

Chemistry - PI 24

CHEMICAL ANALYSIS - GENERAL

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Objectives:

1. List three methods for the isotopic analysis of heavy water, outline in a sentence or two the basic principle behind each method.
  2. List ten chemical items or species monitored in the primary heat transport system. State the reason each is monitored.
  3. List seven items or species of a chemical nature monitored in the Moderator. State the reason for each.
  4. List four major sample points in the secondary heat transport system, four items (chemical) monitored at each point and the reason for monitoring each item.
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A. ISOTOPIIC ANALYSIS OF WATER

Accurate isotopic analyses of water are absolutely essential to the successful operation of the CANDU system. Their need begins with the production of the heavy water. Every phase of the production must be monitored in order that the plant operates under optimum conditions keeping the production at a maximum and the cost at a minimum. All water added to the reactor must be monitored as even a small amount of downgrading of D<sub>2</sub>O and H<sub>2</sub>O leads to decreased reactivity with the possibility of a forced shutdown. Likewise, any water that is lost from the system (eg, by leakage) must also be monitored to determine whether it can be returned directly to the system or whether it must first go to an upgrading unit or just be discarded.

1. **Density Measurement**

Whatever anyone tells you - let me tell you right now that this is a very accurate method.

The specific gravity or relative density of H<sub>2</sub>O is 0.9971 while that of D<sub>2</sub>O is 1.0775 (both at 25°C). A solution containing both waters will lie

somewhere between the two extremes. The relation between the two is linear making interpolation easy.

Modern digital density meters are fast and accurate.

## 2. Refractive Index

Most measurements of refractive indices are performed by rather simple equipment based upon the measurement of a critical angle, ie, the angle where the incident radiation is either 0° (grazing) or 90° (perpendicular). Precise control must be exercised over both the temperature of the system and the wavelength of the light. The latter is accomplished by the use of a monochromatic light source such as a sodium lamp.

The refractive indices of light and heavy water differ from each other by less than 1%.

$$\text{H}_2\text{O} \text{ --- } n_D^{20} = 1.33300$$

$$\text{D}_2\text{O} \text{ --- } n_D^{20} = 1.32844$$

This difference is sufficient to permit a rough and rapid isotopic analysis (provided the temperature is rigidly controlled). The simple refractometer is capable of giving an isotopic composition to  $\pm 2\%$ . Differential (directly referred to installed standards) refractometers were proposed as a method of increasing accuracy but did not suit Hydro's needs.

Refractometers are subject to large errors from even trace impurities but are very well suited to "quick and dirty" spot checks.

## 3. Infra-Red Analysis

For a detailed description of how infra-red spectrometers work you are referred to 224.30-3. A quick summary of IR for heavy water is as follows.

The three isotopic waters,  $\text{H}_2\text{O}$ ,  $\text{HDO}$  and  $\text{D}_2\text{O}$  will exhibit the same vibrations. The frequencies of these vibrations would; however, be expected to be different due to the different weights of the two hydrogen isotopes. If IR light is passed through a sample containing a mixture of the isotopes, some of the light will be absorbed due to harmonic vibration with the water molecules. If

the sample thickness is kept constant, ie, the same sample cell, then it is possible to obtain the isotopic composition by scanning across a region of the spectrum where there is a reasonable change with composition. By measuring the absorption for various samples of known composition a calibration curve is prepared. Measuring the "unknown" and comparing its absorption with the calibration curve gives its composition.

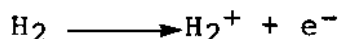
Infra-red analysis is very accurate below 1% D<sub>2</sub>O and above 99% D<sub>2</sub>O; in between the accuracy is about the same as refractive index which is cheaper to do. IR spectrophotometers are designed for laboratory use; most stations have them in the laboratory. Field installed units have been less than satisfactory with respect to their high maintenance requirement.

#### 4. Mass Spectrometry

The mass spectrometer is an instrument that separates ions according to their mass by means of a magnetic field. Once separated it "counts" the number of particules of each mass in order to get the isotopic composition. Ideally the sample should be a gas; if not it is generally converted to a gas by heating. Water is generally converted to hydrogen gas by passage over a hot uranium surface ("uranium furnace"):



Inside the chamber the gas molecules are ionized by bombardment with electrons from a hot filament.



These ions are accelerated and defined into a narrow beam by a series of accelerating slits and sent down the analyzer tube.

Under the influence of a magnetic field perpendicular to the plane of the tube, the paths of the various ions are bent. The amount of "bending" as well as the "counts" may be used to give isotopic analysis.

The mass spectrometer is the most precise of all of the methods except density. It is operable over the whole range 0-100% with analyses good to better than  $\pm 0.01\%$  provided the standards are available. If the sample given to the operator is

hydrogen gas, the analysis is rapid - perhaps two to three minutes. If the sample is water then the time increases to twenty minutes or longer to allow time for conversion of the water to hydrogen.

The machine is expensive and it requires a full-time operator-technician. It suffers from "memory" effects; ie, it remembers part of the last sample due to adsorption on the walls. It thus, cannot take samples of widely varying composition unless one is prepared to extend the time between samples to allow a complete pumping of the system.

If you wish to read more detailed explanations of mass spectrometry, see Lesson 224.30-2.

## B. Heavy Water Systems

The major sample points for PHTS are both reactor outlet headers, purification system inlet and outlet. Species or items monitored are (with variations):

- pH
- Conductivity
- Lithium (Li)
- Chloride (Cl<sup>-</sup>)
- Fluoride (F<sup>-</sup>)
- Deuterium Gas (D<sub>2</sub>)
- Dissolved Oxygen (O<sub>2</sub>)
- Crud
- Fission Products
- D<sub>2</sub>O Isotopic
- Tritium

pH, Conductivity and Li are usually considered together as pH will affect conductivity and Li will affect both pH and conductivity.

A comparison of these three items before and after an IX column in the purification system will give a good indication of the condition of the column resin. In the effluent of a good column, the Li and pH will always be slightly higher than the main system while the conductivity is lower.

Chloride leads to stress corrosion cracking of stainless steels. Historically the source of Cl<sup>-</sup> has been ion exchange resin infra-structure but modern resins are quite low in Cl<sup>-</sup>.

Fluoride will attack Zr in fuel sheaths. Sources of F<sup>-</sup> are teflon tapes and gaskets which are no longer used.

Hydrogen gas is added to remove oxygen and the slight excess added will give dissolved  $H_2$  and  $D_2$  by displacement. It is not realistic to distinguish between  $D_2$  and  $H_2$  by the simple gas chromatographic method used for  $D_2$  determination. As discussed in previous modules excess  $O_2$  leads to general corrosion whereas too high an excess of  $D_2$  leads to hydriding and cracking of pressure tubes.

Crud is collected on filters and from the flow through the filter and the weight gain of the filter one is able to determine the system crud concentration. The main component of crud is Iron Oxide. If the crud is black indicating that the iron oxide is magnetite, then we know there is a low dissolved oxygen. If the crud is brown, hematite, then there is too much dissolved oxygen and something is amiss with hydrogen addition.

The crud on the filter may also be put through analysis for radio-species to check for fission products.

$D_2O$  isotopic is checked by one of the methods in section A of this module.

Tritium may be determined by liquid scintillation.

The moderator system is sampled and analyzed for:

- pH
- Conductivity
- $D_2O$  Isotopic
- Tritium
- Chloride
- Fluoride
- Poisons (Boron or Gadolinium)
- Crud

As well, the cover gas has continuous on-line monitoring of  $D_2$  and  $O_2$ .

The reasons for analysis of the species listed above would follow similar lines as for the PHTS.

### C. Secondary System

Chemical control of the secondary system was covered in modules 21-1 and 21-2.

Sample points are provided at various points throughout the system. Some of the major sample points and major species monitored are outlined on the next page:

(i) **Condensate Extraction Pump Discharge**

Monitoring here will enable us to see if there is condenser leakage especially if we monitor for Sodium, a major component of the chemicals in cooling water. The CEP would routinely be monitored for:

Conductivity - to check water purity.

pH - to keep corrosivity low (check morpholine addition).

Sodium - see above.

Dissolved Oxygen - to see if condenser has gross air in leakage and keep corrosivity low.

(ii) **Boiler Feed Pump Discharge**

Monitored for:

pH

Conductivity

Dissolved Oxygen } - to check efficiency of  
oxygen removal.

Hydrazine } - check Hydrazine injection.

(iii) **Main Steam (Boiler Discharge)**

pH

Conductivity

Various solids - to ensure purity (eg, SiO<sub>2</sub>; Na)

(iv) **Blowdown**

pH

Conductivity

Silica

Chlorides

Solids

} to check on build-up from  
- Feedsystem Corrosion  
- Condenser Leakage  
- Impure Make-up

Other points are monitored and other tests are done, but the list on the previous page will give you an idea of the major items.

The three diagrams on the following pages are schematics of the pH, Sodium and dissolved Oxygen monitoring points at BNGS-A. Note the facility for moving the Sodium monitor to see which condenser water box is leaking.

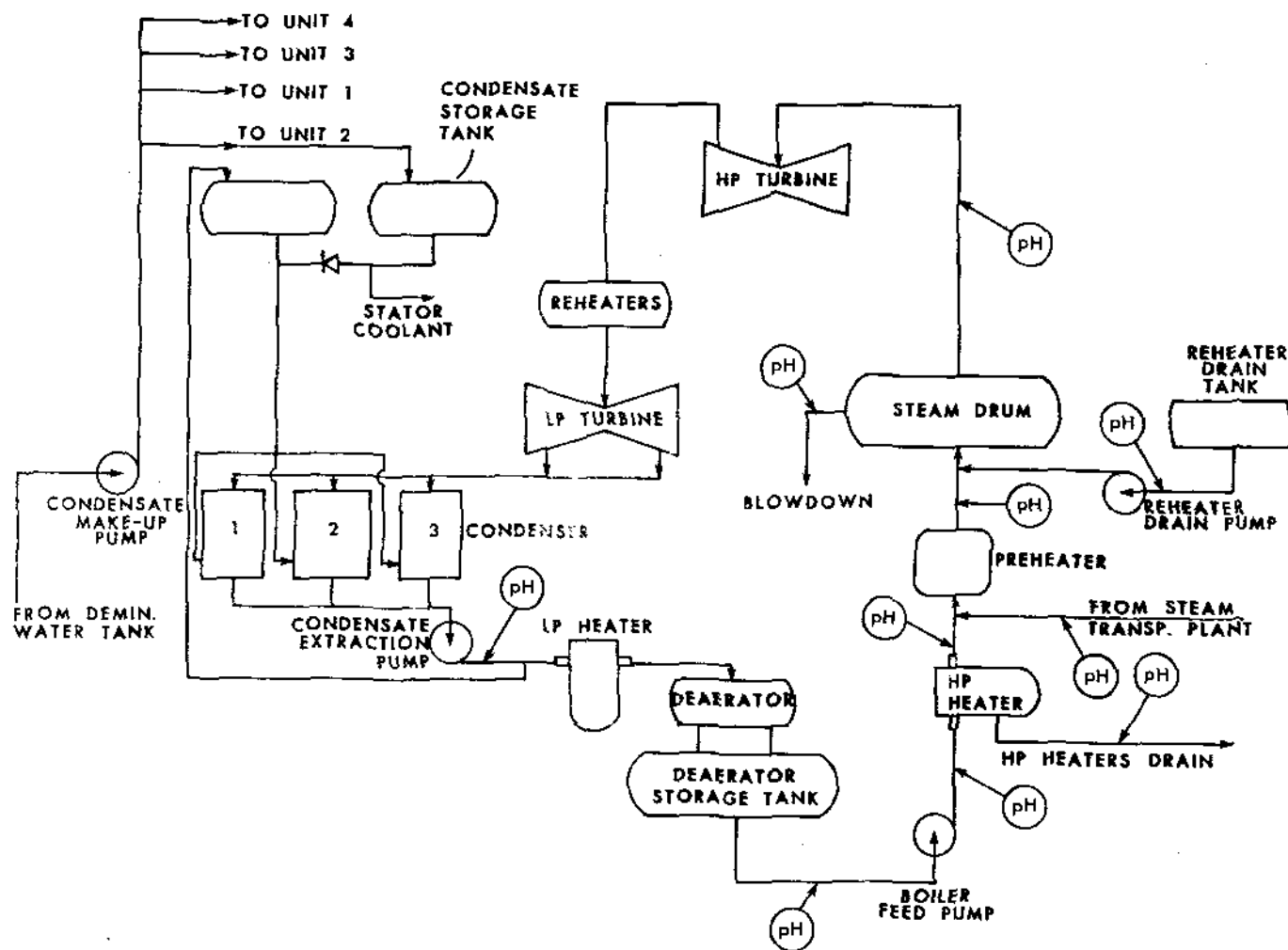


Figure 5

An On-Line pH Monitoring and Control System (BNGS-A)



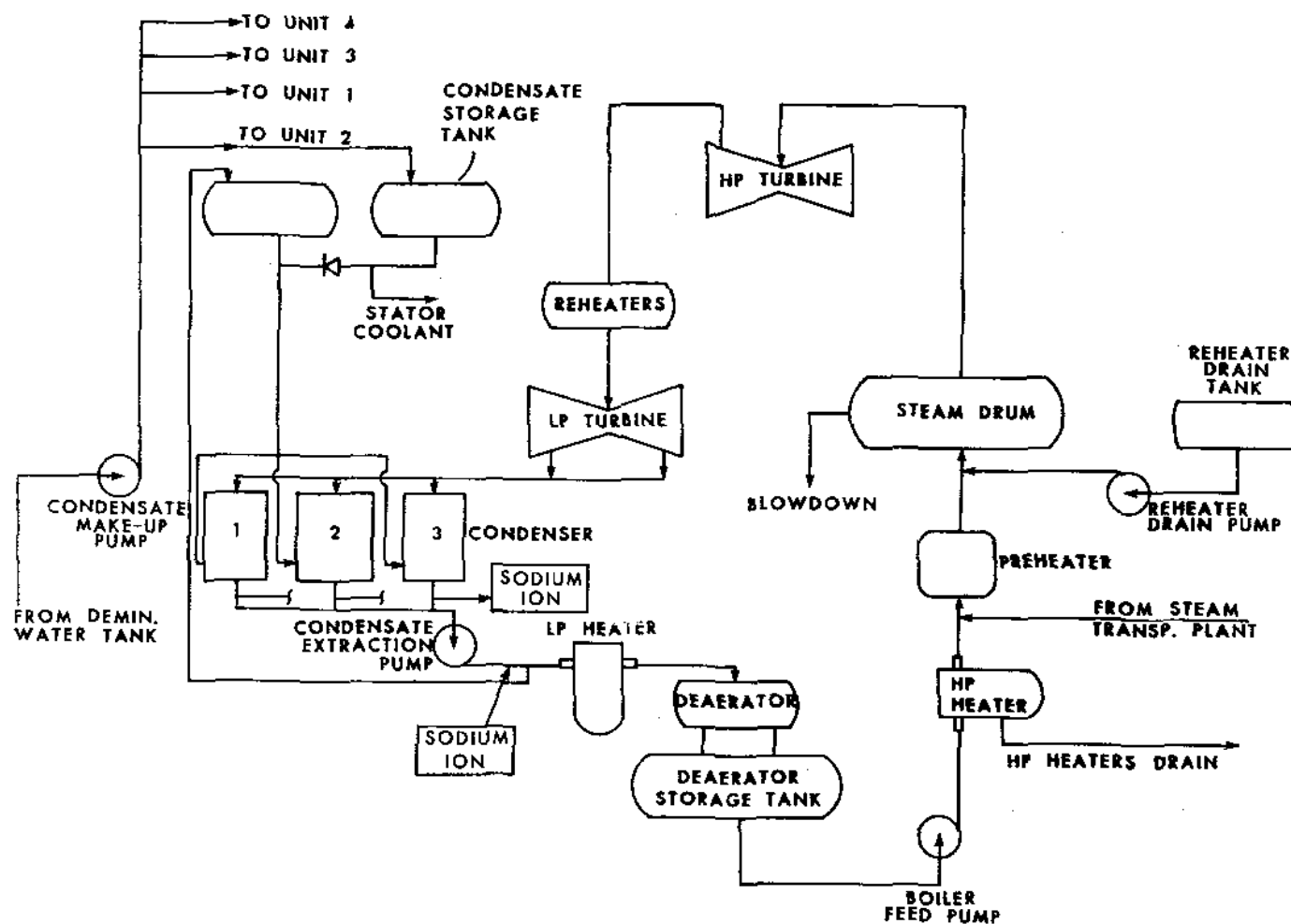


Figure 6

An On-Line Sodium Ion Detection System (BNGS-A)

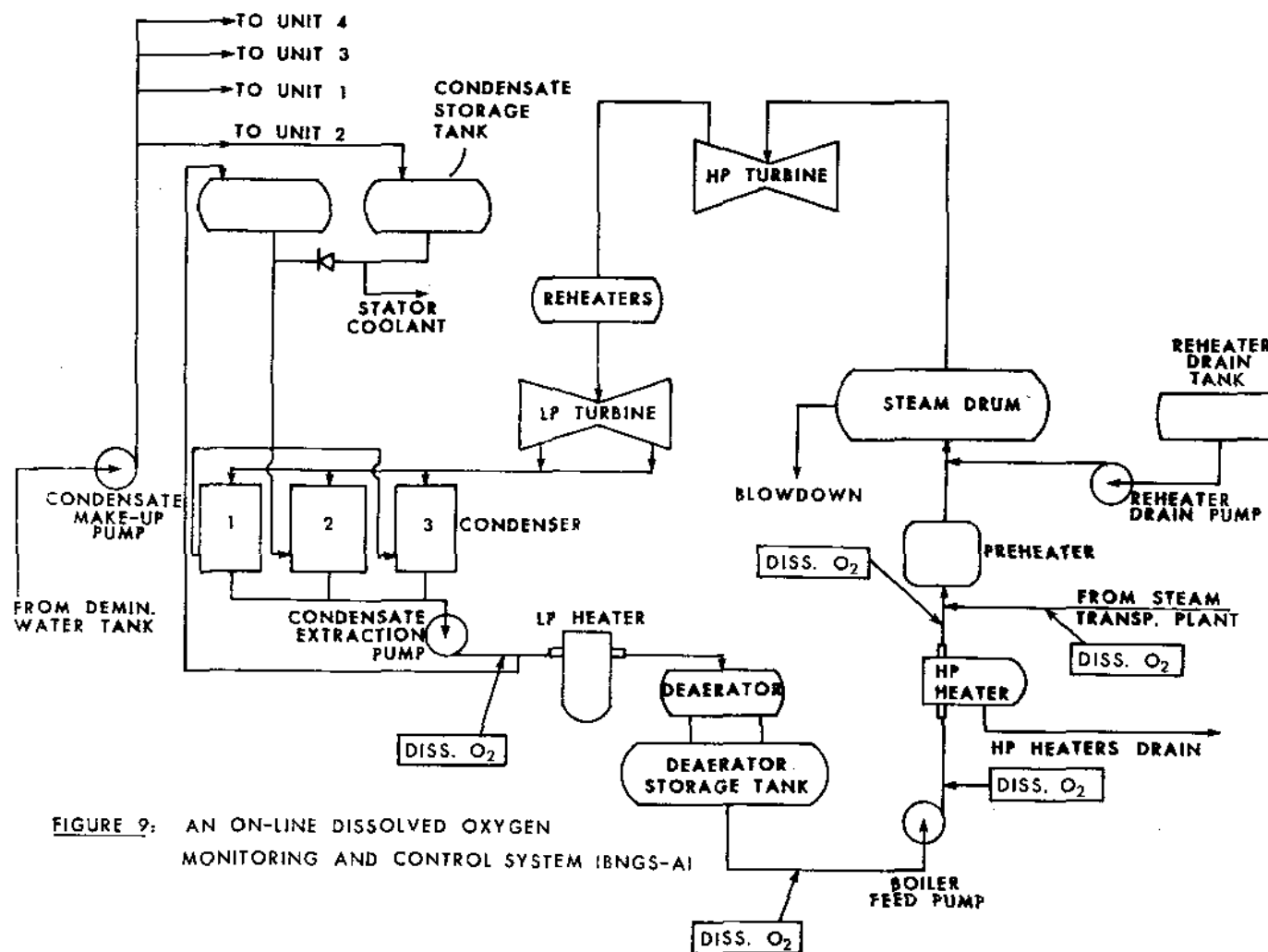


FIGURE 9: AN ON-LINE DISSOLVED OXYGEN  
MONITORING AND CONTROL SYSTEM (BNGS-A)

Figure 9

An On-Line Dissolved Oxygen Monitoring and Control System (BNGS-A)

Practice Exercises:

1. From memory list three methods for the determination of D<sub>2</sub>O Isotopic.

In point form, outline the basis of the method.

2. (a) List ten species monitored in the primary heat transport system. State the reason each is monitored.

(b) List seven species for MOD, state reason.

3. Outline major sample points (4) for the secondary heat transport system. Give four items monitored at each and the reason for each.

Go over your answers for these exercises with a colleague. Make sure that you can co-relate this data with the data on secondary system chemistry in modules 21-1 and 21-2. If you have problems be sure to check with the Course Manager.

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