

LIQUID SCINTILLATION COUNTING
RECENT APPLICATIONS AND DEVELOPMENT
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ROUTINE ANALYSIS OF AMBIENT TRITIUM LEVELS
IN ENVIRONMENTAL WATER SAMPLES

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The measurement of low-level tritium concentrations in discrete environmental water samples has been routinely accomplished by applying standard liquid scintillation counting techniques directly to a small aliquot of the original sample or to a portion of the sample which has been pretreated. Two of the more common sample preparation methods are simple distillation at atmospheric pressure and electrolytic enrichment with a subsequent increase in the tritium content of the sample.

Recently, the Yankee Atomic Electric Company, Environmental Laboratory, has determined the tritium levels in water samples from the environs of several nuclear generating facilities in the New England area by liquid scintillation analysis of high purity tritiated benzene prepared from the water samples to be quantified. A commercially available unit was utilized to facilitate the synthesis of benzene by reacting the water sample with calcium carbide to form tritiated acetylene which is subsequently trimerized on a vanadium catalyst to high purity tritiated benzene.

The University of Georgia, Center for Applied Isotope Studies, has been monitoring a southeastern nuclear power

facility for several years for tritium content of environmental waters. Large volume aqueous samples are counted directly with no pretreatment other than distillation. A special low background liquid scintillation counter has been developed to accommodate increased sample volume.

The method of sample preparation and handling for both methods will be discussed in detail. Typical calibration curves and Minimum Detectable Concentrations (MDC) which can be achieved, along with data reflecting the accuracy of the techniques, will be presented.

I. INTRODUCTION

The vast number of tritium analyses for aqueous samples reported in the literature tend to group in either the relatively high concentration levels of 500 pCi/l or greater, or the extremely low levels of less than 15 pCi/l (1-11). A large proportion of the higher values are reported as being performed by direct aqueous cocktail preparation and liquid scintillation (LS) counting (1-7). The lower levels are usually carried out by electrolytic sample enrichment and counting with low background gas proportional counters (8-11).

This paper addresses two methods available for the routine analysis of aqueous tritium samples at the 100-200 pCi/l level or greater. The development of these methods are particularly timely considering the recent Nuclear Regulatory Commission (NRC) Guide 4.8 (1975) which sets the Minimum Detectable Concentration (MDC) for tritium in environmental waters surrounding nuclear generating stations at 330 pCi/l. These two methods not only meet this MDC for tritium values encountered in varied aquatic environs but also qualify in three other areas: (a) ease of sample preparation, (b) capability to respond to non-routine samples, and (c) the ability to achieve the required MDC in a reasonable counting time.

II. ANALYSIS BY BENZENE SYNTHESIS

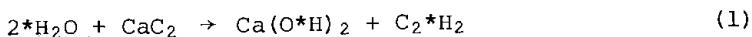
Three methods of tritium analyses were reviewed by the Yankee Atomic Environmental Laboratory (YAEL) prior to selection of a preferred method to use in their tritium analysis program. The first method considered entailed a sample preparation procedure encompassing distillation of the aqueous samples at atmospheric pressure followed by LS counting using an aqueous cocktail. The second procedure reviewed entailed elec-

trolytic enrichment resulting in subsequent increase in the tritium content of the water samples followed by aqueous cocktail preparation and LS counting. The third procedure was to produce high purity benzene from the water samples by a method, developed by Tamers and Bibron (12) and modified by Noakes (13), to count the benzene directly by LS spectrometry.

Calculations for achieving MDC levels for the three methods were carried out using the capabilities of selected cocktails and estimated counting efficiency and background of present day commercial LS counters. The sample distillation procedure with LS counting was evaluated as being only marginal with extended sample counting time. The electrolytic enrichment treatment and LS counting did achieve the required MDC with an acceptable counting period but extended sample processing time was unacceptable for routine analysis. The benzene method appeared to qualify for both achieving MDC levels with a minimum count period with a reasonable sample processing time, and, therefore, was selected as the method of choice.

A. Method

An analysis system consisting of a commercially available TASK Benzene Synthesizer and a Packard Model-C 2425 Liquid Scintillation Spectrometer was utilized to prepare and quantify the high purity, unquenched tritiated benzene from the environmental waters to be analysed. The reaction sequences and stoichiometry are:



*H indicates that a fraction of the hydrogen atoms are tritium atoms.

In the synthesizer (fig. 1), the water sample is reacted with calcium carbide in a steel chamber under vacuum conditions to produce acetylene. Any water vapor associated with the evolved acetylene is eliminated by trapping in an iso-propyl alcohol and dry ice bath. Further purification in the acetylene is accomplished by a phosphorous pentoxide-ascarite column. The acetylene is collected as a solid in a liquid nitrogen cooled trap and sublimed directly onto a vanadium oxide catalyst supported by an alumina substrate where polymerization to pure benzene is accomplished. The pure benzene is isolated from the catalyst column by heating at 90 degrees Celsius under vacuum and trapping the pure benzene as a solid in a dry-ice

isopropyl alcohol bath. No serious safety or chemical handling problems have been encountered utilizing the detailed procedure for system siting, ventilation and operation supplied by the unit manufacturer. Utilizing this methodology allowed the processing of three samples in eight hours.

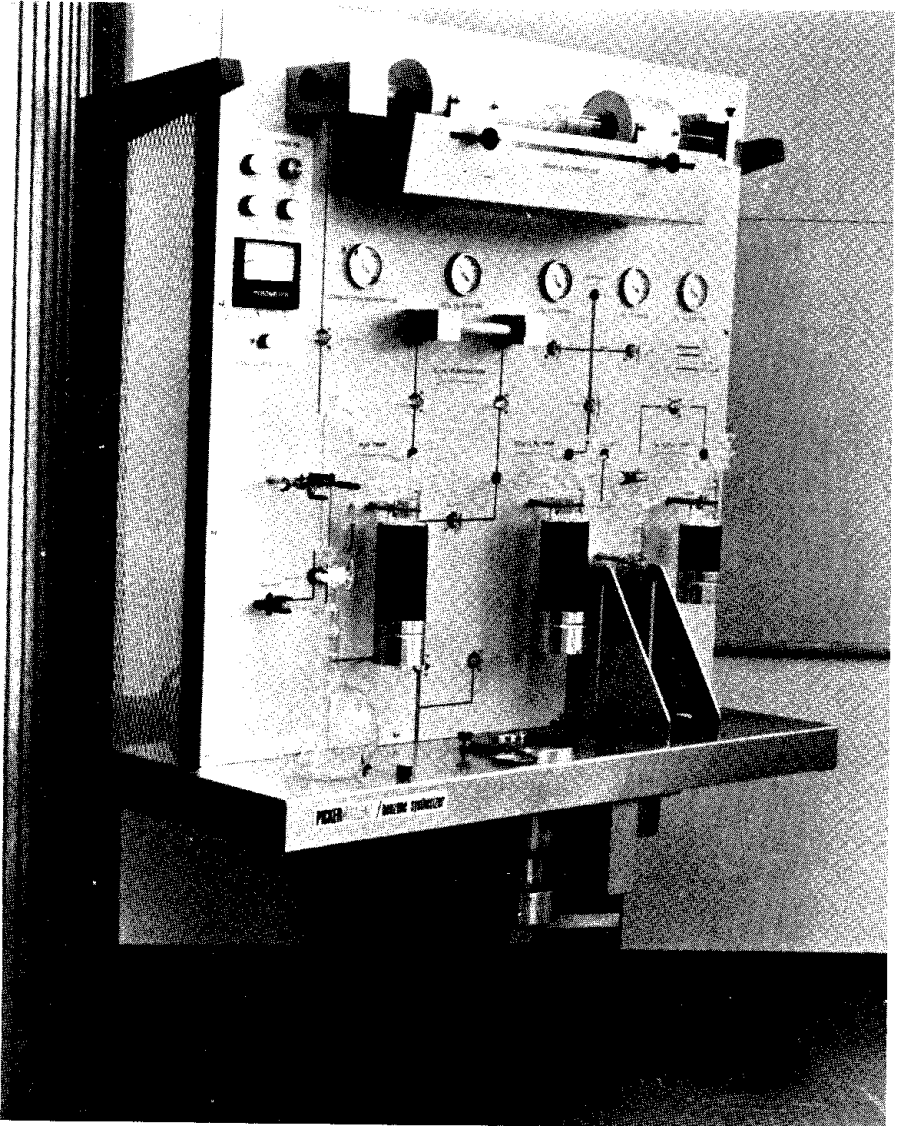


FIGURE 1. Benzene Synthesizer

As indicated in the reaction sequences of equation 1, fractionation of the tritium does occur between the calcium hydroxide and acetylene formed as products of the initial reaction of the water sample with the calcium carbide. However, the isotopic effect was found by Hohndorf and Oro (14) to be constant at 31.4 ± 1.2 percent, thus indicating that the isotope fraction is independent of chemical yield for the reaction. For the system under consideration, the production of a constant volume of benzene was not attainable due to the restrictions of varying sample size, changes in the efficiency of trimerization due to catalyst depletion from previous samples, and the potential for varying rate of reaction of the water-carbide system. This fact, coupled with the lack of adequately documented tritiated benzene standards, led to the adoption of a system calibration rather than a yield determination for each sample in conjunction with a separate instrument calibration.

The system calibration relates the disintegrations per minute per gram of processed water to a count per minute per gram of analyzed high purity benzene. In order to establish this relationship a series of standards, varying in tritiated water specific activity, was processed via the TASK Benzene Synthesizer to obtain tritiated benzene. A normal analysis matrix consists of 13 grams (15 ml) of benzene sample mixed with 4.4 grams (5 ml) of a liquid scintillation cocktail containing 32 milligrams of butyl PBD per milliliter of benzene. The solution is counted in a standard low potassium Wheaton scintillation vial. Plastic vials were not chosen because of the capability of benzene to permeate through the plastic. The samples were routinely analyzed for 200 minutes in the liquid scintillation spectrometer in a series of five samples preceded and followed by backgrounds prepared concurrently with the samples. The analysis system has a demonstrated figure of merit (E^2/B) of greater than 220 which results from the unquenched nature of the system, the high energy transmittance of benzene, and the low optical density of benzene. Spectral grade benzene must be utilized for the preparation of scintillation solutions for background measurements, and to adjust the weight of any tritiated benzene sample to thirteen grams.

B. Results

A graphical representation of the calibration data are shown in fig. 2. It is worth noting that the efficiency ratio is a constant which is solely dependent on the fractionation ratio and the measurement system characteristics.

The adequacy of the technique with regard to accuracy and precision has been tested under routine operating conditions

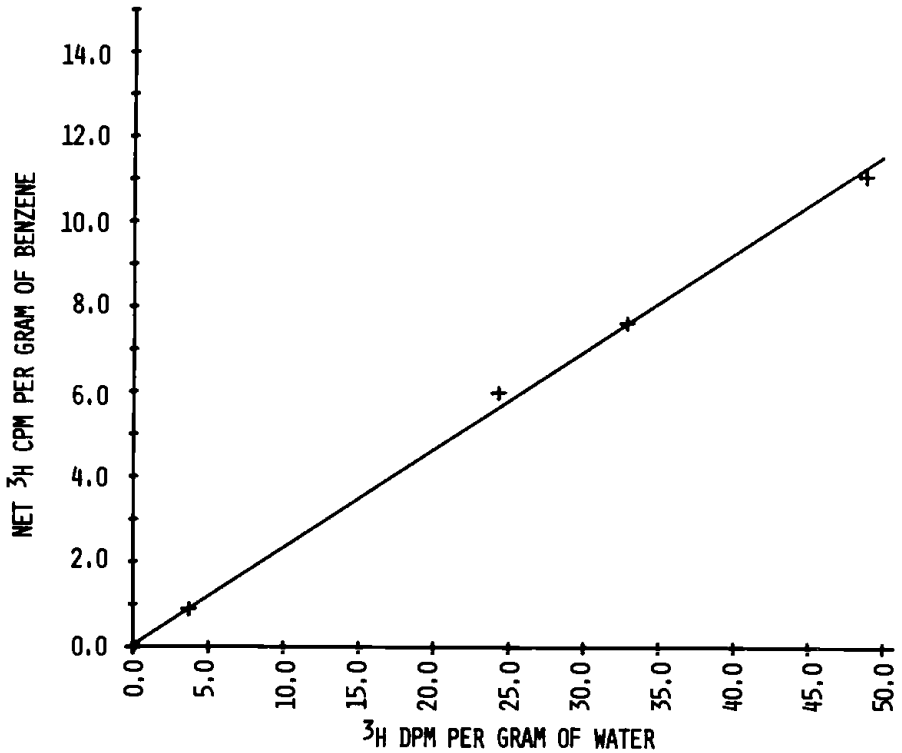


FIGURE 2. Calibration curve - weight of benzene vs. net instrument response.

with both internally initiated and interlaboratory cross check samples. The results of two series of laboratory prepared unknown samples and five series of Environmental Protection Agency intercomparison samples are displayed in Table I. The uncertainty terms associated with the laboratory initiated samples represents a linear sum of random and systematic uncertainties for the preparation of the unknowns whereas the uncertainties listed for the EPA initiated cross checks are historically developed based upon the particular analysis in question (15). For accuracy, the maximum deviation of the individual values from the known value is fifteen percent with the average being eight percent and the maximum deviation of the mean value from the known value is approximately seven percent with the average deviation approaching four percent. For precision, the maximum deviation of any individual value from the mean is approximately nine percent with the average value approaching six percent. These results are acceptable when viewed in the light of the average single standard

TABLE I. Results of Intercomparison Studies -- Benzene Synthesis Method

Initiating Lab and known value	Results (DPM/g)					Mean 10	Deviation (%) of mean from known	Maximum deviation (%) from known	Maximum deviation (%) from mean
	1	2	3	4	5				
YABC 22.1±0.9	21.9 ±0.3	22.5 ±0.4	23.2 ±0.3			22.5 ±0.6	1.8	5.0	3.1
YABC 4.35±0.13	4.37 ±0.22	4.15 ±0.20	4.06 ±0.20	4.64 ±0.22	4.13 ±0.33	4.26 ±0.24	2.0	6.6	8.9
EPA 3.73±0.45	3.73 ±0.13	3.51 ±0.13	3.68 ±0.13			3.64 ±0.13	2.4	5.9	3.5
EPA 4.93±0.42	4.71 ±0.42	4.75 ±0.38	4.80 ±0.33			4.75 ±0.04	3.6	4.5	1.0
EPA 5.04±0.45	4.57 ±0.22	4.64 ±0.22	5.26 ±0.15			4.82 ±0.38	4.4	9.5	9.1
EPA 2.73±0.44	2.89 ±0.29	3.15 ±0.31	2.66 ±0.33			2.91 ±0.24	6.6	15	8.6
EPA 4.51±0.45	4.06 ±0.44	4.17 ±0.31	4.46 ±0.29			4.24 ±0.22	6.0	9.9	5.2

deviation of eight percent attributable to the measurement of the random decay process alone.

The usefulness of the benzene synthesis technique for routine measurements is also dependent on the minimum detectable concentration (MDC) achieved by the technique. The MDC at 95% confidence level adapted for the benzene synthesis system is defined as:

$$MDC \text{ (pCi/l)} = \frac{4.66s_B}{(ER) (2.22) (Bg) (0.001)} \quad (3)$$

Where s_B is the standard deviation of the background count rate

$$ER \text{ is the efficiency ratio} = \frac{(\text{cpm/gram benzene})}{\text{dpm/gram H}_2\text{O}}$$

and Bg is the weight of sample benzene being analyzed

Under routine operating conditions consisting of a stable instrument background count rate of 14.5 cpm for two hundred minutes, the MDC is inversely proportional to the weight of the benzene obtained. The average weight of benzene obtained under routine operating conditions has been eleven grams which will result in a MDC of 220 pCi/l. If the yield of benzene is held constant at eleven grams and the analysis time is varied, the MDC is inversely proportional to the square root of the counting time in minutes. It can be predicted from fig. 3 that an analysis time of eight-five minutes would be required to achieve a MDC of 330 pCi/l.

III. TRITIUM ANALYSIS BY DISCRETE AQUEOUS COUNTING

The University of Georgia, Center for Applied Isotope Studies (CAIS) uses a large volume low-background LS counter which was developed by Noakes, et al (16). The LS counter is especially designed to count large size samples up to 100 ml volume with low background and high stability for long counting times. Low background is achieved by massive shielding (four inches lead), coincidence time of 15 ns and the use of anti-coincidence annulus surrounding the sample vial. High-quality matched phototubes (RCA 4501/V4), picked for their low dark current and high quantum efficiency, contribute greatly to the performance of the system.

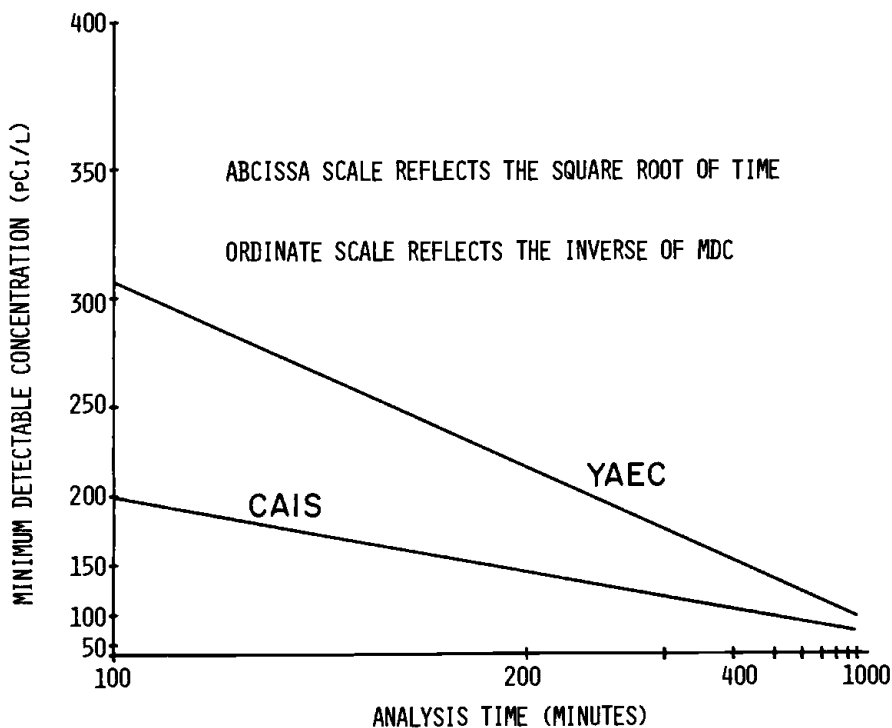


FIGURE 3. Minimum detectable concentration as a function of analysis time under routine conditions.

A. Method

Sample preparation is carried out by atmospheric distillation on a 250 ml aqueous sample. From the distillate a 25 ml aliquot is extracted and mixed with 75 ml of Packard's Monophase-40 cocktail in a 100 ml quartz counting vial (see fig. 4). The samples prepared in this manner are initially cloudy and are stored for 5-10 minutes and then counted for four to ten 100-minute intervals depending on the MDC wanted. Counting repeatedly for 100 minutes allows one to test the data and to discard data which deviates more than ± 2 sigma from the mean. Backgrounds are run using blank (no tritium) water, and standards are made by adding spikes of known amounts of HTO to the background sample.

TABLE II. Results of Intercomparison Studies -- Direct Aqueous Method

Known value	Results (pCi/l)			Mean ± 1σ	Deviation (%) of mean from known	Maximum deviation (%) from known	Maximum deviation (%) from mean
	1	2	3				
2270 ± 349	2404 ± 79	2198 ± 75	2309 ± 76	2304 ± 103	1.5	5.9	4.6
1280 ± 331	1314 ± 64	1229 ± 106	1729 ± 95	1424 ± 268	11.2	35.1	21.4
1230 ± 330	1246 ± 70	1189 ± 69	1093 ± 56	1176 ± 77	4.4	11.1	7.1
2270 ± 349	2485 ± 49	2594 ± 122	2512 ± 115	2530 ± 57	11.4	14.3	2.5
2220 ± 349	2245 ± 54	2021 ± 53	2274 ± 60	2180 ± 138	1.8	9.0	7.3
1680 ± 343	1590 ± 38	1620 ± 54	1760 ± 43	1657 ± 91	1.4	4.8	6.2

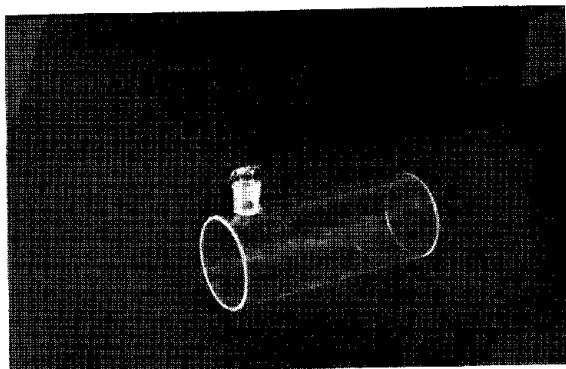


FIGURE 4. 100 ml counting vial.

B. Results

The results of six EPA intercomparison samples are displayed in Table II. The deviation of the means from the known values are well within the uncertainty of the known values. Accuracy is indicated by an average of 5% deviation of the means from the known values. For precision, the maximum deviation of any individual value from the mean is approximately 20%, with the average slightly greater than 8%. The MDC for the 100 ml vial using 25 ml of water and 75 ml monophasic is displayed in fig. 3.

IV. CONCLUSION

In looking at both methods it is clear that either will meet the proposed detection limits of 100-200 pCi/l in a counting interval of 400 minutes or less. The sample preparation time for each method is sufficiently short to allow the processing of several samples per day.

The accuracy of each method is comparable whereas the precision of the benzene synthesis method appears to be slightly superior. The major differences in the two methods is in equipment. The benzene synthesis method uses commercially available hardware whereas the direct aqueous counting method uses an experimental large-volume counter.

It is concluded that either method will satisfy NCR Regulatory Guide 4.8 (1975).

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