

COMMISSIONING OF A QUANTULUS 1220™ LIQUID SCINTILLATION BETA SPECTROMETER FOR MEASURING ¹⁴C AND ³H AT NATURAL ABUNDANCE LEVELS

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ABSTRACT. In 1994, the Gliwice Radiocarbon Laboratory began operating a liquid scintillation spectrometry system, consisting of a Quantulus 1220™ spectrometer and two vacuum rigs for benzene production. This paper describes the procedures used for the benzene synthesis from samples containing <1 g of carbon and in the range 1 to 10 g of carbon. We also present the Quantulus calibration procedures used in the Gliwice Radiocarbon Laboratory and NERC Radiocarbon Laboratory, and compare the calibration parameters.

INTRODUCTION

In 1994, the Gliwice Radiocarbon Laboratory installed a Quantulus 1220™ liquid scintillation spectrometer. The lab immediately began working to calibrate the instrument for the purpose of radiocarbon dating in three different counting geometries. Throughout the process of calibration, comparisons were made with the slightly different procedures and parameters established for the low-level liquid scintillation counting (LSC) of ¹⁴C at the NERC Radiocarbon Laboratory.

In both laboratories, benzene is synthesized using vacuum rigs and procedures designed to optimize the conversion efficiency for predetermined amounts of carbon in a given sample. Gliwice operates two rigs that enable processing of samples containing 1 to 10 g of carbon and <1 g of carbon, respectively. In East Kilbride, only samples that yield >1 g of carbon are prepared for radiometric counting; smaller amounts of carbon are consigned to the laboratory's accelerator mass spectrometry (AMS) program. To determine the optimum settings as a function of counting geometry, we investigated the influence of several factors, including PAC setting, energy discrimination and vial construction and alignment on the ¹⁴C spectral response of the Quantulus 1220™. We also investigated the factor of vial construction (PTFE or glass) and the use of masked holders. The response was compared for all three Quantulus systems (one in Gliwice and two in East Kilbride) in terms of background count rates, ¹⁴C detection efficiencies and quench tolerance.

Assessment of the analytical accuracy and precision achieved in routine LSC were based on the results of measurements for TIRI intercalibration samples and on the comparison of results obtained from the well-established gas proportional counting (GPC) performed at the Gliwice laboratory. Recently the Quantulus spectrometer in Gliwice was calibrated to allow the measurement of environmental concentrations of tritium. The capability and precision achieved in monitoring environmental levels of tritium without prior sample enrichment is illustrated using tritium activity data measured for precipitation water sampled in Upper Silesia (Poland).

Benzene Synthesis

Figures 1 and 2 show the Gliwice Radiocarbon Laboratory's two benzene rigs. Both were designed by Vadim Skripkin from Kiev. We slightly modified them for our needs. Prior to the benzene synthesis, all samples are pretreated using standard methods. After pretreatment, organic samples are carbonized in a steel reactor vessel at *ca.* 650°C. The production of lithium carbide is carried out in

the stainless steel reactor vessel heated in an electrical furnace. One gram of metallic lithium per 1 g of carbonized sample are mixed in the reactor, and after evacuation, are heated to 800–850°C. For carbonized organic samples containing < 1 g of carbon, we use a 0.02-liter reactor vessel.

Inorganic samples are combusted and the resulting CO_2 is purified in vacuum lines used for the GPC system. The production of lithium carbide is carried out in the same type of reactor vessel as that used for “large” carbonized samples. For 1 liter of CO_2 , 2.5 g of metallic lithium is required. The metallic lithium is placed in the reactor vessel, which is evacuated and heated to 650°C. In the next stage, CO_2 is let into the vessel. After completion of the reaction, the vessel is heated to 850°C and evacuated for 30 min (Mestres *et al.* 1991). Subsequently, acetylene is produced in the reaction of the obtained lithium carbide with water. The acetylene is purified in a chromic acid absorption bulb. In case of acetylene production from “small” samples, the acetylene is also dried on a sodium swarf.

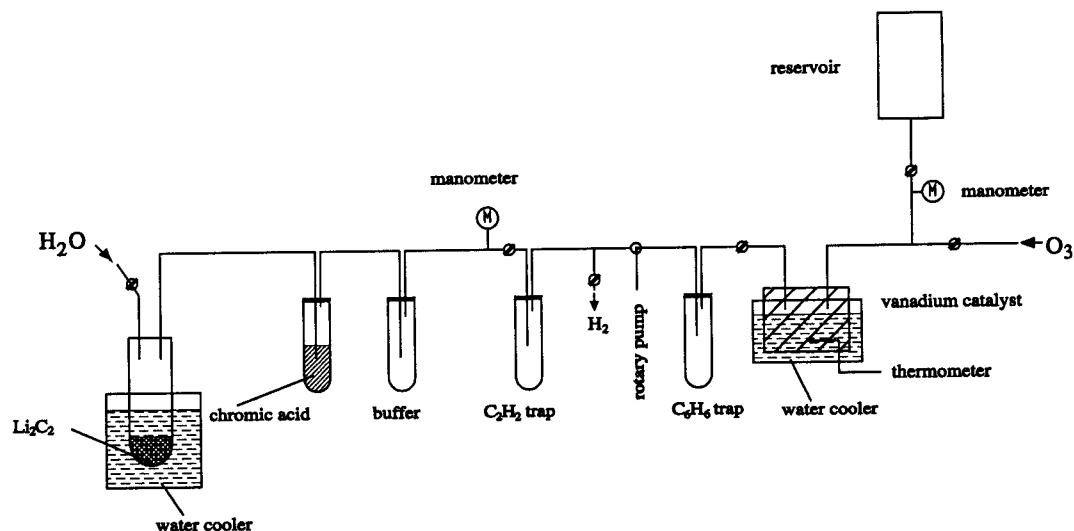


Fig. 1. Vacuum line for benzene synthesis from samples >1 g carbon

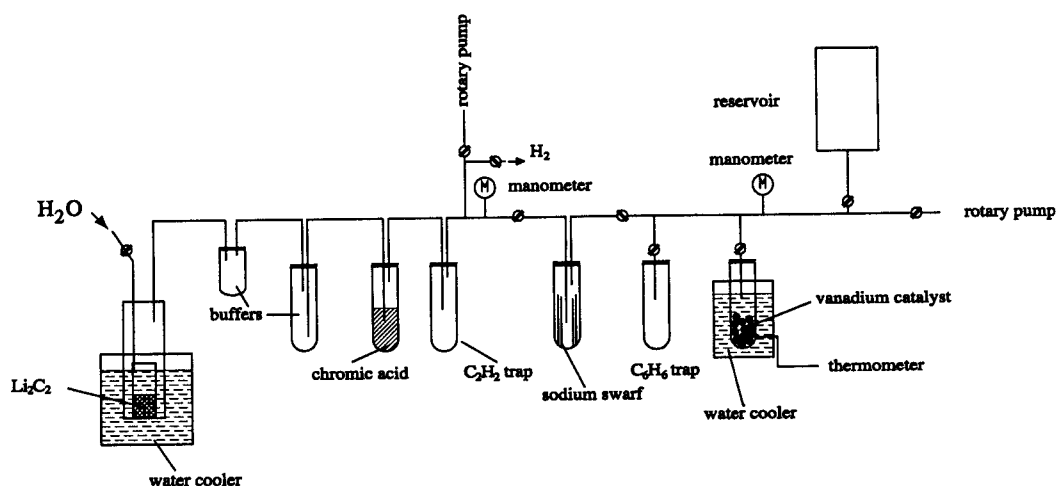


Fig. 2. Vacuum line for benzene synthesis from samples <1 g carbon

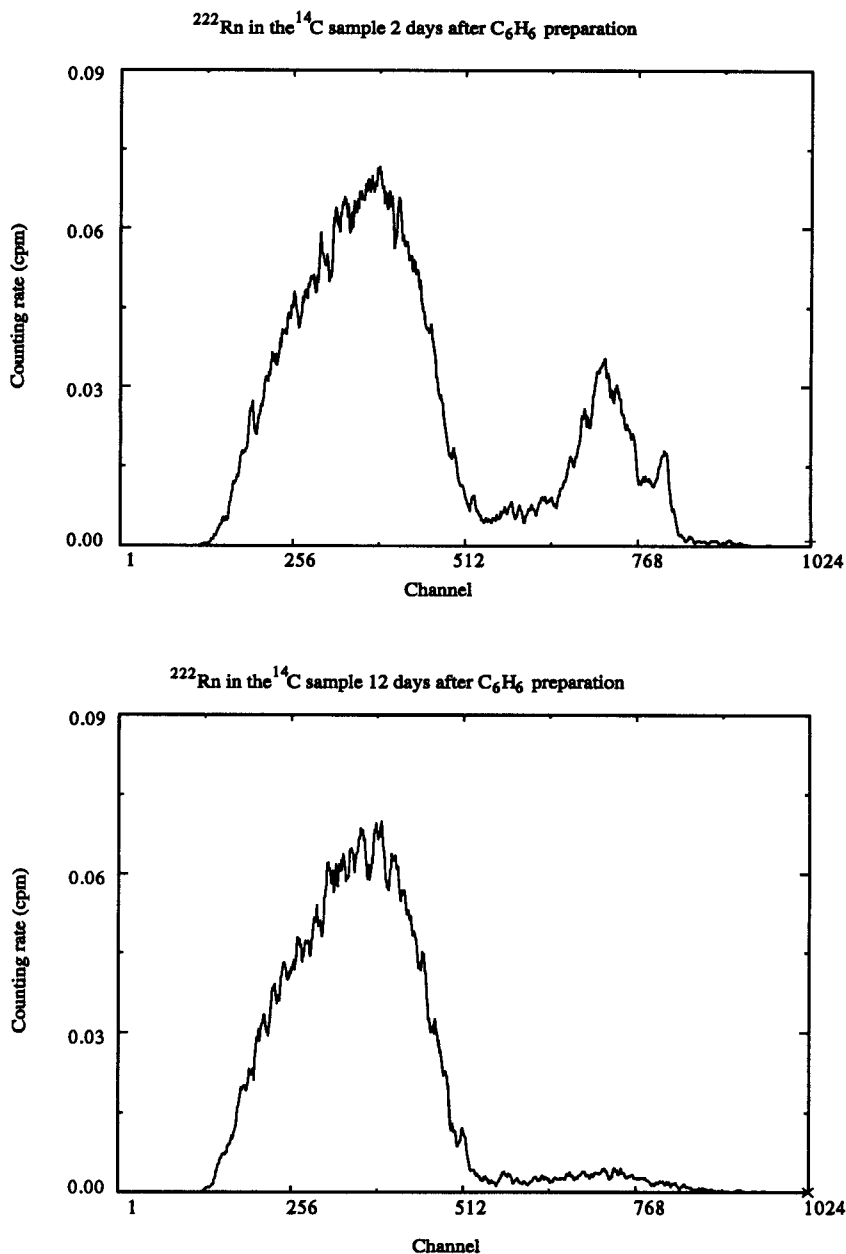


Fig. 3. Presence of ^{222}Rn and daughter isotopes in the sample benzene ^{14}C spectra, two days and two weeks after benzene synthesis

In the final stage, benzene is obtained by the catalytic trimerization of acetylene with the application of Arslanov's vanadium catalyst. Prior to trimerization, the catalyst is preheated in a vacuum to 300°C . One portion of the catalyst can be reused several times. After every 10th sample, the catalyst is "cleaned" by purging with ozone. The obtained benzene is dried and purified with the use of a sodium swarf and a sublimation/resublimation procedure. To allow the radon present in the benzene to decay (Fig. 3) the purified benzene is stored in a freezer for no less than 3 weeks.

The procedures used for benzene synthesis are being improved continuously. Currently, the benzene yield is up to 92%. The yield of the benzene rig designed for samples containing <1 g of carbon is higher than that of the bigger one.

Calibration Procedure for Radiocarbon

The Quantulus ultra low-level liquid scintillation beta spectrometer uses multiparameter, multichannel counting techniques (Kojola *et al.* 1984, 1985; Polach *et al.* 1984). The low background levels of the spectrometer are obtained by application of the passive material shield, active anticoincidence shield, radio frequency noise discriminator and pulse amplitude comparator (PAC). We used the following procedure to set up the spectrometer for routine ^{14}C activity measurements (for ^{14}C dating):

- Definition of the counting geometry. Because samples routinely dated in the Gliwice Radiocarbon Laboratory contain <2.5 g of pure carbon, we decided to use 3 mL, 2 mL and 0.8 mL volumes of benzene as counting geometries (Gupta and Polach 1985). For convenience, low potassium 7 mL PICO glass vials from Packard were chosen for 3 and 2 mL counting geometries. To achieve low background counting rate, we chose small PTFE vials for the 0.8 mL geometry (Skripkin *et al.* 1995). Pico glass vials are filled to less than half of the volume and inserted in the Packard vial holders. The upper part of the holders was masked with black tape or black mat lead-free paint to reduce photomultiplier crosstalk.
- Choice of the scintillator. Butyl-PBD was chosen as the scintillator for all counting geometries because of its high counting efficiency. It is used in the proportion of 13 mg per 1 mL of benzene.
- Selection of the standard and background samples. We decided to use ANU Sucrose and NBS Oxalic Acid II as the modern activity standards. As background samples, we used commercial Polish Analar-grade benzene. We used samples prepared from coal, graphite and calcite.
- Determination of the counting window for ^{14}C measurements. Spectra of modern standard, tritium and background were collected for each counting geometry. The window was set to contain <1% of the total tritium spectrum and *ca.* 80% of the total ^{14}C spectrum, which gives total efficiency *ca.* 60% (Fig. 4; Tables 1 and 2).
- Choice of the optimal PAC level. The optimal PAC value is that one that minimizes the function $B/\text{Eff}^2(\text{PAC})$, where B is the background count rate and Eff is the relative efficiency (Fig. 5; Tables 1 and 2).
- Determination of the quench correction curve. The variation of benzene purity from sample to sample and therefore the variation of quenching may cause changes of detection efficiency (McCormac 1992). These changes should be compensated by multiplying the sample count rate by an adequate quench correction factor. Quench correction curve is the relationship between the reciprocal of the relative counting efficiency and the SQP parameter. To obtain the quench correction curve, the counting rate for a high activity sample is determined. Subsequently, a drop of a 5% acetone solution is added and the count rate is determined again. This procedure is repeated a few times. The relative efficiency is then calculated and the quench correction curve is plotted (Fig. 6).
- Test of the stability of counting. The stability of the apparatus was checked by repeated measurements over few months using background and modern standard samples. (Stability is also continuously checked by comparing standard and background count rates obtained from each counting protocol with previous values). From these results, the maximum determinable age, counting efficiency and factor of merit were calculated for each counting geometry (Tables 3 and 4).

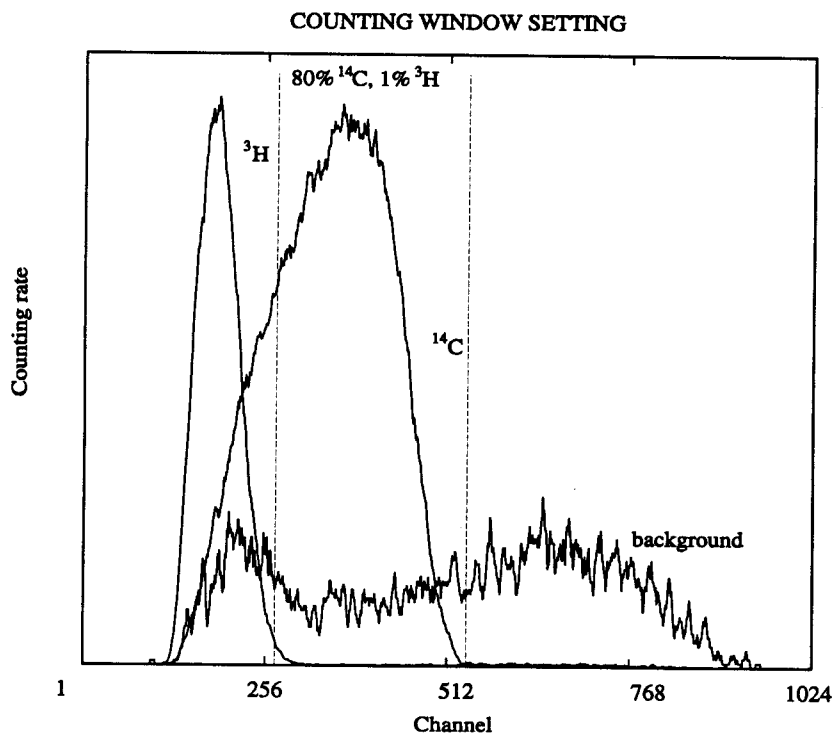


Fig. 4. Determination of counting window for 3 mL counting geometry

TABLE 1. Counting Parameters of Different Counting Geometries at the Gliwice Radiocarbon Laboratory

Counting geometry	Type of counting vial	Counting window	PAC value
0.8 mL	0.8 PTFE vial	275–545	110
2 mL	7 mL Packard Pico Low K Glass vial in Pico Holder	305–570	150
3 mL	7 mL Packard Pico Low K Glass vial in Pico Holder	271–540	152

TABLE 2. Counting Parameters of Different Counting Geometries at NERC Radiocarbon Laboratory

Counter	Counting geometry	Type of counting vial	Counting window	PAC value
Quantulus 1	4 mL	7 mL Packard Pico Low K Glass vial in Pico Holder	247–525	120
Quantulus 2	2 mL	7 mL Packard Pico Low K Glass vial in Pico Holder	268–550	120
Quantulus 2	4 mL	7 mL Packard Pico Low K Glass vial in Pico Holder	260–530	120

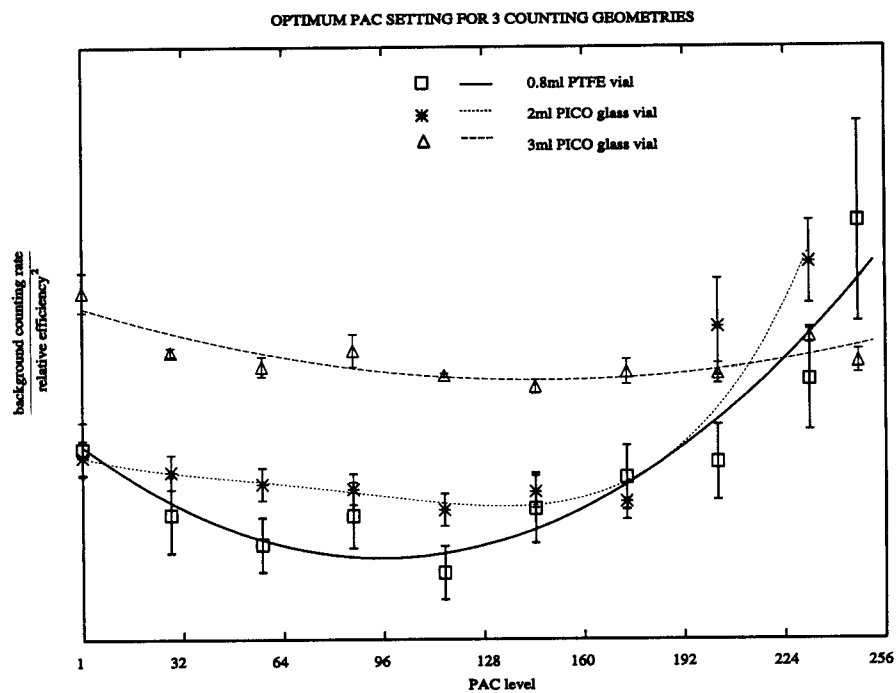


Fig. 5. Choice of the optimal PAC level for three counting geometries

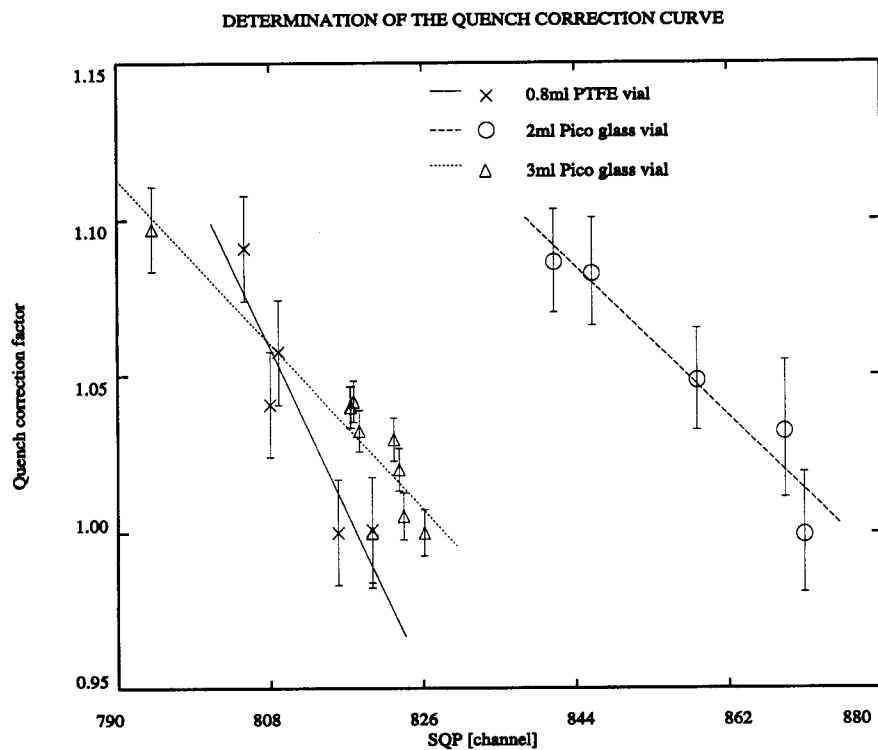


Fig. 6. Determination of quench correction curve for three counting geometries

- Checking the calibration. As a check of the calibration, the results of age determination were compared with the ages of a few well-known samples from the TIRI project, and comparison with results obtained using the well-established Gliwice GPC system (Table 5).

Table 3. Liquid Scintillation Beta Spectrometer Quantulus at the Gliwice Radiocarbon Laboratory

Counting geometry	Mass of carbon (g)	Background (B) (cpm)	Modern (So) (cpm)	¹⁴ C Efficiency (%)	Factor of merit (So/√B)	T _{max} * (yr)
0.8 mL	0.65	0.061 ± 0.006	5.266 ± 0.085	59.6	21.3	43,900
2 mL	1.62	0.252 ± 0.007	12.393 ± 0.047	56.3	24.7	45,100
3 mL	2.43	0.357 ± 0.008	20.795 ± 0.055	62.9	34.8	47,900

*To calculate T_{max} we used t = 1000 min

TABLE 4. Liquid Scintillation Beta Spectrometer Quantulus at NERC Radiocarbon Laboratory

Counter	Counting geometry	Mass of carbon (g)	Background (B) (cpm)	Modern (So) (cpm)	¹⁴ C Efficiency (%)	Factor of merit (So/√B)	T _{max} * (yr)
Quantulus 1	4 mL	3.24	0.663 ± 0.009	28.668 ± 0.050	65.1	35.2	52,000
Quantulus 2	2 mL	1.62	0.364 ± 0.004	14.384 ± 0.039	65.3	23.8	56,000
Quantulus 2	4 mL	3.24	0.573 ± 0.010	28.652 ± 0.049	65.0	37.8	55,000

*To calculate T_{max} we used t = 6000 min

TABLE 5. Comparison of Dating Results for Quantulus GPC at Gliwice and TIRI Consensus Values

Sample name	Quantulus at Gliwice (BP)	GPC at Gliwice (BP)	TIRI project (BP)
TIRI I	10,930 ± 75	11,070 ± 70	11,060 ± 17
TIRI J	1530 ± 50	--	1605 ± 8
TIRI L	13,090 ± 170	13,330 ± 90	12,790 ± 30
CAH 91/30	1750 ± 70	1710 ± 50	--
CAH 91/31	1730 ± 70	1840 ± 50	--
CAH 91/32	2045 ± 70	2045 ± 50	--
Strzegocice	1200 ± 80	970 ± 30	--
OB3	4535 ± 80	4500 ± 60	--
NASZ 58/88 spag	1020 ± 110	1020 ± 40	--
M17A/2	7135 ± 130	7320 ± 80	--

Calibration Procedure for Tritium

Setting up the spectrometer for measurements of tritium activity at natural abundance level requires:

- Definition of the counting geometry. Because of the low concentration of tritium in precipitation, we decided to use the largest possible sample volume. Therefore, we chose 8 mL of sample water and 12 mL of scintillator (HiSafe 3) geometry. We chose the 20-mL Wallac PTFE vials because of the low background count rates.
- Choice of background and standard samples. As a background sample, we use geologically old distilled water. The standard of tritium activity was prepared by mixing background water with tritiated water of known activity. To avoid contamination of the counting chamber, the activity of the prepared standard is <100 dpm per vial.

- Determination of the counting window for tritium measurements. Spectra of tritium and background were collected and the window was set to maximize the figure of merit.
- Determination of the quenching correction curve. The value of the quenching correction factor was estimated for each sample using the quenching correction *versus* SQP value plot. The data for this graph were obtained from repeated measurements of the count rate for the pure tritium activity standard and after addition of CCl₄ solution.
- As a check of Quantulus capabilities for tritium activity determination at natural abundance level, we attempted to find out whether it is possible to detect seasonal variations of tritium concentration in the precipitation sampled from the highly polluted Upper Silesia (Rank 1992). To accomplish this, we collected precipitation samples every two weeks during one year. Because Upper Silesia is the most polluted region in Poland, all collected samples were distilled prior to counting in order to remove impurities from the water. Figure 7 shows the results of the test. They were obtained without application of any isotopic enrichment procedure. Counting time for each sample was 1000 min.

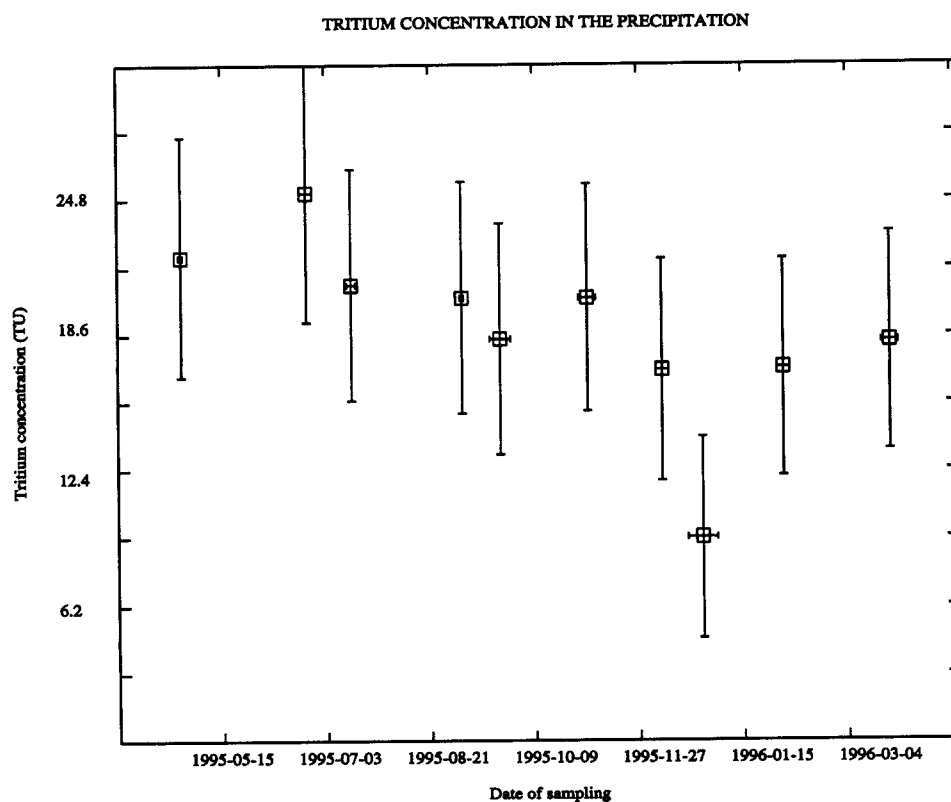


Fig. 7. Seasonal variations of tritium concentration in the precipitation water sampled in Upper Silesia, Poland

CONCLUSION

During the exercise of setting up the liquid scintillation method at the Gliwice Radiocarbon Laboratory we found that:

1. The use of GPC CO₂ vacuum lines for preparation of CO₂ from inorganic samples provides an easy way to produce high-purity benzene.

2. The use of the carbonization procedure minimizes of the amount of lithium needed for benzene synthesis.
3. Our laboratory needed the samples to be aged prior to counting. One can also monitor eventual change of counting rate in the "radon counting window" during sample counting to detect presence of ^{222}Rn .
4. Determination of each of the counting parameters for Quantulus LSS should be done separately for all counting geometries.
5. Calibration tests show good agreement with dates obtained with the Gliwice GPC system and the results of TIRI project.
6. Quantulus can be used for easy and inexpensive tritium concentration measurements in environmental investigations.

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