These mid-range samples are difficult to categorize because practices and sampling frequency vary widely from station to station. Improved vapour recovery and cleanup systems for the later reactors have considerably reduced the sampling requirements compared with Pickering A. For operational purposes, analysis of the majority of the samples from these systems requires an accuracy of ± 0.5 wt% D₂O. Improved accuracy (± 0.01 wt% D₂O) may be required on an infrequent basis for inventory control purposes. However, under normal operation, precise inventory management for the heavy water recovery and cleanup system can be achieved through accurate measurements of the concentrations of the bottom and top (tails) product from the upgrader. Laboratory analysis is generally done with a refractometer. However, the deuteration/dedeuteration systems use an on-line density hydrometer as a gauge.

The light water range (0-1 wt% D₂O) includes all the service water systems, the main steam system, and liquid and vapour discharges from the station (see Table 1(c)). Numerous other light water systems, such as the liquid zone controllers, the shield cooling and the poison injection mixing tanks, were also included in the review but are not sampled frequently enough (i.e. less than once per week) to warrant being included in the Table. The frequency of sampling the various light water systems is different in the different stations. This is particularly evident for service water systems. These include coolers and heat exchangers, which in some stations are sampled individually with a set frequency (from once per shift to once per week). In others, only the bulk service water is sampled regularly and the individual components are sampled only when a leak is detected. Except for the moderator heat exchangers, the accuracy required

TABLE 1(a)
HEAVY WATER ANALYSIS IN TYPICAL CANDU-PHW POWER REACTORS
(a) Heavy Water Range (>95 wt% D₂O)

Source	Range (wt% D ₂ O)	Accuracy (wt% D ₂ O)	Frequency (per week)	Present Analysis	SAMPLE CONDITIONS			Amenable to on-line monitoring
					Pressure (kPa)	Temp. (°C)	Quality	
Heat Transport System: - main circuit - collection tank - purification	>97.5	±0.01	3-7 ⁽¹⁾	Lab I.R.	atmos 600	30-300	Clean, pH ~10-10.5 Li ~1-2 mg/kg Cond. ~1-4 mS/m	yes
Moderator System - main circuit - collection tank - purification	>99.7	±0.01	3-7 ⁽¹⁾	Lab I.R.	100-200	25-65	Clean, pH 5-8 Crud <100 µg/kg Cond. <1 mS/m	yes
D ₂ O Supply - new D ₂ O - upgrading product	>99.7 >99.7	±0.01 ±0.01	as required 21 ⁽²⁾	Lab I.R. on-line I.R.	atmos 40	25 70	Clean Clean	no yes

NOTES

- (1) Frequency per system. Higher frequency associated with collection tanks.
(2) Sampling frequency for those systems which do not have on-line monitor

TABLE 1(b)
HEAVY WATER ANALYSIS IN A TYPICAL CANDU-PHW POWER REACTOR
(b) Mid-Range (1-95 wt% D₂O)

Source	Range (wt% D ₂ O)	Accuracy (wt% D ₂ O)	Frequency ⁽¹⁾ (per week)	Present Analysis	SAMPLE CONDITIONS			Amenable to on-line Monitoring
					Pressure	Temp. (°C)	Quality	
Upgrader Feed	1-95	± 1.0	7-20	Refractometer	atmos	25	Clean	-
Vapour recovery	1-95	± 0.5	7-60	Refractometer	atmos	25	Often contaminated Cond. 40-100 mS/m	-
Cleanup System	1-95	± 0.5	7-30	Refractometer	atmos	25	Clean	-
Deuteration/ Dedeuteration	1-95	± 2.0	3	On-Line Density	atmos	25	Clean	Yes

NOTES:

- (1) The higher frequencies are for Pickering A, the lower limit for Bruce A and 600 MWe reactors.

TABLE 1(c)
HEAVY WATER ANALYSIS IN A TYPICAL CANDU-PHW POWER REACTOR
(c) Low Concentration Range (<1 wt% D₂O)

Source	Range (wt% D ₂ O)	Accuracy (wt% D ₂ O)	Frequency (per week)	Present Analysis	SAMPLE CONDITIONS			Amenable to on-line Monitoring
					Pressure (k Pa)	Temp. (°C)	Quality	
Service Water - high pressure - low pressure	0.014	±0.001 (1)	1-21 (2)	On-Line I.R.	200 -700	25	Depends on station	Yes
	-0.020							
Main Steam System	0.014 -0.100	±0.001	21	On-Line I.R.	200	25	Clean pH ~9	Yes
Upgrader Tails	< 1	±0.01	21	On-Line I.R.	16	55	Clean	Yes
Active Drainage Sumps	< 1	±0.01	21	Lab I.R.	atmos	25	High in dissolved and undissolved solids	-
Stack	< 1	0.001	7	Lab ³ H ₁	atmos	25	Clean	Yes

NOTES:

- (1) Moderator heat exchangers require analysis with an accuracy of ±0.00001 wt% D₂O (i.e. 0.1 ppm) on a daily basis.
- (2) The frequency range shown here represents the range per component.

for heavy water leak detection is ± 0.001 wt% D_2O (i.e. ± 10 ppm). However, for the moderator heat exchangers, an accuracy of ± 0.1 ppm is required daily to provide protection against chronic low level leakage. Such precision is achieved by tritium analysis of grab samples. The stations are currently designed for on-line analysis of the main steam and service water systems for detecting heavy water leaks. The on-line infrared monitors, with an accuracy of ± 10 ppm, provide continuous protection against major leaks from all heat exchangers. They also monitor for chronic leaks from all heat exchangers but the moderator. The other liquid effluents i.e. the active drainage sumps and the upgrader tails have much lower discharge rates and consequently only require an accuracy of ± 0.01 wt% D_2O . Present upgraders have provisions for an on-line infrared tails monitoring system which is primarily used for process control.

Analysis of the water vapour content in the stack effluent has been included in Table 1(c). These samples are collected on silica gel and/or a cold finger to provide information on integrated heavy water losses and tritium releases. Laboratory tritium analyses are presently required to achieve the necessary high precision. However, considerable benefit would be realized from an on-line stack-loss monitor measuring heavy water losses directly since:

- estimating D_2O losses from tritium release data is not sufficiently accurate, and
- minimal protection is offered by tritium analysis in early reactor life.

On reviewing this data, it has been concluded that for heavy water leak detection, no practical manual sampling program matches the protection offered by a continuous monitor. Thus on-line analysis is essential for those process streams capable of releasing heavy water to the environment, viz.

- the service water systems,
- the main steam system, and
- the stack exhaust.

These streams must be monitored with an accuracy of ± 0.001 wt% D_2O or better. For those systems that require heavy water concentration analyses for process control purposes, on-line instruments should be used and grab samples should only be taken to monitor the performance of the on-line instrument and not to control the process. Thus on-line instruments are required for:

- the upgrader bottom product,
- the upgrader tails, and
- the deuteration/dedeuteration units.

The upgrader analyses are required with an accuracy of ± 0.01 wt% D_2O and the deuteration/dedeuteration units require ± 2 wt% D_2O .

Thus, six systems have been identified as definitely requiring on-line monitoring.

In assessing the remaining systems against the secondary advantages, the frequency of analysis dictates the potential value of on-line instruments. However, since the sampling frequency and practices vary greatly, individual station preferences will determine whether on-line analysis is desirable for

specific systems. However, the following general conclusions can be drawn for those systems of secondary importance:

- (i) In the high concentration range, the present 3-7 samples per week from each of the moderator or heat transport systems does not justify on-line analysis.
- (ii) The large number of mid-range samples (from the collection and cleanup operations) appears to justify on-line analysis. However, they originate from many sources and the accuracy requirements are modest so that on-line analysis is unlikely to be practical. A simple portable instrument calibrated directly in wt% D₂O may be operationally more convenient for some of these systems.
- (iii) In some stations where sampling frequency is high, batch processes such as the vapour recovery and the active drainage tanks will benefit from on-line analysis. This would reduce routine work loads and allow liquid transfers, without laboratory analysis, at operationally convenient times. Such a scheme has proven very successful on the evaporator drain tank on the NRU reactor [2]. For the power reactor application, although the absolute accuracy requirements are modest, a resolution of 0.05 wt% D₂O would alert the staff to sudden changes in process conditions.

3. REVIEW OF DENSITY INSTRUMENTS

In relating the density of a sample to the isotopic composition, it is important to note that H₂O-D₂O mixtures form a perfect solution with no measurable volume change on mixing [3]. Thus, the volume percent D₂O is a linear function of the density.

However, in the power reactor program, except for analyses close to pure H₂O, the D₂O concentration is conventionally expressed in terms of weight percent. Kirshenbaum [4] has derived the following expression to relate the sample density to the concentration at 25°C:-

$$\text{Weight percent D}_2\text{O} = \frac{1027.91 \Delta d}{\Delta d + 997.05}$$

where Δd is the difference between the density of the mixture and that of pure H₂O (997.05 kg/m³ at 25°C).

This non-linearity between heavy water concentration and the density of the H₂O/D₂O mixture amounts to an error of ~2.8 wt% D₂O for a 50 wt% D₂O sample if a linear relationship is assumed. Thus, an important feature that has been included in the assessment of density instruments is their capability to compensate for the small but significant non-linearity so that the instrument reads directly in wt% D₂O.

The precise data of Kell [5] on the densities of H₂O and D₂O at a series of temperatures from 0 - 100°C was used to determine the temperature coefficient of the density for 0, 50 and 100 wt% D₂O over the range 0 - 50°C. The maximum density of ordinary water occurs at 4°C. This is, therefore, a point of zero temperature coefficient (see Fig. 1). The corresponding point for D₂O is at 11.2°C. To minimize the effect of sample temperature on the measured density requires either:

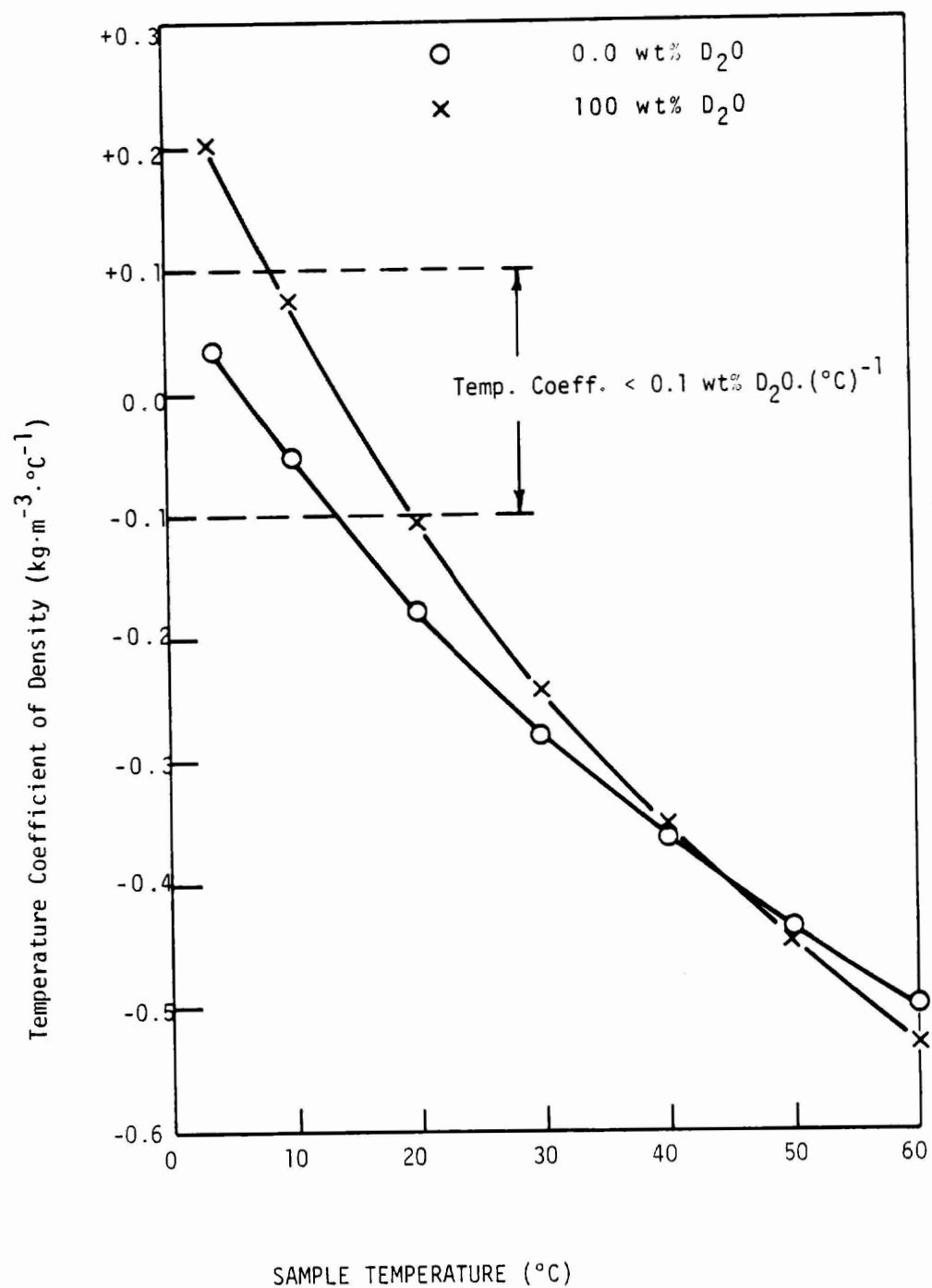


FIGURE 1: Temperature Coefficient of Density as a Function of Sample Temperature for Light and Heavy Water

- very precise temperature control, or
- temperature compensation.

(i) Temperature Control

To reduce the effect of sample temperature variations the densitometer must operate at a temperature which minimizes the temperature coefficient. At 10°C the temperature coefficient varies from $-0.05 \text{ kg.m}^{-3}.\text{°C}^{-1}$ to $+0.07 \text{ kg.m}^{-3}.\text{°C}^{-1}$ as the concentration varies from 0 to 100 wt% D₂O. Hence, near 10°C the magnitude of the temperature coefficient for all concentrations is less than $0.1 \text{ wt\% D}_2\text{O}.\text{(°C)}^{-1}$. Consequently, to achieve analysis with a resolution of 0.01 wt% D₂O, sample temperature control to within $\pm 0.1^\circ\text{C}$ is required. This can be achieved for process system applications, but does impose additional complexity on the installation design.

(ii) Temperature Compensation

Since the magnitude of the temperature coefficient depends both on sample concentration and temperature, temperature compensation is also complex. Precise values of the density of various heavy water/light water mixtures over a temperature range from 5-50°C were calculated from the published data. The results are summarized in Table 2. Any compensation scheme must be capable of coping with the variations depicted by this Table.

Because of their significance in heavy water isotopic analysis these fundamental principles were taken into consideration during the commercial instrument review.

Requests for literature were sent to 123 potential suppliers of density instruments based on a list generated from trade literature and directories. From the letters of enquiry, 53 responses were received leading to 25 different products.

The instruments divide into six classes, each characterized by the principle of the measurement as described below.

(a) Direct Weighing

Weighing a sample of a known volume is a simple method for density or specific gravity determinations. Although often used for laboratory samples, it is seldom practical for measuring the density of a flowing fluid. However, process instruments for the continuous weighing of a flowing sample were offered for this application by two suppliers.

(b) Buoyancy

Buoyancy transmitters based upon Archimedes' Principle have been adapted to the measurement of liquid density or specific gravity. For density measurements, a cylindrical displacer is located so as to be fully submerged. The buoyant force on the displacer changes only as a function of changing liquid density and is independent of changing liquid level in the vessel. Three process instruments based on this measurement principle were offered.

TABLE 2

TABULATION OF THE DENSITY OF $\text{H}_2\text{O}/\text{D}_2\text{O}$ MIXTURES FOR VARIOUS CONCENTRATIONS AND SAMPLE TEMPERATURES

Density is expressed in kg.m^3

TEMP.	CONCENTRATION (wt% D ₂ O)										
	0%	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
5°C	999.96	1009.61	1019.44	1029.47	1039.70	1050.14	1060.79	1071.65	1082.74	1094.06	1105.62
10°C	999.70	1009.40	1019.29	1029.38	1039.67	1050.16	1060.87	1071.80	1082.96	1094.35	1105.99
15°C	999.10	1008.84	1018.77	1028.90	1039.23	1049.78	1060.54	1071.52	1082.73	1094.18	1105.87
20°C	998.21	1007.98	1017.94	1028.10	1038.47	1049.05	1059.84	1070.86	1082.11	1093.60	1105.34
25°C	997.05	1006.84	1016.83	1027.01	1037.40	1048.01	1058.83	1069.88	1081.16	1092.68	1104.45
30°C	995.65	1005.45	1015.45	1025.65	1036.06	1046.68	1057.52	1068.59	1079.89	1091.44	1103.23
35°C	994.04	1003.85	1013.86	1024.07	1034.49	1045.12	1055.97	1067.05	1078.36	1089.92	1101.73
40°C	992.22	1002.03	1012.05	1022.26	1032.68	1043.32	1054.17	1065.26	1076.58	1088.14	1099.96
45°C	990.22	1000.03	1010.04	1020.25	1030.67	1041.30	1052.16	1063.24	1074.56	1086.12	1097.94
50°C	988.04	997.84	1007.85	1018.05	1028.46	1039.09	1049.94	1061.02	1072.33	1083.89	1095.70

(c) Hydrostatic Head

The difference in pressure between any two elevations below the surface of a fluid is equal to the difference in liquid head, and is independent of variations in the liquid level. The dimensional difference between the two elevations multiplied by the specific gravity of the liquid gives the difference in head and is usually expressed in inches or metres of water, the standard units for the calibration of such instruments. Density measurement systems based on Δp cells were offered by three suppliers.

(d) Vibration

The damping of a vibrating object in contact with the process fluid increases as the density of the fluid increases. This principle has been applied to industrial density measurement in several ways. In general, the object which vibrates is externally stimulated and is either:

- an immersed reed or plate, or
- a tube or cylinder which conducts or which is filled with the process fluid.

The actual fluid density can be inferred from one of two measurements:

- changes in the natural frequency of vibration when the stimulus is applied constantly, or
- changes in the amplitude of vibration when the object is "rung" periodically in the bell mode.

Since frequency is a basic physical parameter which can be measured very precisely, this approach is used in five instruments that were proposed for this application.

(e) Radiation

The intensity of the gamma-rays transmitted through a fixed thickness of sample is exponentially dependent on the density of the fluid. The application of this principle to the measurement of the density of H_2O/D_2O mixtures was offered by eight suppliers.

(f) Others

In addition to the twenty-one density instruments already described, four other devices which could be applied to heavy water analysis were also offered.

The speed, V , at which sound travels through a liquid is an inherent physical property of the liquid and is dependent on its density, d , as follows: $V = (k/d)^{1/2}$ where k is the bulk modulus. Thus, a precise measurement of the velocity of sound in a water sample can be used to analyze for heavy water concentration [6]. Instruments based on this principle were offered by two suppliers.

An instrument based on neutron moderation and a fluidic device complete the list of monitors that were reviewed.

In each class, the instruments were compared in detail and the one most applicable to heavy water concentration measurements was selected for comparison with instruments from each of the other classes. The results of this comparison are summarized in Table 3.

For comparison purposes, it was assumed that the instruments would be required to operate over the entire range from 0-100 wt% D₂O with corresponding density extremes of 988.04 kg.m⁻³ and 1105.99 kg.m⁻³. To accommodate those applications for which a narrower span is appropriate, consideration was given to the resolution and accuracy specified for a narrower span wherever possible. Approximate instrument costs have been included for comparison.

As can be seen from Table 3, the resolution offered by the instruments based on vibration far exceed that of the other devices. However, the price is also correspondingly higher.

4. REVIEW OF REFRACTOMETERS

The refractive index of a water sample not only depends on its isotopic composition but also on the sample temperature and measurement wavelength [7]. At the sodium wavelength of 589 nm and at a sample temperature of 30°C, the refractive indices are as follows [8];

Refractive index of H₂O, $n_1 = 1.33194$, and
Refractive index of D₂O, $n_2 = 1.32752$.

For the concentration dependence, Djurle [9] has established a quadratic relationship between the refractive index of an H₂O/D₂O mixture and the deuterium content. However, the quadratic term is small and can be ignored for this application. Consequently, the refractive index, n , of a sample with deuterium atomic percentage, p is

$$n = 1.33194 - 4.42 \times 10^{-3} p.$$

Thus, like the density dependence, the relationship between the refractive index and the concentration of H₂O/D₂O mixtures in the conventional units of wt% D₂O is non-linear and similar considerations have to be given in the selection of a suitable instrument.

The wavelength dependence presents no major instrumentation problems since most sources, either white light or monochromatic, are sufficiently stable for this measurement. However, it should be noted that the difference between the refractive index of H₂O and D₂O increases with decreasing wavelength (see Fig. 2). Thus, improvements in resolution can be achieved by operating at shorter wavelengths.

The temperature dependence of the refractive index of H₂O/D₂O mixtures is very large ($\sim 3 \text{ wt\% D}_2\text{O} \cdot (^\circ\text{C})^{-1}$) and eliminates direct refractive index measurements as a practical analytical approach. On the other hand, the differential refractive index has a temperature coefficient equivalent

TABLE 3
SUMMARY OF DENSITY INSTRUMENTS

PRINCIPLE OF MEASUREMENT	NUMBER OF SUPPLIERS	SELECTED UNIT	ACCURACY wt% D ₂ O	RESOLUTION wt% D ₂ O	RESOLUTION ON REDUCED SPAN	LINEARIZATION	APPROXIMATE COST K\$
Weighing	2	Halliburton	+2.0	0.2	Same ⁽¹⁾	NO	4
Buoyancy	3	Princo	+3.0	0.5	0.05	NO	5
Hydrostatic	3	Foxboro	+10.0	5.0	Same	NO	-
Vibration	4	Agar	+0.5	0.02	0.004 ⁽²⁾	YES	20
Radiation	8	Berthold	+0.6	0.3	Same	YES	10
Others	4	Musonics	+0.3	0.1	Same	NO	10

NOTES:

- (1) Minimum span equivalent to 50 wt% D₂O.
(2) Resolution for minimum span of 20 wt% D₂O.

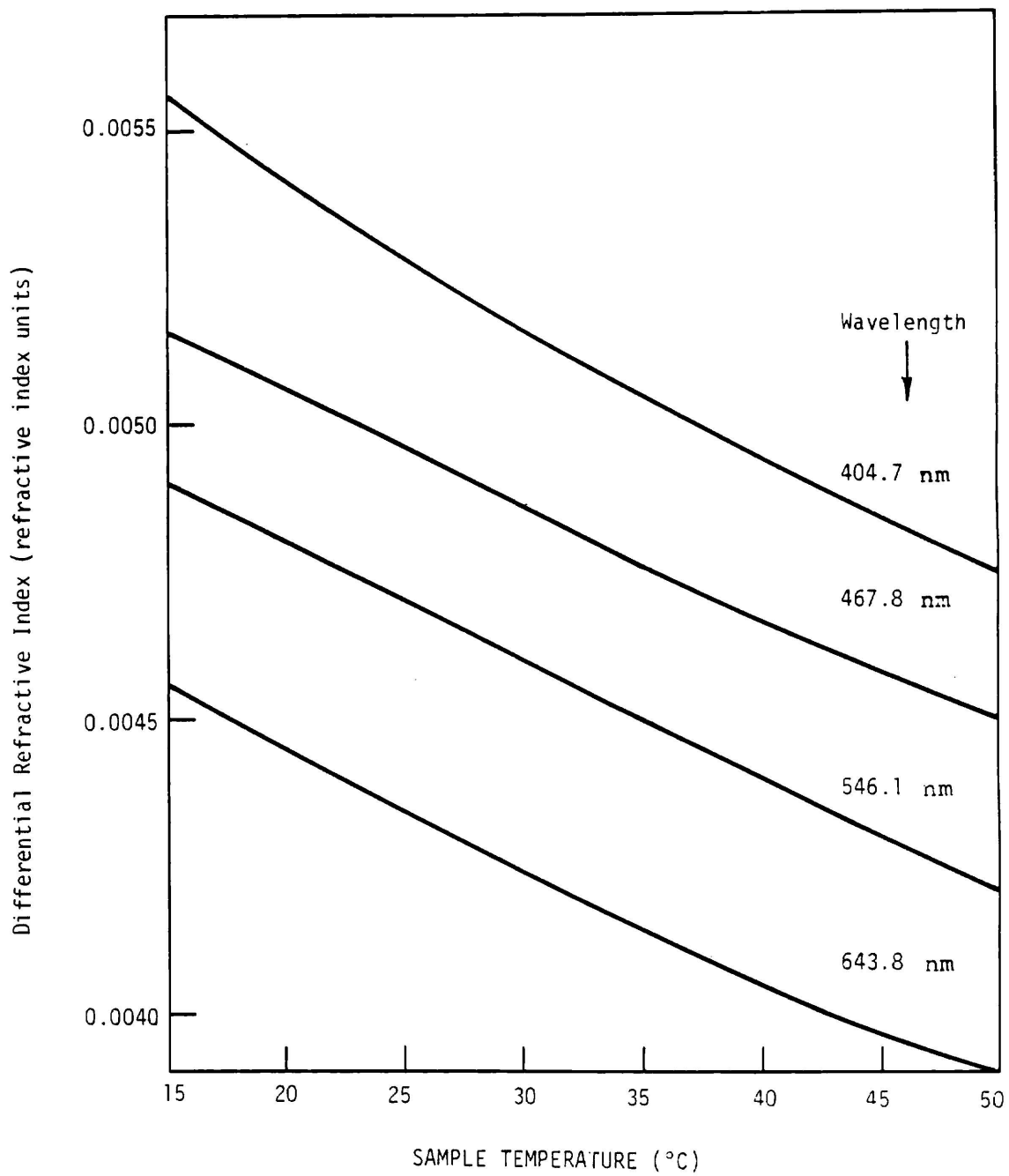


FIGURE 2: The Differential Refractive Index ($n_1 - n_2$) as a Function of Sample Temperature for Various Measurement Wavelengths.

to 0.4 wt% D₂O.(°C)⁻¹. This is virtually independent of deuterium content, sample temperature and operating wavelength. Therefore differential refractometry is a practical approach and temperature compensation or sample temperature control can be used to reduce the effects to acceptable limits.

Fifty-two potential suppliers of refractive index measuring instruments were surveyed.

From these letters of enquiry, 21 responses were received leading to 14 different products.

Although refractometers are normally divided into four scientific classes: spectrometer, interferometer, critical angle and differential; all the instruments offered fell into the latter two categories. Thus, for the purposes of this review, the instruments that were offered were classified into the four practical categories described below. Once again, a wide range (0-100 wt% D₂O) application was used for comparison purposes and the effect of reducing the span by a factor of ten was considered.

(a) Abbe Refractometer

The minimum angle of incidence whereby a ray is totally internally reflected is the parameter measured in a large number of refractive index instruments. Of the critical-angle refractometers, the Abbe type is by far the most common. Three different manufacturers offered this approach.

(b) Dipping Refractometer

For process applications, the dipping critical angle refractometer is the most practical. In this instrument a single measurement prism which penetrates the process pipe is normally used. As the stream concentration changes, the critical angle changes and the amount of light reflected changes proportionally. Process instruments based on this approach were offered by three suppliers.

(c) Differential Refractometer

For applications in which changes in refractive index, rather than the absolute value, are of prime importance, differential refractometers are more practical. These instruments measure the difference between angles of refraction in a sample and a reference standard. Suitable instruments employing this principle were offered by five suppliers.

(d) Hand Refractometers

Three hand refractometers were offered. These portable instruments, which are critical-angle refractometers with Abbe-type prism boxes, provide resolution which is comparable with the more expensive laboratory instruments. Although these would appear to be very convenient portable instruments, with an inherent resolution of 2 wt% D₂O, the effect of impurities would likely add a considerable error to the reading. Moreover, unsealed tritiated samples could present a radiation exposure problem.

The capabilities of these instruments are summarized in Table 4. Of the refractometers that were reviewed the differential type are obviously best suited to heavy water analysis. However, they do not have the precision of the vibrational densitometers.

5. INSTRUMENT SELECTION

On the basis of the comparison of the specifications of densitometers and refractometers summarized in Tables 3 and 4, the Agar (Model 800) vibrational density meter was selected as the most suitable instrument for on-line heavy water analysis of process streams in CANDU nuclear reactors.

In addition to sensitivity, two other factors favour the use of density measurements over refractive index.

- The temperature coefficient for the density measurement is a factor of four smaller than for refractive index.
- Although the effects of impurities are very important for both measurements, laboratory experience shows that they are less significant for density techniques.

As a result of this study an Agar densitometer was procured and subjected to laboratory evaluation as discussed in Section 6.

In conducting this instrument review, two other factors became apparent. Firstly, specifications written by manufacturers with one application in mind cannot always be interpreted literally for a different application. Secondly, for instruments of this type and complexity, the process models are almost twice the cost of comparable laboratory models.

Several of the products offered were laboratory instruments and not suitable for process monitoring. However, laboratory analyses are important at power reactors, so these instruments were included in the review for completeness.

Because of the inherent advantages of using density rather than refractive index measurements to determine D_2O concentration, the Anton Paar densitometers are the most suitable for laboratory analyses in the intermediate concentration range. These are vibration-type density meters [10] with one model (DMA-60/601) having six-place precision and a quoted accuracy of ± 0.0015 wt% D_2O . However, to achieve this, an external sample temperature controller is required to maintain the measurement cell to within $\pm 0.01^\circ C$. For less demanding applications other models are available.

It should be noted that the accuracy and resolution of laboratory instruments are normally comparable, because frequent calibration is possible. By comparison, the accuracy of a process instrument is typically ten times poorer than the resolution due to environmental effects, instrument drift, and unreliable sample quality. This is the most important consideration which precludes the possibility of modifying laboratory instruments for field use.

TABLE 4
SUMMARY OF REFRACTIVE INDEX INSTRUMENTS

PRINCIPLE OF MEASUREMENT	NUMBER OF SUPPLIERS	SELECTED UNIT	ACCURACY wt% D ₂ O	RESOLUTION wt% D ₂ O	REDUCED SPAN	LINEARIZATION	APPROX. COST
Abbe	3	Bellingham & Stanley	+2.0	-	-	No	\$3000
Dipping	3	Anacon	+0.5	0.5	approx. same	No	\$5000
Differential	5	Anacon	+1.0	0.25	0.03 ⁽¹⁾	No	\$6000
Hand Held	3	-	+2.0	-	-	No	\$ 300

NOTES:

(1) Equivalent Resolution for Operation on 10 wt% D₂O Span.

It should also be noted that a two column manometer-type D₂O analyzer has been developed at CRNL and is currently in use in the laboratories at several reactor sites. Although it is not a process monitor, it is inexpensive and can be used whenever D₂O analysis to ± 1 wt% D₂O is required.

6. RESULTS FROM THE LABORATORY EVALUATION

The Agar densitometer that was purchased consisted of two major components, a Model FD881ABSTV density transducer and a Model HC900 electronic conversion unit. These particular units were selected since they offer key features, as described below, that make them particularly suitable for heavy water analysis.

The Agar transducer, shown in the photograph in Fig. 3, maintains a thin walled stainless steel tube in transverse oscillation by an electromagnetic driving field. The tube oscillates at its resonant frequency, this being dependent on the density of the fluid flowing through the tube. To counterbalance the oscillations, the sample flows in series through two other tubes which are mechanically mounted in parallel with the sensing element [11], as shown in Fig. 4.

The liquid path through the sensor is a clear passage containing no obstructions, and no removable or moving parts. The pressure drop is equivalent to 1.4 m of 19 mm diameter smooth bore pipe with two 180° bends. The ports are designed to be self purging and offer considerable immunity to the accumulation of deposits.

The sensing assembly is connected to the supporting framework and the coupling flanges by isolating bellows thus reducing the effects of vibration. The entire assembly is mounted inside a sealed cylindrical case providing protection against dust and moisture.

The instrument was supplied with a three-wire platinum resistance thermometer (100) whose primary function was to provide a signal for transducer temperature compensation. However, this signal is also used to convert the measured density to the required concentration units.

The standard transducer has been mechanically designed to operate with sample pressures up to 8000 kPa and sample temperatures in the range from -30°C to +200°C. The unit provides a frequency modulated output signal which can be related to the fluid density. For this application, the sensitivity is approximately 2.7 kg/m³ per microsecond change in period-ic time.

The microprocessor based electronic unit, shown in Fig. 5, was designed and programmed to perform three major functions, viz:

- the conversion of the period measured by the transducer to sample density in the appropriate engineering units (kg/m³);
- the subsequent calculation of the heavy water concentration in wt% D₂O; and
- output displays and alarms for the primary functions.

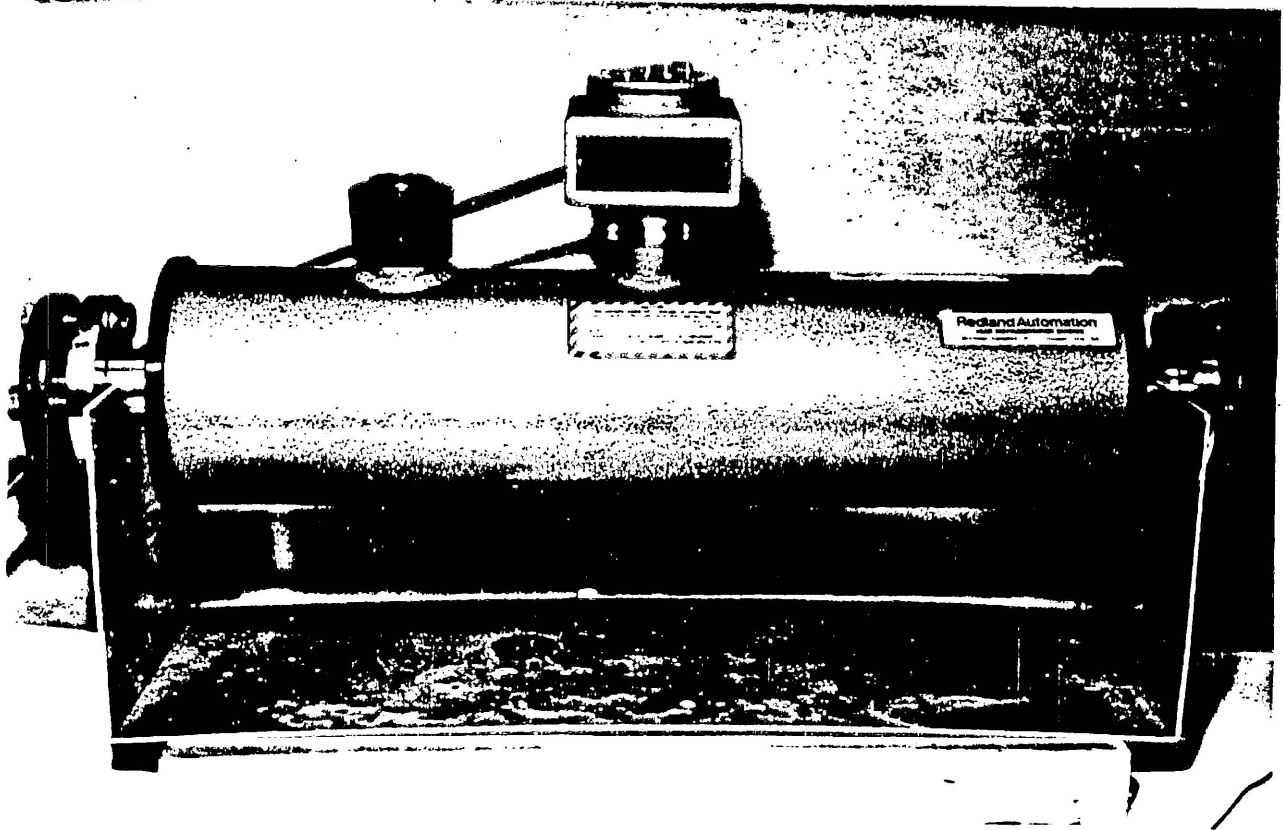


FIGURE 3: PHOTOGRAPH OF AGAR MODEL FD 881 ABSTV DENSITY TRANSMITTER

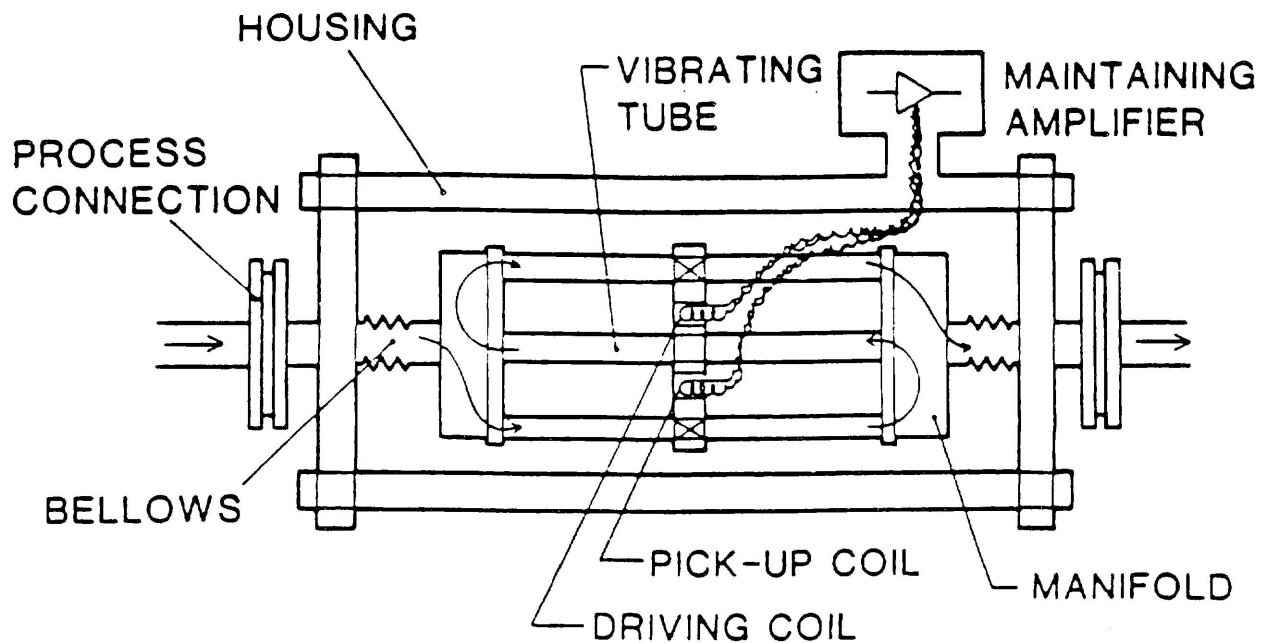


FIGURE 4: SCHEMATIC DIAGRAM OF AGAR DENSITY TRANSDUCER

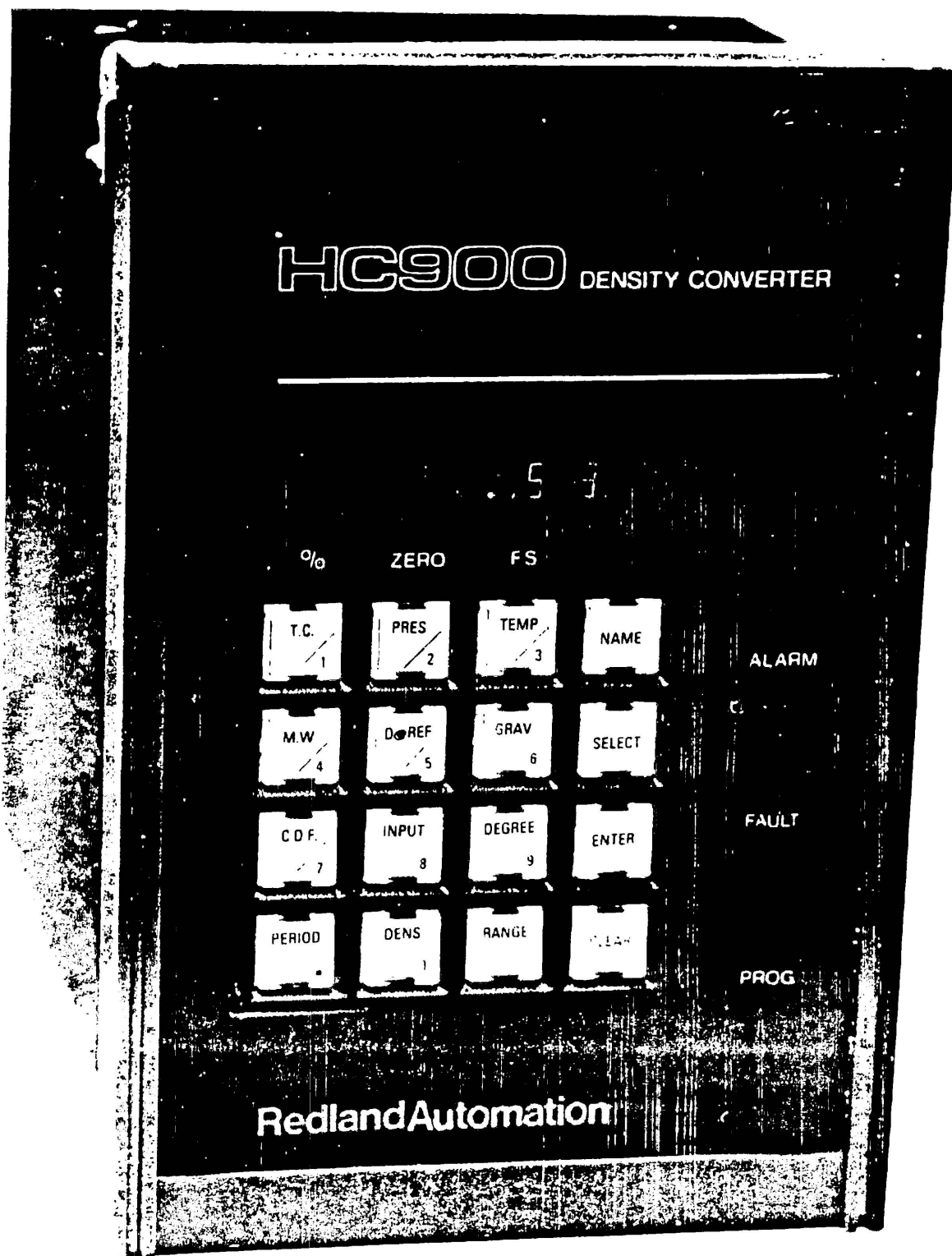


FIGURE 5: PHOTOGRAPH OF FRONT PANEL OF ELECTRONIC CONVERSION UNIT

When operated in the narrow range required for heavy water analysis (approximately 1000-1100 kg/m³), the transducer exhibits a large variation of measured period with sample temperature (see Fig. 6). This variation is much larger than the change in sample density as shown by the data points on the same figure, and confirms that transducer temperature compensation is essential. The laboratory tests confirmed that linear compensation for the effect of temperature on the instruments accuracy for density determinations is adequate.

The effect of sample pressure on the measured period was also determined to be linear for pressures above 35 kPa (gauge). However, the measured pressure coefficient is small. Consequently, dynamic compensation for sample pressure variations is not considered necessary, thus eliminating the need for an electronic pressure sensor in routine applications.

For sample pressures below 35 kPa (gauge), slight non-linear behaviour was observed in some instances particularly at elevated temperatures. This has been attributed to sample effervescence in the vicinity of the vibrating element. Consequently, operation with sample pressures greater than 70 kPa (gauge) is recommended.

The calculational capabilities of the electronic unit are used effectively in converting the measured sample density and temperature to heavy water concentration in the required engineering units (wt% D₂O). This is accomplished by taking into account both the non-linearity discussed in Section 3 and the fact that the concentration is a complex function of density and temperature as described by Table 2.

The manufacturer converted the tabulated density data of Table 2 to the format suitable for storage in the microprocessor memory. The electronic unit was programmed to perform linear interpolations between the tabulated parameters for density and temperature to determine the value of the heavy water concentration.

Since considerable care is taken in determining a precise value of the absolute density, the use of a look-up table is a satisfactory approach to determining the heavy water concentration. This feature is unique in the instruments that were reviewed and considerably simplifies the application of density measurements to heavy water analysis by eliminating the need for precise sample temperature control.

The performance of the instrument was measured on a laboratory test loop which was capable of simulating a wide range of operating conditions. These tests were aimed at assessing the fundamental limits of the instruments performance when it is operated in an industrial environment. The results are described under the following headings.

(i) Resolution

The instrument resolution was determined to be 0.02 wt% D₂O confirming the manufacturer's specifications. The factor limiting the resolution was found to be the temperature measuring circuit. However, without corresponding improvements to the accuracy, further improvements to the resolution are not considered necessary.

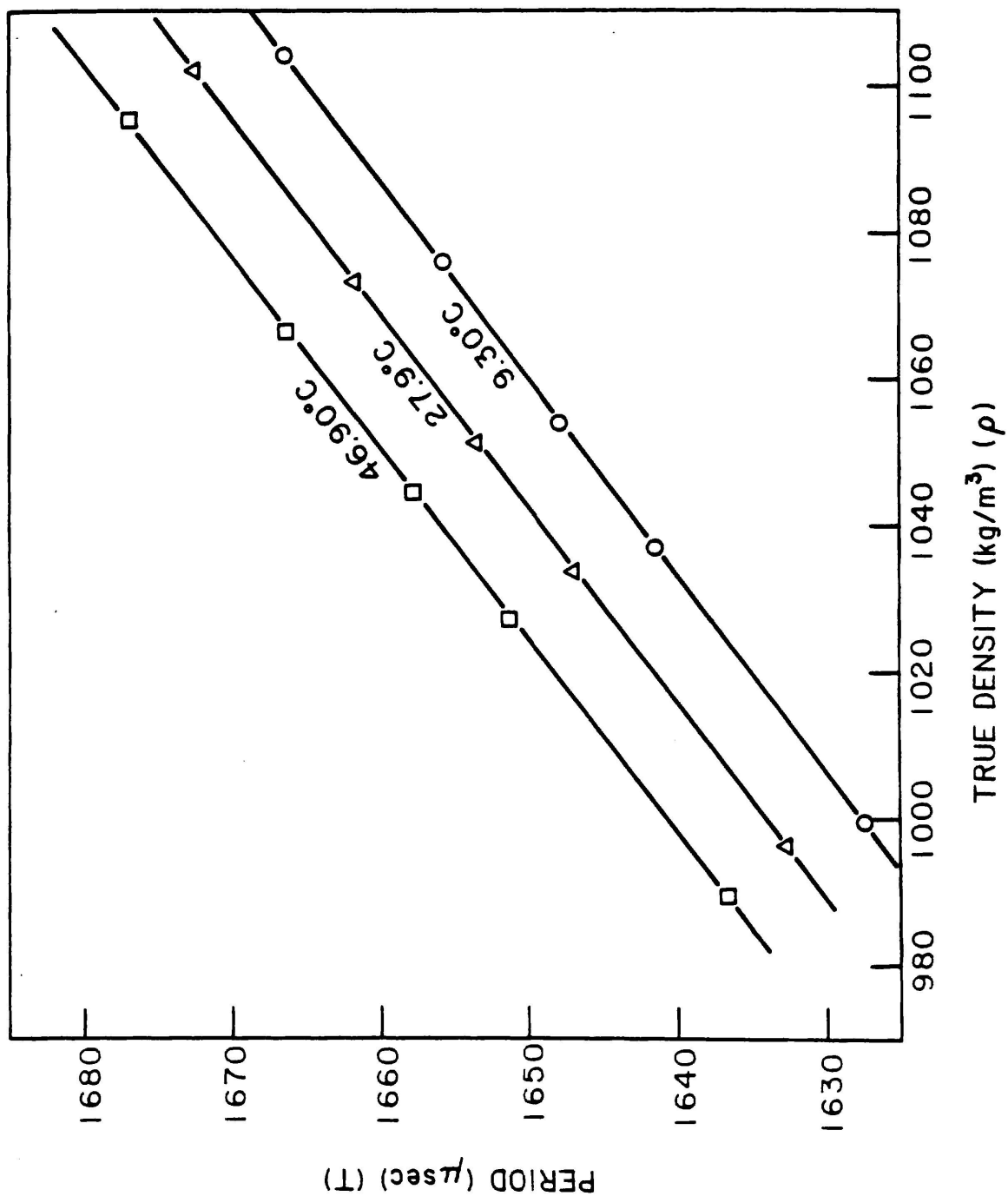


FIGURE 6 : THE VARIATION OF MEASURED PERIOD WITH DENSITY AS A FUNCTION OF SAMPLE TEMPERATURE

(ii) Accuracy

The major limitation on the accuracy of the instrument was the ability of the calibration algorithm to fit the experimental data. The test data confirmed that accuracies of ± 0.1 wt% D₂O are achievable. However, the calibration is not considered amenable to field adjustment.

The instrument was programmed by the manufacturer with three parameters for the calibration algorithm. The electronic unit computes the density from an algorithm which has a physical basis but which is not suitable for simple adjustment by an operator.

Each of the parameters are interrelated in such a way that each calibration produces an entirely new set of values. It would have been far simpler to linearize the calibration curve and then provide the operator with simple zero and span adjustments to scale the output to the desired values. This would reduce the number of calibration samples required from four to two and provide simple adjustments.

(iii) Drift

Operating the instrument under stable sample and environmental conditions, the calibration was monitored continuously for 71 days. During this period the calibration drifted by less than 0.01 wt% D₂O per day. This is to be compared with the manufacturer's quoted value of 0.003 wt% D₂O per day. Although higher than expected, the instrument is sufficiently stable, that detailed recalibration every two months will be adequate, with a weekly single point calibration check also being recommended.

(iv) Response Time

With the test loop that was used, it was not possible to accurately measure the transducer's response time to step changes in density. The liquid hold-up volume and subsequent mixing of the samples limited this measurement to confirming that the response time is less than 5 minutes independent of direction of the change. Since the measurement is based on a period measurement, there is no reason to suspect that the manufacturer's quoted response time of milliseconds cannot be achieved.

(v) Variation of Operating Parameters

The sample flow, temperature and pressure were each varied in turn while the other two operating parameters were held constant. The dependence of the instrument output on the variation of these parameters was determined to be sufficiently small to permit the instrument to be used in a power reactor environment without serious restrictions on the tolerances required for operator adjustments (see Table 5). The single environmental parameter for which detailed performance measurements were made was ambient temperature. The output dependency was determined to be $+0.005$ wt%D₂O (°C)⁻¹. This very low value confirms the adequacy of the temperature compensation and the suitability of the instrument for use in an industrial environment.

TABLE 5
VARIATION OF OPERATING PARAMETERS

Parameter	Range	Output Coefficient
Sample Flow	0.5 L.min ⁻¹	0.004% D ₂ O.L ⁻¹ .min
Sample Temperature	10-45°C	-0.035% D ₂ O.(°C) ⁻¹
Sample Pressure	35-200 kPa	0.01% D ₂ O/kPa

(vii) Effects of Sample Purity

Any impurity in the water can cause a change in density which will register as a change in D₂O concentration. The density change will depend on the density of the impurity and its concentration, and for this reason can be readily predicted.

Although each application must be considered in detail, the effects of sample purity are not considered to be insurmountable. Normal filtering and degassing procedures will eliminate the major problems to be expected from particulates. Moreover, the normal concentrations of dissolved solids used for chemical control of the process systems are sufficiently low that variations in the output will be less than 0.1 wt% D₂O. This is well within the accuracy tolerance.

On the basis of this laboratory test program it is therefore concluded that the Agar densitometer is well suited to monitoring those process streams that require heavy water analyses with an accuracy of ± 0.5 wt% D₂O.

7. CONCLUSION

The review of the heavy water analytical requirements for Canadian power reactors has concluded that the processes for which on-line analyses are essential are those capable of heavy water leakage to the environment and those whose concentration are used for process control. All these systems require analyses to an accuracy better than ± 0.01 wt% D₂O which exceeds the capabilities of density and refractive index monitors. All other processes are of secondary importance and individual station preferences will determine whether on-line analysis is required for heavy water management or operational reasons.

The survey of commercial refractive index and density instruments resulted in 39 different products being reviewed in detail. From these, the Agar (Model FD800) vibrational densitometer was selected as the most sensitive instrument for wide range heavy water analysis.

The evaluation test program established that the unique computational capabilities of the Agar densitometer allow it to be calibrated in the required concentration units with a resolution of 0.02 wt% D₂O and an accuracy of ± 0.5 wt% D₂O for a wide range of operating and sample conditions. Consequently, it is recommended that this instrument be included in the list of potential monitors available to system designers and plant operators.

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