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# TRITIUM ANALYSIS OF SAMPLES OBTAINED FROM VARIOUS ELECTROLYSIS EXPERIMENTS AT BARC

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## Scope

The report summarises the methodology and techniques adopted for the determination of tritium content in various samples obtained during the initial sets of experiments conducted at Trombay in connection with studies on the feasibility of 'Cold Fusion'.

The analyses were carried out at the Isotope Division and Health Physics Division.

## Sample Preparation Technique

Sample preparation techniques involved use of the appropriate scintillation 'cocktail' and wherever applicable, the samples were distilled before use. Diluting the sample with double distilled water, even while reducing the number of signal pulses per unit volume of sample, helped in reducing the pH as well as quenching impurities present in the sample. Alternately the sample could be kept for 'chemiluminescence cooling' so that the contribution from the same, if any, is reduced to a negligible level with respect to the sample under counting.

40K free vials are used for low background. Use of Dioxane as solvent was avoided wherever direct counting was adopted, as it tends to show chemiluminescent properties when used in certain samples. The commercially available scintillation 'cocktail' INSTAGEL, (containing a surfactant such as Triton —X—100) was found to be suitable for counting in such situations.

Standardized procedures involved addition of 0.1 to 2 ml of sample in appropriate volume of scintillator in cases where the count rates were high. Larger quantity of sample was taken (8 to 12 ml of sample) in the case of low level samples for better detection limit.

## Counting System

There are several LSS systems available for estimation of low-energy beta emitters like  $^3\text{H}$ ,  $^{14}\text{C}$  etc. In the present case the LSS system manufactured by M/S Packard Inst. Co. (Model 4530) and LKB system (Model 1215 RACKBETA-II) were used (Some samples were analysed in an alternate LSS Packard 4530 too, for confirmation of reliability of the method.) The LSS used has facilities for automatic quench correction. The probable errors due to interference due to chemiluminescence is also avoided by adopting appropriate chemical counting methods.

The system stability is checked everyday using sealed tritium standards and sealed background samples in a 'calibration' mode, so that normalization is effected by adjusting the

two PMT voltages automatically by the LSS system itself. Standardisation and efficiency of each sample is determined using quench curves developed for each batch of experimental samples by using Quench Standards of the appropriate chemical form.

In the case of heavy water samples used for each set of electrolytic experiments initial samples were drawn and kept aside and counted along with the samples drawn during the course of the experiments.

The rooms where the experiments are conducted were constantly monitored for tritium contamination from air.

In almost all the experiments samples were drawn at appropriate intervals to follow up the trend in tritium concentration values.

Experiments which have shown definite increase in tritium concentration values are listed separately.

In all the tritium measurements the following factors were considered in arriving at the excess tritium content produced (if any) in the experiment.

- a) initial tritium content in the heavy water used for each experiment.
- b) concentration of tritium content due to electrolysis.
- c) concentration effects due to make-up volumes of the heavy water.

## **Materials And Method**

**Tritium Content in Heavy Water Before Electrolysis:** Heavy Water used for electrolysis experiments at the Analytical Chemistry Division and Reactor Operations Division are analysed for tritium content. In these two Divisions (ACD and ROD) almost all the experiments were conducted using the heavy water from these stock solutions.

**Tritium Content in Palladium Cathodes:** For the electrolysis experiments at the Analytical Chemistry Division palladium metal has been used mostly as cathode in different shapes. Before the cathodes were prepared samples of palladium metal was collected for tritium assay. In addition, samples of palladium metal and palladium salts from Radiation Technology Division were also collected and analysed for tritium content.

Palladium metal was dissolved in aqua regia, while palladium salts were dissolved in water and nitric acid. From these solutions suitable stock solutions were prepared. These include

- a) acidic solutions
- b) neutralised solutions
- c) diluted solutions and
- d) diluted and neutralised solutions finally made for counting.

In addition, dummy stock solutions were also made with the reagents used except palladium.

The counting was continued for a period of one week. Acidic solutions have shown initially very high chemiluminescence; diluted and neutralised samples after prolonged counting have shown that the palladium and palladium salt do not contain any tritium contamination.

Checking of Lithium Electrolyte: Generally, lithium salts (LiOD) have been used as electrolyte (0.1 Molar) in the electrolysis experiments. In view of this, the lithium solutions were checked for

- a) tritium contamination,
- b) chemical effects including chemiluminescence etc., in the counting of samples from the cells.

For this purpose lithium deuterioxide solution (0.2 M) were prepared with known heavy water ( $D_2O$ ) stock solution and analysed for both a) and b).

From the counting data the following observations are made:

1. Immediately after preparation, high chemiluminescence was observed. However with passage of time this chemiluminescence came down to negligible amounts (in about 10 days time). When these lithium stock solutions were neutralised, the chemiluminescence effect was greatly reduced to negligible values.
2. When these samples were subjected to distillation and water was collected and counted, no chemiluminescence was observed. The distilled samples have shown the original tritium content of the heavy water ( $D_2O$ -4) used for this purpose. Therefore no tritium contamination was noticed in lithium salts used for the electrolysis.
3. However, it has been observed that the electrolyte samples which have been subjected to a few days of electrolysis have shown small amounts of chemiluminescence when compared to unelectrolysed lithium deuterioxide samples. Initial chemiluminescence which was observed in some of the electrolysed samples was found to decay rapidly within 24 hours.
4. Therefore, tritium content in the final samples from cells was confirmed by counting the  $D_2O$  distilled from these samples.

## Quench Corrections

Due to the presence of chemical impurities even in trace quantities chemical quenching possibilities exist, which in turn reduce the pulse output. In impurity quench the components which quench the sample do so either by competing with the fluors for energy transfer, or by chemically interacting with the fluor molecules to make them less reactive to energy transfer. Oxidizing agents at high pH can alter oxygen atoms in many of the fluors so that the fluorescent properties are also changed.

In colour quench, the quenching component absorbs the photons produced by the scintillation process, before they can be detected by the PMTs. Colour quench usually does not interfere with the scintillation process but exerts its effect by preventing the photon being seen by the detector system of the LSS.

In both the above cases the resultant effect will be a compression of the beta spectrum of tritium and reduction in pulse output, thereby reducing the efficiency of the LSS. Thus it becomes necessary to correct for such quench errors and arrive at the efficiency of each one of the samples being counted.

Quench corrections are carried out by any one of the following methods

- i. Standard Addition Technique wherein a known amount of standard of appropriate concentration is added to the sample which determines the efficiency for that particular sample. In this 'spike method' the sample becomes irretrievable.
- ii. Sample Channels Ratio Method effectively takes the ratio of two preset channels of the beta spectrum for the sample and comparing it with a 'calibration curve' developed with a series of known quenchers of appropriate chemical form whose efficiency have been determined previously. For very highly quenched samples this technique is not quite suitable as the ratio of the two channels will not reflect a true picture of the actual situations.
- iii. Many LSS have built in 'Automatic External Standard Channels Ratio' Technique provided as a facility for quench corrections. The principle depends on pneumatically shooting a gamma emitting pellet which occupies a place very near the counting vial for a very short period and produces compton electrons which also undergoes similar quench effects as that of the sample. Here again a 'calibration curve' with a known set of 'Quenched Standards' of appropriate chemical composition helps in determining the efficiency of the sample being counted.

A later version of the same technique developed by Donald Horrocks uses the compton edge count rates for fixing the channel position for the quenched standards and calls it 'H Number'. Each sample being counted will record its H number which provides a method for determining the efficiency.

## Results

Table—I gives the tritium content in the heavy water stock solutions used for electrolysis experiments conducted at Analytical Chemistry Division and Reactor Operations Division, and Heavy Water Division, BARC.

Table—II gives the data pertaining to 10 electrolysis experiments conducted at Analytical Chemistry Division and Reactor Operations Division, BARC.

Table—III From the set of values given in Table II the data where excess tritium has been observed in the electrolyte solution after electrolysis have been summarised and given.

Table—IV The data from experiments conducted at Heavy Water Division, BARC are tabulated. It may be pointed out that the correction factors due to make—up volume contribution in the final tritium content have not been reflected in the table.

Table—V Information regarding the experiments conducted at various Division/ Sections have been given. The samples counted from these experiments have not shown any apparent increase in tritium values.

**TABLE I**  
**TRITIUM CONTENT OF INITIAL HEAVY WATER USED**

STOCK NO.	TRITIUM CONCENTRATION (in $\mu\text{Ci/ml}$ )
D <sub>2</sub> O – 1	$1.16 \times 10^{-3}$
D <sub>2</sub> O – 2	$0.489 \times 10^{-3}$
D <sub>2</sub> O – 3	$0.845 \times 10^{-3}$
D <sub>2</sub> O – 4	$0.076 \times 10^{-3}$
D <sub>2</sub> O – 5	$0.117 \times 10^{-3}$
D <sub>2</sub> O – 6	$0.27 \times 10^{-3}$
D <sub>2</sub> O – 7	$0.045 \times 10^{-3}$
D <sub>2</sub> O – 8*	$0.055 \times 10^{-3}$

\* This value was given by HWD as the average value of initial tritium content in D<sub>2</sub>O used for the experiments HWD (B) and HWD (C).

**TABLE - II**  
**TRITIUM COUNTING DATA IN ANALYTICAL CHEMISTRY DIVISION**  
**EXPERIMENTS**

All cathodes: palladium metal All anodes: platinum

	Initial volume of D <sub>2</sub> O (ml)	D <sub>2</sub> O added (ml)	Final D <sub>2</sub> O volume (ml)	Amp. hrs.	Electrolyte	D <sub>2</sub> O used $\mu$ Ci/ml A	Tritium data Electrolysis end sample $\mu$ Ci/ml B	D <sub>2</sub> O activity after volume correction $\mu$ Ci/ml C	Net tritium activity $\mu$ Ci/ml B-C	Remarks
Expt. (i) ACD	45	50	45	52.2	0.1 M LiOD	$0.845 \times 10^{-3}$	0.45	$1.78 \times 10^{-3}$	0.448	Excess tritium observed
Expt. (ii) ACD	65	52.6	65	296	0.1 M LiOD	$0.489 \times 10^{-3}$	0.239	$0.885 \times 10^{-3}$	0.238	Excess tritium observed.
Expt. (iii) ACD	60	85	60	231	0.1 M NaOD	$0.076 \times 10^{-3}$	$0.1 \times 10^{-3}$	$0.183 \times 10^{-3}$	-	Excess tritium <u>not</u> observed.
Expt. (iii) a ACD RC-2	75	55	75	174.08	0.1 M LiOD	$0.076 \times 10^{-3}$	$0.116 \times 10^{-3}$	$0.131 \times 10^{-3}$	-	Electrolyte solution boiled off.
Expt. (iv) ACD RC-II	75	326	75	844	0.113 M LiOD	$0.076 \times 10^{-3}$	$0.114 \times 10^{-3}$	$0.406 \times 10^{-3}$	-	Black coating formed on electrode surface.
TC-I	100	1113.2	100	2510.7	0.1 M LiOD	$0.076 \times 10^{-3}$	$0.119 \times 10^{-3}$	$0.922 \times 10^{-3}$	-	Stopped due to accident.
TC-II ACD RC-III	100	40	100	61.83	0.1 M LiOD	$0.076 \times 10^{-3}$	$0.092 \times 10^{-3}$	$0.106 \times 10^{-3}$	-	Excess tritium <u>not</u> observed.
	75	345	75	1032.9	0.1 M LiOD	$0.076 \times 10^{-3}$	$0.239 \times 10^{-3}$	$0.426 \times 10^{-3}$	-	Experiment continuing.
<b>ROD - samples</b>										
RCS-2	237	74	237	73.3	0.1 M LiOH	$0.076 \times 10^{-3}$	$2.6 \times 10^{-3}$	$0.1 \times 10^{-3}$	$2.5 \times 10^{-3}$	Excess tritium observed.
RCS-3	78	20	76	25.6	0.1 M LiOH	$0.076 \times 10^{-3}$	$6.83 \times 10^{-3}$	$0.098 \times 10^{-3}$	$6.73 \times 10^{-3}$	Excess tritium observed.

**TABLE - III**  
**TRITIUM COUNTING DATA IN EXPERIMENTS WHERE EXCESS TRITIUM WAS OBSERVED**

All cathodes: palladium metal All anodes: platinum

	Initial volume of D <sub>2</sub> O (ml)	D <sub>2</sub> O added (ml)	Final D <sub>2</sub> O volume (ml)	Amp. hrs.	Electro-lyte	D <sub>2</sub> O used $\mu$ Ci/ml A	Tritium data			Remarks
							Electrolysis end sample $\mu$ Ci/ml B	D <sub>2</sub> O activity after volume correction $\mu$ Ci/ml C	Net tritium activity $\mu$ Ci/ml B-C	
Expt. (i) ACD	45	50	45	52.2	0.1 M LiOD	$0.845 \times 10^{-3}$	0.45	$1.78 \times 10^{-3}$	0.448	Excess tritium observed
Expt. (ii) ACD	65	52.6	65	296	0.1 M LiOD	$0.489 \times 10^{-3}$	0.239	$0.885 \times 10^{-3}$	0.238	Excess tritium observed.
ROD - samples										
RCS-2	237	74	237	73.3	0.1 M LiOH	$0.076 \times 10^{-3}$	$2.6 \times 10^{-3}$	$0.1 \times 10^{-3}$	$2.5 \times 10^{-3}$	Excess tritium observed.
RCS-3	78	20	76	25.6	0.1 M LiOH	$0.076 \times 10^{-3}$	$6.83 \times 10^{-3}$	$0.098 \times 10^{-3}$	$6.73 \times 10^{-3}$	Excess tritium observed.

**TABLE - IV**  
**TRITIUM COUNTING DATA IN EXPERIMENTS WHERE TRITIUM HAS OBSERVED**  
**(HEAVY WATER DIVISION)**

Initial volume of D <sub>2</sub> O (ml)	D <sub>2</sub> O added (ml)	Final D <sub>2</sub> O volume (ml)	Final D <sub>2</sub> O volume (ml)	D <sub>2</sub> O used $\mu$ Ci/ml A	Tritium data			Remarks
					Electrolysis end sample $\mu$ Ci/ml B	D <sub>2</sub> O activity after volume correction $\mu$ Ci/ml C	Net tritium activity $\mu$ Ci/ml B-C	
Expt. (A) HWD	250	1650	250	$0.045 \times 10^{-3}$	1.505	$0.342 \times 10^{-3}$	1.503	Excess tritium observed
Expt. (B) HWD	135	300	135	$*0.055 \times 10^{-3}$	$48.15 \times 10^{-3}$	$0.177 \times 10^{-3}$	$47.97 \times 10^{-3}$	Excess tritium observed
Expt. (C) HWD	1000	6000	1000	$*0.055 \times 10^{-3}$	$190.3 \times 10^{-3}$	$0.385 \times 10^{-3}$	$189.92 \times 10^{-3}$	Excess tritium observed
Expt. (D) HWD	250	1296	250	$0.27 \times 10^{-3}$	$121.0 \times 10^{-3}$	$1.669 \times 10^{-3}$	$119.33 \times 10^{-3}$	Excess tritium observed

\* These two values were given by HWD as the average values of initial tritium content in D<sub>2</sub>O used for the experiments HWD (B) and HWD (C).

**TABLE V**  
**TRITIUM CONCENTRATION DATA IN OTHER ELECTROLYSIS EXPERIMENTS**

Division	No. of Expts.	No. of samples Collected	Remarks
Physic. Chem. Sec.	2	20	Pd-Ni system: LiOD (0.1 M): Ionic membrane used between electrodes: Vol. and cell dimensions changed in different cells.
Radiation Chem. Sec.	2	14	Pt-Pd system: LiOD 0.01 M Control Exp. with D <sub>2</sub> SO <sub>4</sub>
Water Chem. Div.	3	33	Pt-Pd system: LiOD 0.1 M Electrode size varied: One cell exploded.

NOTE: NO APPARENT INCREASE IN TRITIUM CONCENTRATION WAS OBSERVED IN THE ABOVE EXPERIMENTS.

## ANNEXURE

### LIST OF SAMPLES ANALYSED FOR TRITIUM CONTENT AT HEALTH PHYSICS DIVISION (BARC) BY LIQUID SCINTILLATION COUNTING

LSS Used	:	Packard (Model 4530)
System Bkg for full Channel (0-19 keV)	:	<12 cpm
Real Time Monitoring for ambient gamma fields?	:	Yes (in 3 rd channel)
System Stability Check?	:	Yes (everyday)
Corrections made for	:	a) Chemi- and Photo-luminescence b) H <sub>2</sub> O <sub>2</sub> /D <sub>2</sub> O <sub>2</sub> presence if any c) Chemical and Photon quenching d) Volume Quenching (D <sub>2</sub> O)
Quench Corrections	:	By Spectral Index Sample

(SIS) and Spectral External Standard (SES) in the Packard LS System. Cross check with Sample Channels Ratio (0-19 keV and 2-19 keV regions) is also done.

Division	Experiment Ref.	No. of Samples
Heavy Water Div. *	M Series	55
Chemistry Div. *	V Series	50
"	D Series	35
"	P Series	44
"	H/HN Series	30
"	Gp Series	8
"	CG Series	15
"	K Series	20
"	R Series	2
Analyt. Chem. Div.	S Series	4
Metallurgy Div.	G Series	3

\* The identification and interpretation of various sets of experiments are given by the respective groups separately, elsewhere.

NOTE Chemistry Division Experiments are planned such that different parameters are studied independently by different groups.