

Assessment and Assurance of the Quality in the Determination of Low Contents of Tritium in Groundwater

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INTRODUCTION

In the last few years it has become clear that groundwater resources are in danger of becoming unfit sources of drinking water as a result of human activities, e.g., waste dumps for hazardous materials and agricultural activities involving extensive use of fertilizers. In Denmark, the environmental protection authorities have launched a major program for monitoring and ensuring the quality of groundwater. The program involves periodic measurements of some 80 parameters of interest, e.g., nutrients, organic pollutants, trace and ultratrace metals, and tritium, in approximately 1000 positions covering the types of aquifers seen in the country.¹

Tritium released into the atmosphere by the testing of thermonuclear weapons in the 1950s and early 1960s, and subsequently incorporated in atmospheric water and precipitation, has proven very useful in hydrological research over the last decades. In hydrological research the tritium content is often expressed in tritium units (TU), 1 TU being equivalent to 1 tritium nucleus per 10^{18} hydrogen nuclei and approx. 0.118 Bq/L. In many cases a profile of the tritium content in the groundwater, as shown in Figure 1, gives a quite precise dating of the groundwater and furthermore can give valuable hydrological information. Figure 1 shows tritium profiles from two geologically different locations common in Denmark. The vulnerability of a well in case of the threat of pollution may be assessed by a single tritium measurement. A content of tritium approaching 1 TU, would indicate that the water originates from the time before the atmospheric bomb testing; consequently, that resource is relatively well protected. The interpretation of tritium data is beyond the scope of this chapter, but examples of such work may be found in the IAEA series of publications on isotope hydrology.²

Awareness of the need to ensure and document the quality of environmental

TRITIUM PROFILES

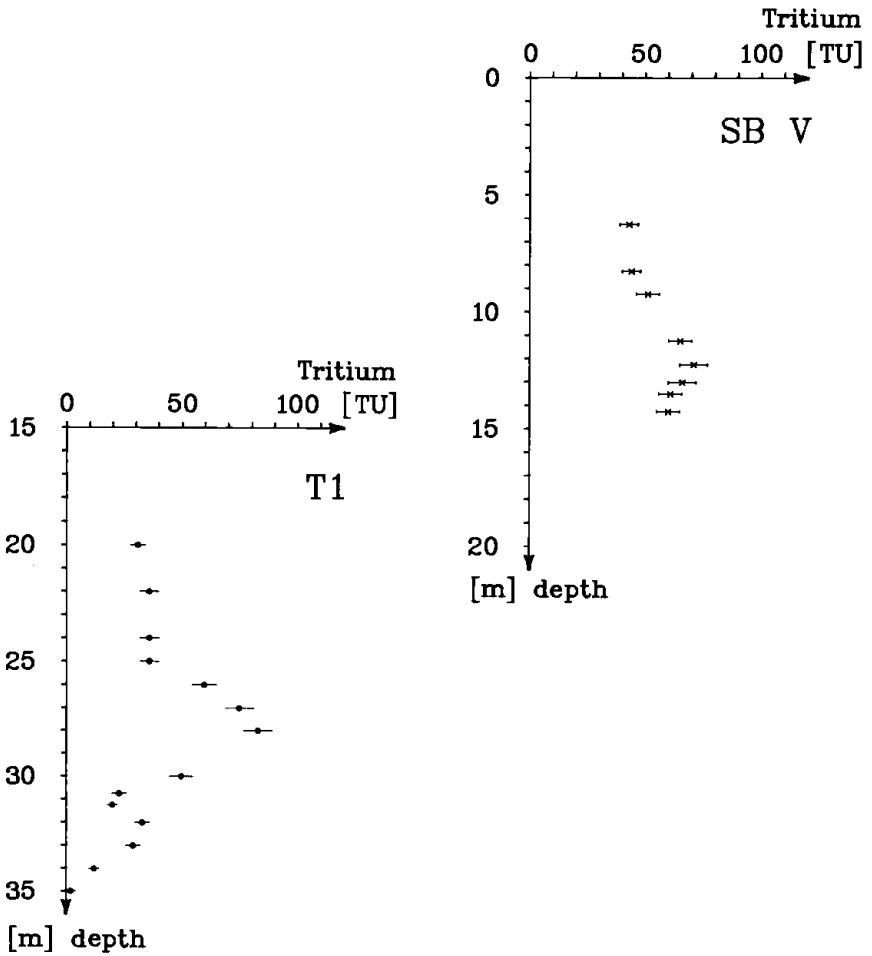


Figure 1. Tritium in groundwater profiles from an area by Syv Baek, Zealand (SB V), a glacial clay deposit (moraine), and an area by Rabis Baek, Jutland (T I) a sandy aquifer, 1988.

measurements is growing as the consequences of decisions based upon such measurements for human health, quality of life, and economy are becoming more widespread and complex. This chapter reports our attempt at assessing and assuring the quality of measurements we believe will be of growing importance in the work done to understand the mechanisms of groundwater pollution in the years to come.

Table 1. Summary of Method**Electrolytical Enrichment:**

1. Distillation of water sample.
2. Addition of Na_2O_2 .
3. Electrolysis in IAEA cell (Mild steel cathode, stainless steel anode), volume: 300 mL, 850 Ah, $t = 0-5^\circ\text{C}$. Enrichment Factor (EF): approximately 14.
4. Distillation of enriched sample, volume: approximately 20 mL.

Liquid Scintillation Spectrometry:

- 12 mL sample in 10 mL Pico-Fluor LLT (Packard).
- Low potassium glass vials.
- Spectrometer: Packard 2000 CA/LL.
- Counting time: 300-500 min. $t = 15^\circ\text{C}$.
- Efficiency (ϵ): approx. 0.18.
- Background (tritium free water): 2.4 CPM.

METHOD

The method for determining the content of tritium in groundwater is well established and commonly used. It is based on IAEA's method for the electrolytic enrichment of tritium in water,³ followed by liquid scintillation counting. This method is regarded as applicable to the determination of tritium contents in water samples down to 1 TU.⁴ Table 1 gives an outline of the method as it is routinely applied. It should be noted that multiple calibration standards are used and that the enrichment of samples with regard to tritium in the electrolysis is determined experimentally in each run by five identical samples of tritiated water. The liquid scintillation counting is done on uniformly quenched samples so that errors introduced by incorrect or poorly defined efficiency correction are avoided.

QUALITY ASSURANCE

Probably the most important aspect of any measurement quality is the reliability of its associated statement of uncertainty, which must be an integral part of reporting any result. This aspect has been discussed thoroughly in a book on neutron activation analysis in which it is shown that "... the precision of a single analytical result is determined by the method with which it is found. When all sources of variability are properly taken into account, the estimated precision will account for all the observed variability of analytical results."⁵ This would seem to hold for most types of measurements and certainly for the measurements discussed here.

As can be seen in Table 1 several processes are involved in a measurement; that may contribute to the observed variability. The processes are the calibration of the spectrometer, the handling of samples, including the electrolytical enrichment, the determination of the enrichment factor, and finally the counting of the sample. This is also indicated by the expression used to convert counting results into tritium content (A), in the original sample:

$$A = (C - C_b) * \epsilon^{-1} * EF^{-1} * K$$

Where C is the observed count rate in the sample, C_b is the background count rate, ϵ is the efficiency of the spectrometer, EF is the degree of enrichment by the electrolysis, and K is a factor for unit conversion, decay time correction etc. In our method EF is determined by the actual enrichment of five identical samples of tritiated water in each run; thus:

$$EF = C_e * C_0^{-1}$$

Where C_0 is the mean count rate of the sample of tritiated water before electrolysis and C_e is the mean count rate of the same sample after electrolysis. An estimate of the standard deviation of an individual result, s_A may be calculated from this expression:

$$s_A = A * ((s_c^2 + s_{Cb}^2) / (C - C_b)^2 + (s_e / \epsilon)^2 + (s_{C_0} / C_0)^2 + (s_{C_e} / C_e)^2)^{1/2}$$

Contributions from the counting process, s_C and s_{Cb} , may be calculated from the counting statistics assuming identity between the total number of counts observed and variance. In estimating the contributions from the enrichment factor, s_{C_e} and s_{C_0} , and calibration, s_e , Shewart control charts of standard deviations are used.

Figure 2 shows such a control chart for the relative standard deviation of ϵ . It can be seen how a minor modification of the spectrometer, involving improved grounding, has improved the precision of the calibration; over the last 10 runs the precision has been homogeneous with a relative standard deviation of 0.4%.

In a similar way the contributions from the enrichment may be found. The result is summarized in Table 2. When the standard deviation of the single result has been estimated, the ability of this estimate to account for the observed variability may be tested by the analysis of precision, using the T statistic. In the case of independent duplicate measurements of M different samples, the statistic T is determined as:⁵

$$T = \sum_{i=1}^M ((A_{i1} - A_{i2})^2 / (s_{i1}^2 + s_{i2}^2))$$

Where A_{i1} and A_{i2} are the two independent results and s_{i1} and s_{i2} are the estimated standard deviations of the two results. T is approximated by an X^2 distribution with M degrees of freedom. Figure 3 shows T as a function of the number of duplicate determinations made over a 10 month period, in which approximately 10% of the determinations were done in duplicate. The individual results range from below 1 TU to 45 TU. As T is not significantly different from an X^2 distribution, it may be assumed that the estimated standard devia-

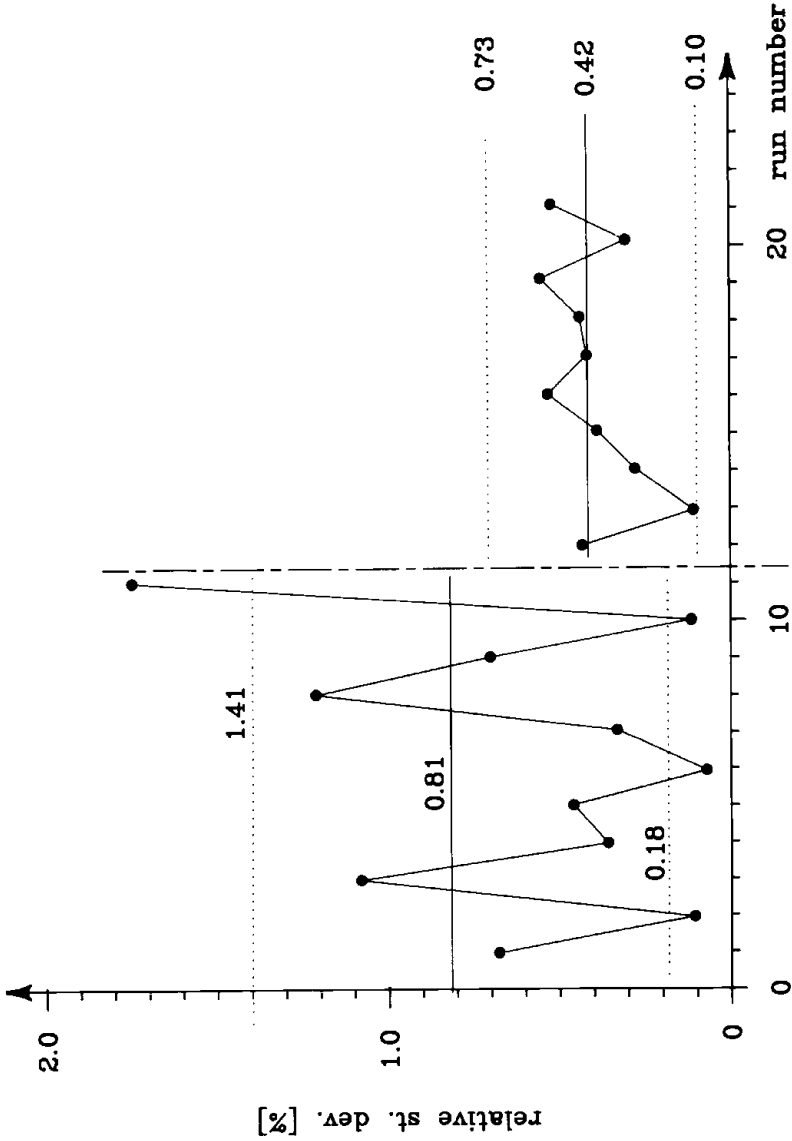


Figure 2. Control chart for the relative standard deviation of the counter efficiency, ϵ , as calculated from three independent calibration standards per run. The vertical dotted line coincides with the time of modification of the spectrometer. Control limits are given as 0.05α .

Table 2. Individual Error Contributions

	Rel. Std. Dev. [%]
Efficiency	0.4
Tritiated water	1.2
- " - after enrichment	4

tions of individual results do account for the observed variability in the duplicate results; consequently, no other significant source of variability is present.

In Figure 4 the calculated standard deviation for the samples is shown as a function of tritium content. s_A/A varies between approximately 0.5 for a content of 1 TU to approximately 0.05 at 45 TU. When the random error has been determined, what remains to be shown is that systematic errors or bias do not affect the results. An important source of bias would be the presence of a significant blank value in the determinations. This is checked by routinely measuring samples of supposedly tritium free groundwater. These measurements give results well below 1 TU and it is assumed that the blank can be neglected. The absence of systematic error can be demonstrated by measuring reference samples with certified tritium contents, similar to those usually measured in the laboratory, or by the participation in interlaboratory comparison exercises. The laboratory has participated in an intercomparison organized by the IAEA in which no systematic error was detected.⁶

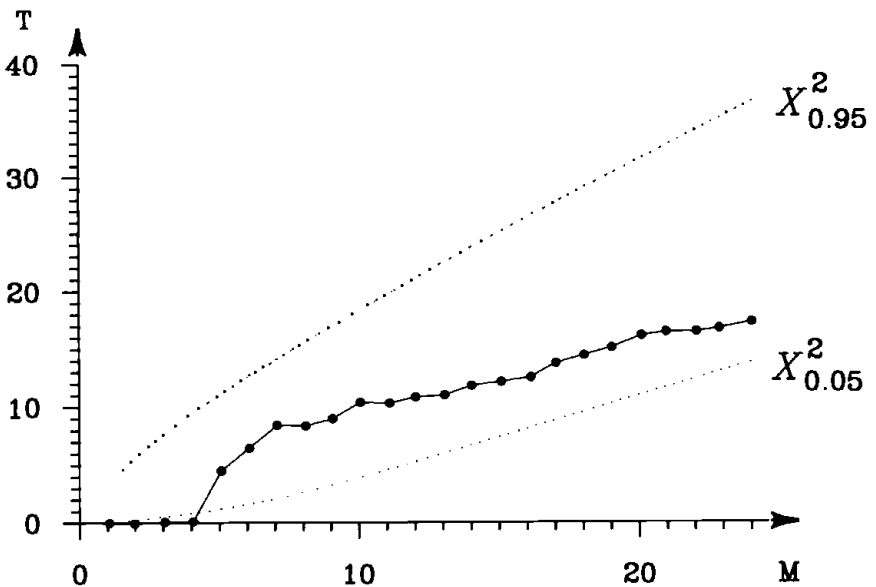


Figure 3. The statistic T , calculated from duplicate determinations plotted as a function of M , the number of duplicate determinations. Dotted lines represent the 5% and 95% fractiles in the X^2 distribution with M degrees of freedom.

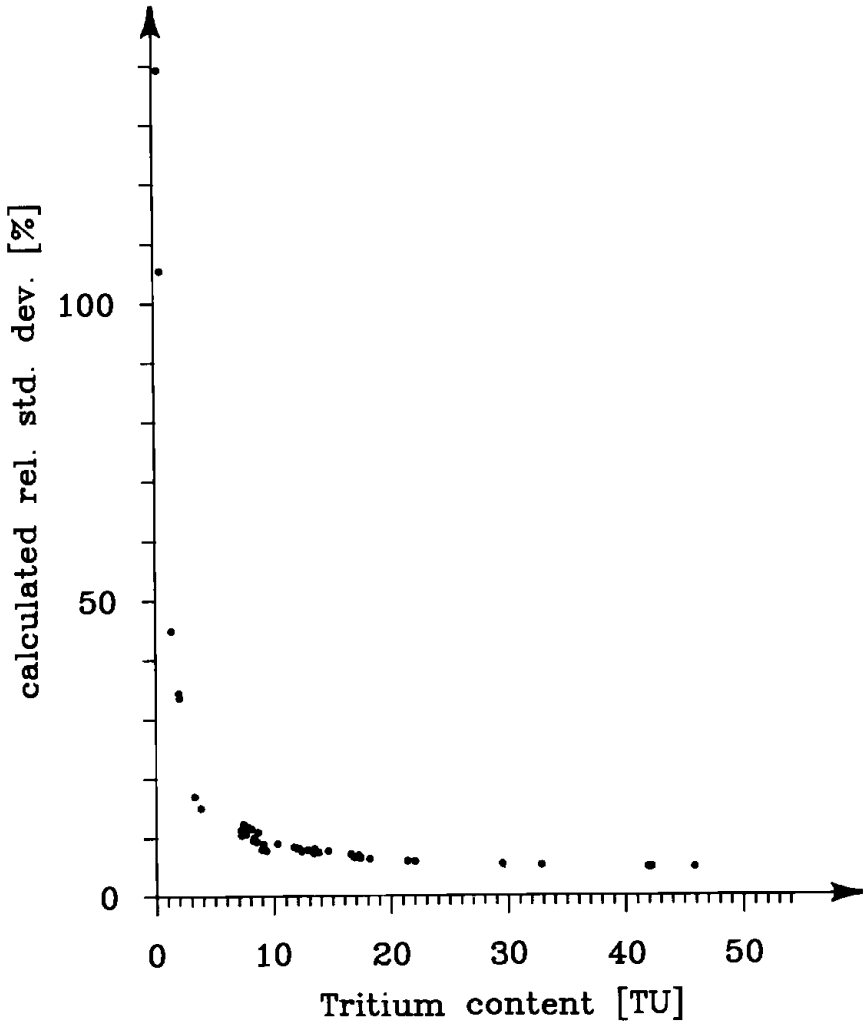


Figure 4. Calculated standard deviations as a function of tritium content.

CONCLUSION

The measurement quality of low tritium contents in groundwater can be controlled by comparing expected and observed variability in duplicate determinations of randomly selected samples. The analysis of precision shows that the identified sources of random error account for the observed variability, and the method may be said to be in statistical control.

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