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THE USE OF THE SMALL GAS PROPORTIONAL COUNTERS FOR THE CARBON-14 MEASUREMENT OF VERY SMALL SAMPLES

DISCLAIMER

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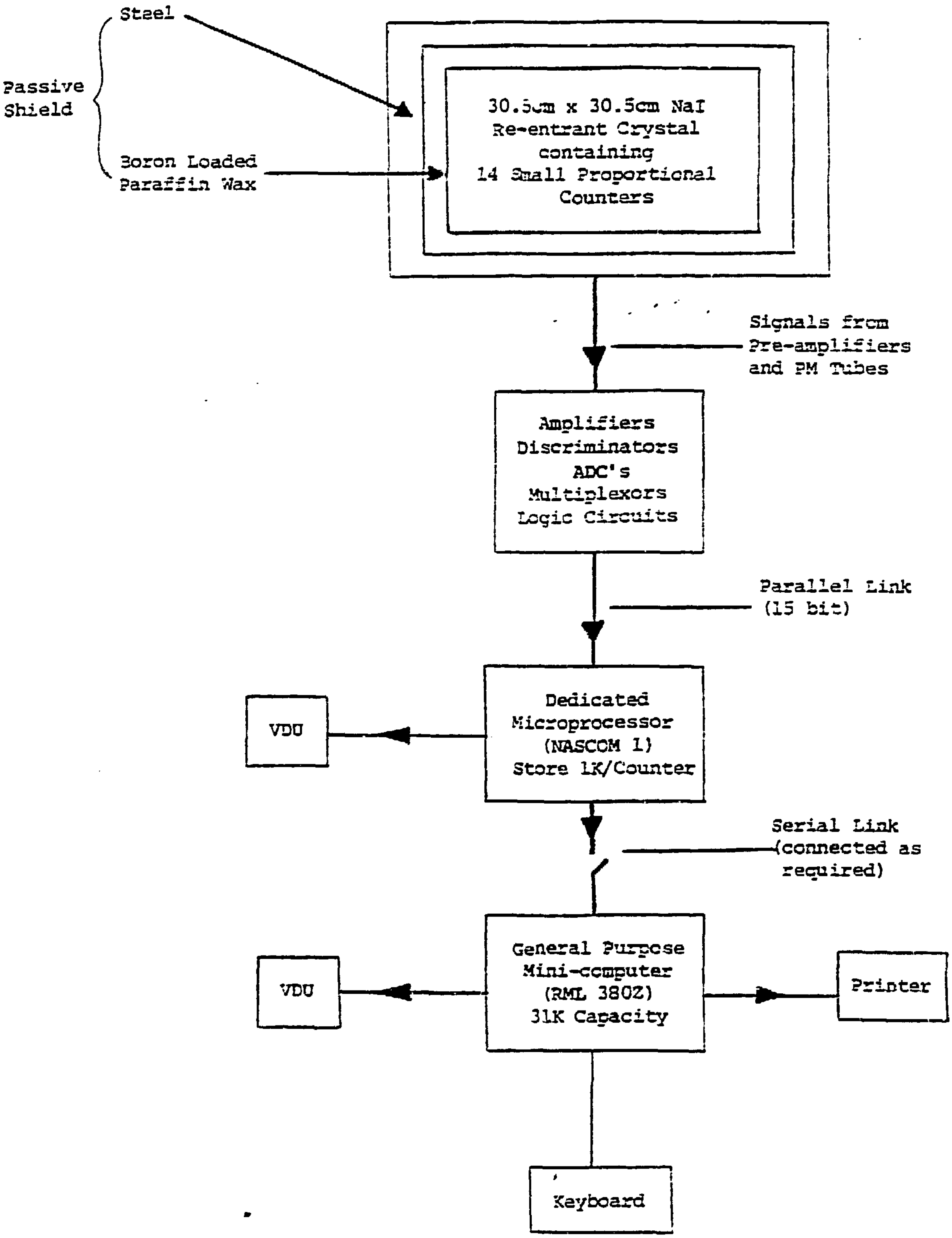

Fig. 3 Schematic Diagram of Harwell Small Counter Facility

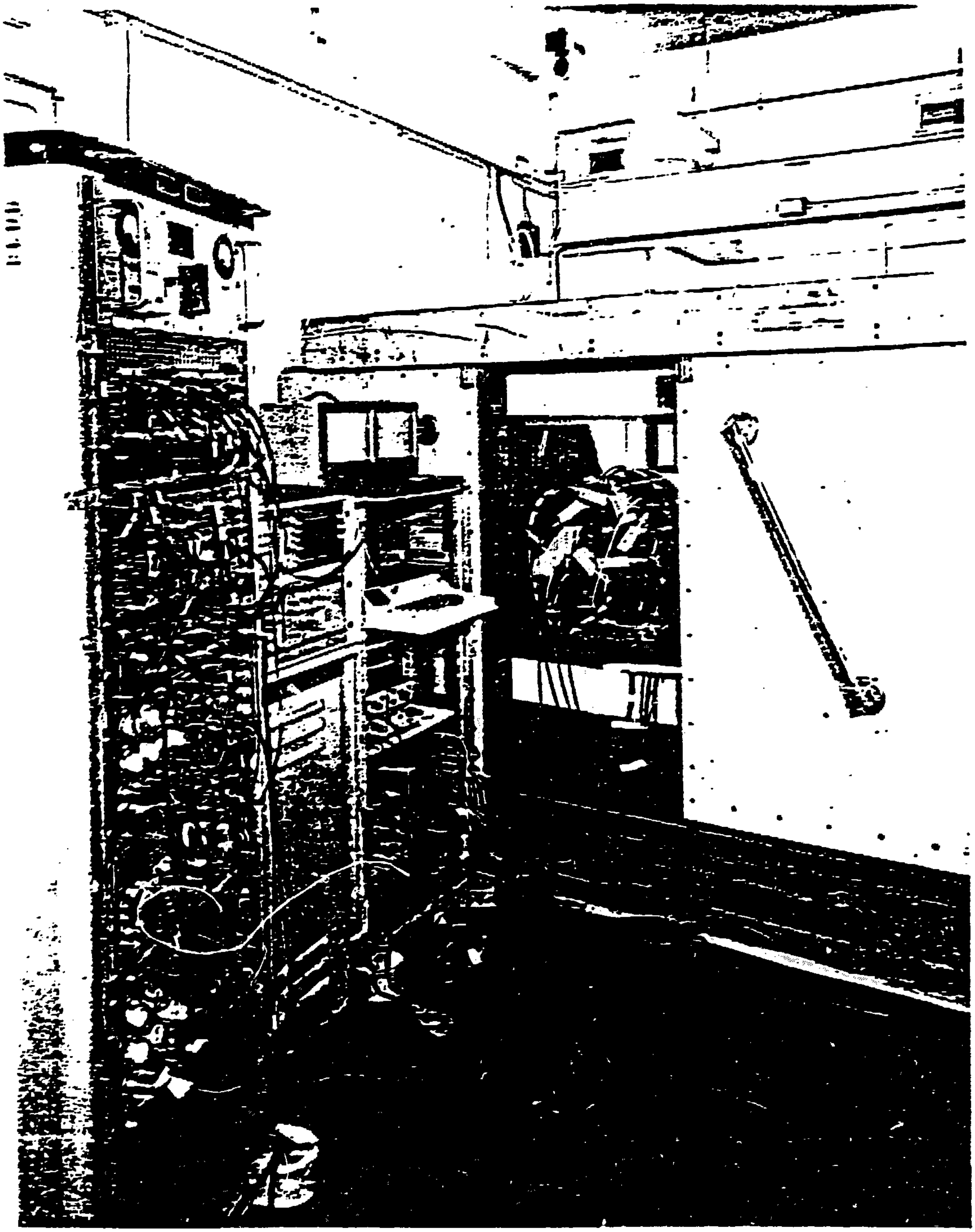

Fig. 2 The Harwell Small Counter Facility

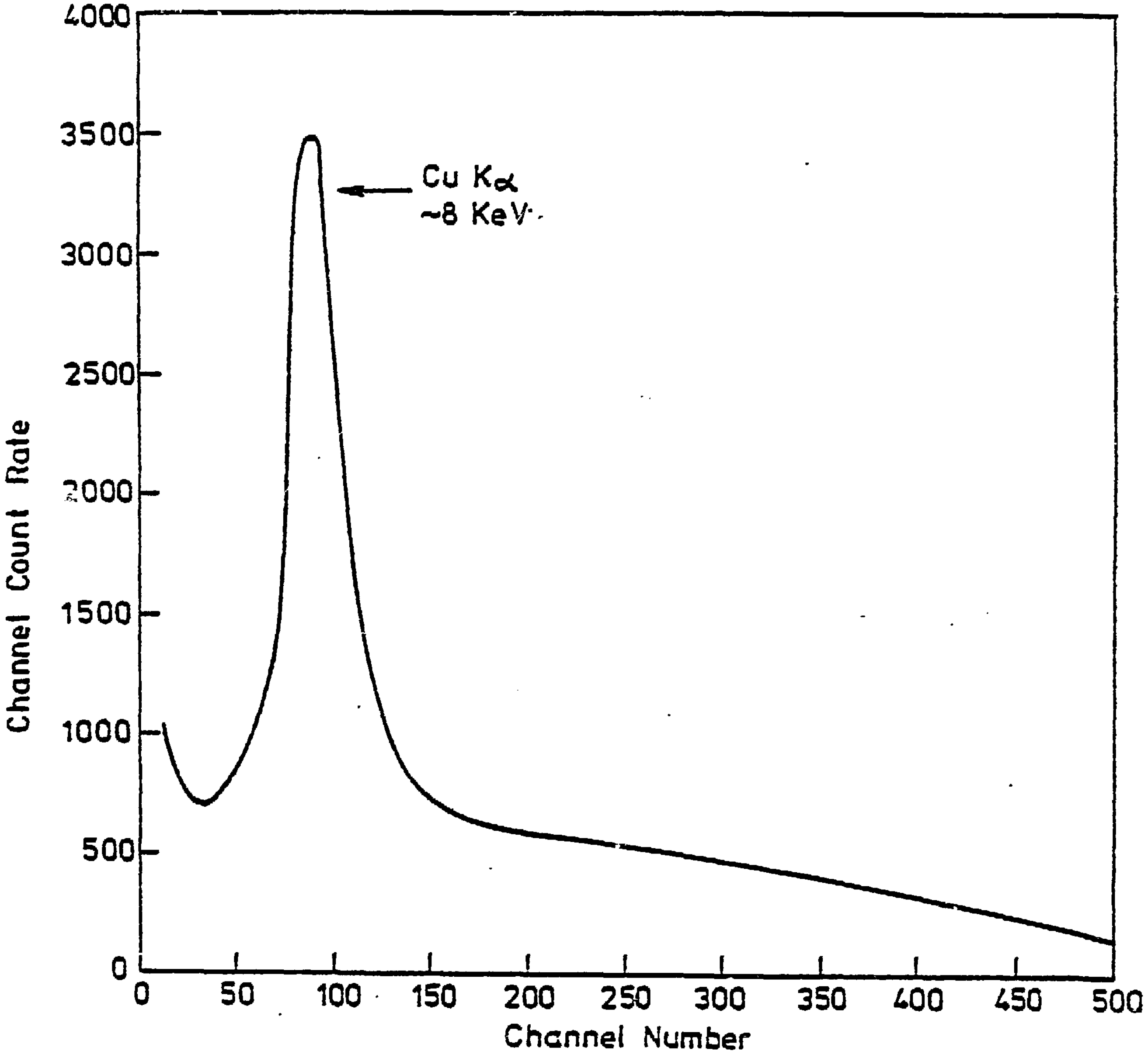

FIG.1. BROOKHAVEN MINIATURE GAS COUNTER (5cc VOLUME)
Excitation spectrum using a ^{238}Pu external source after
~ 4 months counting

TABLE I

CHARACTERISTICS OF SOME SMALL ^{14}C PROPORTIONAL COUNTERS

Volume (cm^3)	Pressure (atm)	Counting Gas	Weight of Carbon (mg)	Counts/Day (net) of Modern C	Counts/Day Background	Modern Carbon / Background	Reference
35	1	CO_2	19	288	403	0.72	(10)
30	1	$C_2H_4+C_2H_2$	32	446	360	1.2	(11)
40	1	C_2H_6	43	439	360	1.2	(11)
40	0.6	C_2H_4	26	288	173	1.7	(12)
10	6	CH_4	32	446	58	7.8	(29)
40	2.1	CH_4	45	576	346	1.7	(2
15	1.2	CH_4	10	176	173	1.	(14)
5	4	CO_2	10.7	178	100	1.7	(30)
5	4	CO_2	10.7	186	56	3.3	(9)
5	4	CO_2	10.7	186	21	8.9	(9)
7.5	4	CO_2	16	269	77	3.5	(9)

A VDU monitor gives indication of the mode of operation being employed. Full display, analysis of data and long term (back-up) storage is obtained as and when required using a rather more sophisticated general purpose mini-computer (RML 380Z). At the rate of data accummulation expected, read out for the purposes of quality control will only be necessary once or twice a week with a more detailed analysis at the end of the long count. The RML 380Z which includes facilities for graphics display is ideally suited for this and is available, furthermore, for many other functions of a general purpose computer by the laboratory for most of its operational time.

Summarising, therefore, the Harwell set-up is designed to provide a viable turnover of small sample measurements of around 250 samples per year. This will be achieved by using different counter sizes and only the smallest samples will need the very long counting times discussed elsewhere in this paper. No economies have been made in the choice of shielding arrangements as it is firmly believed that the background level and its stability are vital to the success of the operation. The use of a dedicated microprocessor for data capture is an inexpensive alternative to conventional multi-single channel systems. Used in conjunction with a simple general purpose computer having graphics display, it is entirely adequate for this work and is an attractive alternative to very much more sophisticated and more expensive 'routing' type of multichannel analysers.

4.2 Other Planned Facilities

At Brookhaven a plan is under consideration for a unit that would contain 16 small counters in a "cosmic ray counter" anti-coincidence ring shielded by massive iron. Except for this feature it would, in electronics, amplification and multichannel analysis, resemble the Harwell installation. It would serve to determine ^{14}C contents in over 600 samples of milligram size generated by an oceanographic project. Dr. Lloyd Currie of the US National Bureau of Standards is planning a unit of 20 small proportional counters to use in his environmental research.

5 Conclusions

Since the large-scale units for small-sample counting, and the accelerator-mass spectrometric devices are each only beginning to come on-line, it is premature to attempt to compare the two methods for cost-effectiveness. One fact is certain: the cost alone of the accelerators will place them outside the reach of many radiocarbon laboratories. For very small (less than 10 mg) and/or very old samples, the accelerator will be the only feasible approach. On the other hand, a clearly defined role has been identified for small proportional counters in ^{14}C dating studies within a number of disciplines. Samples of down to 10 mg size can be measured reliably and a sample of 100 mg of modern carbon can be counted to 2% precision in under two days. For such samples, one must believe that the queuing time rather than the measuring time will be the limiting factor.

Consequently, one can expect an increasing demand for ^{14}C measurements as the relevance of the increased dimension of dating capability is realised.

perceptible deterioration.

The demonstration was convincing and accordingly a complete set-up was planned which, using 14 counters (purchased from Brookhaven) of two sizes, would enable a turnover of approximately 250 samples per year. This set-up, shown in Fig. 2, is in an advanced state of construction and is presently undergoing commissioning prior to full scale operation.

Figure 3 gives an outline schematic of the shield, counter system, electronics and the data management. The shields, meaning the conventional passive shielding and the anticoincidence guard counter, are very much the most expensive components of the complete set-up. Many laboratories may already possess a suitable passive shield left from earlier work with large gas counters. Harwell was fortunate in being able to acquire a shield once used by the National Physical Laboratory at Teddington for ^{14}C gas counting.

For the anticoincidence counter, the choice was made to purchase a large NaI crystal. This was obviously very much more expensive than the more usual multi-geiger counter array or the integral multi-wire proportional counter assembly but, on the Brookhaven results, the significant background reduction obtained with the crystal set-up seemed to justify the additional expense. This lower background reflects in the counting time, and hence, in the long run, the 'turnover' time for samples. It is also of interest to note that the signal (modern rate) to background ratio, achieved with the crystal, of 9:1 compares favourably with the same ratio for a standard liquid scintillation counter. Thus, in a suitably sized counter and with the total time of count not the limiting factor, no less precision ought to be obtained. The sample processing for such a small counter is clearly considerably simpler than for the large sample liquid scintillation counter.

Beyond the shield and counter assembly, the system comprises the electronics, logic circuits, data storage and display. Here, recent improvements in technology, eg. monolithic integrated circuit components and microprocessor data capture, have been fully exploited. Essentially the system provides the facilities of 14 multichannel analysers each of 512 channels and capable of dividing the pulse input from each counter into separate coincident (cosmic) and anticoincident (sample) spectra.

Following the pre-amplifiers and EHT filter circuits, which are specific to each counter and physically located as closely as possible to the counter terminations, the signals are passed into a single electronics/logic unit. The circuit accepts 16 input channels, 14 from the counters, one from the anticoincidence counter plus an internal timing channel. A common logic board collects the signals from the separate amplifier/discriminator sections and encodes them in a manner acceptable to a small dedicated (ie. used for no other purpose) microprocessor (NASCOM 1). The coding describes the counter origin, the pulse amplitude and adds flag bits indicating whether the pulse occurred in coincidence with the guard counter or with any other counter of the assembly. The NASCOM interprets the output 'word' and passes the pulse for addition into the appropriate location of the 512 x 16 store.

into existing radiocarbon laboratories at relatively little expense. However, there are plans under-way for several new installations specifically designed for the small counters. The most advanced unit is at the Low Level Measurements Laboratory at Harwell in the UK.

4.1 Harwell Small Counter Facility

Harwell's needs for the measurement of ^{14}C in very small samples are similar to those outlined in the introduction. The laboratory has operated a commercial radiocarbon dating service since 1973 and holds contracts for dating work for archaeology, hydrology, environmental and industrial applications. In addition, it has run its own research programmes in subjects related to the commercial operations and activities of interest to the nuclear industry, of which it is a part.

Over the years, the need for a small sample system has become increasingly apparent and experiments had been in hand for some-time to set up a single-line gas proportional counter (300 ml volume), counting methane, to cope with some of them. The standard method for ^{14}C measurements employed, however, has been liquid scintillation counting(28). The system which, in full, includes the sample processing and the counting, is orientated to a normal sample size of about 5 g equivalent carbon. Measurements are routinely undertaken with samples down to 2 or even 1 g carbon but with considerably less confidence than the larger samples, not especially because of the less favourable counting conditions but rather because of the more insiduous and unquantifiable uncertainties in the sample preparation process, eg. memory. Such effect on the sample result is inevitably magnified at the smaller end of the sample size scale. There is, thus, a very big gap between the fail-point of the liquid scintillation system (around ¼ to 1 g carbon) and the potential of the smallest Brookhaven counter at around 10 mg carbon. Over the years, many samples have been acummulated which, generally after pretreatment, have been found to be inadequate for the standard process. It is also clear from our communications with would be submitters that the occurrence of samples which contain quite visible amounts of perfectly good carbon (charcoal), but well below the minimum required for a good liquid scintillation counter measurement, is all too frequent. In addition, there is new work, for example, the ^{14}C dating of water having low carbonate content or the measurement of individual tree rings in environmental studies, with samples taken from core extractions, in which the ability to make measurements from samples yielding down to 10 mg carbon would be of immediate practical value.

The first response to the announcement by Brookhaven of measurements in such small counters was, it has to be admitted, not without some scepticism. The idea of a counter filling, especially of a gas as electronegatively sensitive as CO_2, remaining stable and countable over a period in excess of two months was totally unexpected. A counter supplied by Brookhaven was put on test at Harwell in September, 1979. It had already been counting at Brookhaven for 83 days before dispatch. The $K\alpha$ X-ray peak obtained by excitation of the cathode material (Cu in this counter) by an external ^{238}Pu source is given in Fig. 1. The resolution ($\sim$ 25%) is a good indicator of the counting quality of the gas + counter, which even after a further 2 months showed no

3. Dating Applications

Since the development of the improved miniature counter at BNL, we have carried out three dating studies on actual museum objects, as opposed to laboratory feasibility tests. In the first of these, a sample containing about 16 mg carbon removed from a wooden Eskimo mask of considerable archaeological significance, in the Kraemer collection of New York University, was counted for 89 days. It was felt by the curator, on stylistic grounds, that only two dates were possible - 18th century AD or 5-6th century AD. We obtained a date of 1610 AD ± 105 years, clearly in disagreement with the 5-6th century range(20).

The second sample was art-historical in nature. The Stavelot Triptych is a celebrated 12th century reliquary associated with the Benedictine Abbey of Stavelot on the Meuse River in Belgium and is the centrepiece of the collection at the Pierpont Morgan Library in New York City(21). Very little information was available to the curator concerning possible reconstruction of the oak panels forming the backing of the enamelled metal, preceeding its acquisition by the Morgan Library in 1913. We found that the centre panel had a date of 1333 AD ± 115 (uncorrected) while the right panel was modern; ie. the ^{14}C was essentially contemporary. As a sidelight, we dated a minute piece of the "robe of the Virgin Mary" found in the reliquary: it came out 1160 AD ± 150, which places it definitely in the period of the Crusaders.

The third example was an extraordinary hemispherical piece of iron weighing about 9 kg (20 lb), found on a desolate island in Frobisher Bay, Baffin Island, in the Arctic North America by C.F. Hall in the 1860's, and presently in the Smithsonian Institution(22). It was assumed by Hall, and all other authorities until recently, to be a relic of one of the three expeditions of Sir Martin Frobisher, the Elizabethan explorer who visited this area in 1576, 1577, and 1578 in search of gold(23,24,25). But, the recent discovery of Viking remains in the New World(26) motivated the Smithsonian Conservation-Analytical Laboratory to re-examine the iron "bloom" and to ^{14}C date it following the technique of N. Van der Merwe(27). The problem was the small content of carbon in bloom iron; approximately 0.05% by weight.

By combusting three 10 g samples of the iron, about 10 mg of carbon as CO_2 was obtained and counted: the experiment was duplicated and 17 mg resulted. These samples were counted for about 100 days each and dates of 1271 AD ± 133 and 1158 AD ± 107 obtained. Although these dates are well within the Viking exploration period, the iron bloom could still have been Frobisher's, if 16th century ironmakers in England had used charcoal made of wood from very old trees. The object is being investigated metallurgically and a complete report will be issued in due course.

4. Current Developments

The Brookhaven developments made use of existing anticoincidence equipment, amplifiers etc. and, for this reason, it is the authors' belief that small counters of this type could be incorporated

The cathode is ∿ 0.05 mm (0.002 in) iron foil and the anode is ∿ 0.005mm (0.0002in) tungsten wire. Prior to assembly, the quartz parts are immersed in concentrated hydrofluoric acid for a few minutes, rinsed and dried, while the iron is degreased in n-hexane and etched with boiling 2M HCl, rinsed and dried. The exact step-by-step procedures for assembling the counters are available from the Brookhaven authors.

One important design feature of these counters, typically of 5 ml volume and capable of holding 10 mg of carbon as CO_2 at 4 atm, is that they are entirely free of any plastic or organic matter in contact with the counting gases, and are routinely baked out before filling, at 300°C in high vacuum. This procedure seems necessary if the counters are to operate stably over a number of months on one filling (9,15). Sample preparation basically follows the well established procedures used for conventional ^{14}C gas counting but using rigs suitably scaled down for the smaller samples being handled.

Samples are combusted in a stream of oxygen at a partial pressure of ∿ 130 mm Hg, and afterwards passed through a Pt black gauze and a CuO furnace, each at 600°C. Separation of the resultant CO_2 is achieved by using a trap containing glass wool at liquid nitrogen temperature. Final purification is obtained in a second stage in which the general methods of Srdoč and Sliepčević (17) are employed. For the final purification, the CO_2 is passed through activated charcoal at 0°C as Bruns (18). Finally, the CO_2 is forced into the counter with a Toepler-type pump at 4 atm pressure: the counter's response to the KαX-rays of iron fluoresced by an iodine-125 source forms a stringent test of the gas's freedom from electron-attaching impurities (9) in the gas filling prior to counting.

Following normal low background counting techniques, the counters are enclosed in a combination shield employing passive and anticoincidence guarding: two types of anticoincidence guard counter (for ionizing radiation cancellation) have been investigated. In the first, the counters were placed in a low level shield consisting of a ring of long, 5 cm diameter proportional ("cosmic ray") counters. In the second, the counters were inside the well of a large cylindrical NaI crystal (25 x 25 cm). In both cases, the assemblies were contained within a massive iron (γ-ray) shield, 30 cm wall thickness. Data obtained with each method of anticoincidence is presented in Table I: the NaI crystal is seen to be more effective, but it is, also, of course, more expensive initially.

The Brookhaven counters are, as has been mentioned above, the latest development, and certainly not the final one, in a long series of experiments involving ^{14}C measurements in small proportional counters. In Table I, comparative data and references are presented: the advance is seen to be in the use of a NaI shield to obtain signal/background ratios of almost 9/1 for only 10.7 mg of modern carbon. In future research it may be possible to, a) increase the gas pressure a little more, b) reduce background by placing the whole apparatus far underground, and c) apply axial magnetic fields to the counter to produce ^{14}C pulses that are capable of being discriminated from background by means of rise-time analysis (3,19).

2. Development of Small Counters

2.1 Background

The idea of using small counters for measuring ^{14}C in milligram carbon samples is not new. In fact IAEA "Radioactive Dating" conferences in 1962 and 1967, the predecessors of this conference, contained several presentations in which small counters for ^{14}C were described(10,11,12) (see also Table I, this paper). Indeed, Oeschger (op. cit.) remarked that a 40 ml counter filled with methane permitted one to date the 21 mg of carbon contained "if not too high an accuracy is required", and in his 1965 report such a counter was applied to 40 mg of carbon from glacial ice(2). Nearly a tonne of ice had to be melted to apply even this small sample!

Around 1976, just when research was beginning in earnest on the accelerator-mass spectrometer technique for ^{14}C determination, work resumed at Brookhaven on a project started there many years before, namely to extend and improve upon, if possible, the experiments of Oeschger with small proportional counters and conventional anticoincidence methods. This work was sponsored by the Smithsonian Institution(13) in June 1976; by January, 1977 we had built and tested a 5 ml, 4 atm CO_2 counter and in February, 1978 obtained our first dates, of tree-ring samples of 10 mg carbon(9). During this same period, Currie at the National Bureau of Standards built and operated 15 ml counters holding 10 ml of carbon or less(14): he used these to measure the dichotomous mixing ratio between "live" (modern, biogenic) and "dead" (fossil-fuel derived) carbon, when the requirements for precision were not so high. In his actual ^{14}C determinations in milligram carbon samples from air pollutants, counting times of only 23-65 hours were needed(4).

2.2 Brookhaven Developments

The aim at Brookhaven which stemmed from the interest of the Smithsonian Insitute and ourselves in actual archaeological dating, was to use even smaller counters than before but with longer counting times and higher CO_2 pressure to improve the statistical precision of the ^{14}C determination. To facilitate this we investigated, additionally, improved methods of background reduction: this will be especially important in the case of ^{14}C measurements where the specific activity is low ie., old samples.

The design of the counters was orientated toward the requirements outlined above, to maximise our precision in the determination of low-level gaseous activities. This is a field that has been a speciality of the Chemistry Department at Brookhaven, in our research on the detection of solar neutrinos (15,16). All materials of construction were chosen carefully to be as free as possible from naturally occurring contaminants. All parts, excepting the short lengths of glass used in sealing the anode and cathode leads, are of Suprasil fused quartz(9).